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Feasibility study of decomposing methane with hydroxyl radicals ☆

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ABSTRACT

Coal-mine gas disaster is one of the most serious coal-mine disasters in China. The main component of coal-mine gas, methane is chemically stable and very difficult to be degraded by conventional methods. Hydroxyl radical (·OH), due to strong oxidizing ability and high electro-negativity, is the primary degradation source of atmospheric methane. In the present study, methane degradation using hydroxyl radicals generated by Fenton's reagent, Fe^{2+}/H_2O_2, has been carried out in the self-designed bubbling reactor. The effects of H_2O_2 concentration, dosage of $FeSO_4{\cdot}7H_2O$ and initial pH value on methane removal efficiency were investigated respectively. It has been found that the optimal reaction conditions were 100 mM of hydrogen peroxide, 2.00 mM of ferrous ion and initial pH value of 2.5. Under optimal conditions, the removal efficiency of methane reached 25% after 30 min. The preliminary experimental results unambiguously demonstrate that the degradation of methane using hydroxyl radicals generated by Fenton's reagent is feasible.

1. Introduction

Coal-mine gas disaster is one of the most serious coal-mine disasters in China, not only resulting in heavy casualties and tremendous loss of property, but also inducing adverse social impact. At present, the main technologies for controlling coal gas are physical methods, such as prediction of gas outburst, mine ventilation and gas exhaustion (Zhang, 2001). However, due to the complexity of geological conditions and low gas permeability of coal seams, many catastrophic gas accidents still frequently occur. Consequently, the present controlling technologies of coal gas are difficult to assure the safety production of coal mine.

Coal-mine gas is a kind of clean fuel, meanwhile is the major source of atmospheric pollution. The main component of coal-mine gas, methane, is a very important greenhouse gas that needs to be controlled. Intergovernmental Panel on Climate Change (IPCC) have reported that compared to carbon dioxide, warming effect of methane is about 21 times higher than that of carbon dioxide. For a long time, on the one hand, coal mining in China has promoted the rapid development of coal industries and guaranteed the energy supply for the sustaining, high speed and steady development of national economy. On the other hand, coal mining also has resulted in large quantity of environmental pollution and coal-mine disasters. According to a statistic of mining safety field, more than 10 billion m^3 of coal-mine gas cannot be effectively utilized and directly emitted into air, which induces enormous greenhouse effect.

Generally, in coal seams, coal-mine gas mainly occur in form of free and adsorption phases, most of which are extracted or directly discharged into atmosphere by the ventilation system during the coal mining. High content gas in coal seams or released into tunnels, are the key factors to result in coal and gas outburst. However, the chemical reaction activity of methane molecule is very low, which is difficult to be treated by conventional methods. As a result, the reducing discharge of coal-mine methane by effective ways not only can control or prevent coal-mine disasters, but also can decrease environmental pollution.

Presently, methane emitted into air is mainly degraded through the atmospheric hydroxyl radicals, soil microorganism and atmospheric loss. In the recent years, Hou et al. (2008) and Chen et al. (2006) have been devoted to the research of coal-mine gas degradation by microorganism. The preliminary research results

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of microorganism system demonstrated that coal gas can be decomposed by adding methane oxidative bacteria into coal sample. Compared to the microorganism system, hydroxyl radicals in air have stronger oxidizing ability than methane oxidative bacteria in soil. Among of 560 Tg methane totally decomposed every year, about 88% is degraded *via* the hydroxyl radical oxidation (UNEP, 2001). Moreover, in the field of environmental science, the degradation of air pollutant methane with hydroxyl radicals has been investigated through basic experiments (Liu et al., 2006) and theoretic simulation (Nyman and Clary, 1994). However, as to the applying hydroxyl radical oxidation on controlling coal gas is still blank in the field of coal-mine safety.

In general, hydroxyl radicals can be generated by Fenton reagent, TiO_2 photocatalysis, γ-radiolysis, H_2O_2 and O_3 ultraviolet photolysis, etc. Among of these methods, the advantages of Fenton process are the simplicity of equipment, mild operating conditions (atmospheric pressure and room temperature), rapid oxidation rate, and relatively low cost. Consequently, the goal of this work was to study the degradation of methane with hydroxyl radicals generated by Fenton process to explore possible application in coal-mine gas treatment. The primary factors such as H_2O_2 concentration, dosage of Fe^{2+}, initial solution pH value, which would influence the removal efficiency of methane, were investigated in the self-designed bubbling reactor. The experimental results indicate that the hydroxyl radicals generated by Fenton reaction have accomplished the removal of methane under a certain reaction condition. It has been found that H_2O_2 concentration, dosage of Fe^{2+}, and initial pH values have optimal values. Under optimal conditions, the removal efficiency of methane reached 25%. It was proved to be feasible that the hydroxyl radical oxidation *via* Fenton process can be used to decompose coal-mine methane.

2. Materials and methods

2.1. Material and reagents

The hydrogen peroxide solution (30%, v/v) was purchased from Shanghai Yuanda Peroxide Co., Ltd. (Shanghai, China). Ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and perchloric acid were purchased from Shanghai Chemical Reagents Co. (Shanghai, China). The standard gas was purchased from Foshan Kedi Gas Ltd. in China. Deionized-distilled water was used for preparation of all solutions. Unless noted otherwise, the concentration of methane gas was 0.026 g/L (3.7%, v/v).

2.2. Experimental setup

A detailed experimental setup to carry out the advanced oxidation reaction in a continuous gas flow reactor system was shown in Fig. 1. The gas cylinders containing methane, oxygen, nitrogen, and carbon dioxide were used as reactant gas sources. The reactant gas was mixed using different mass flow controllers (Advanced Pollution Instrumentation Inc. Model 700) to form a gas stream. The gas streams were pre-mixed by a gas blender and a desired flow rate was controlled at 10.0 L min^{-1}.

The obtained gas stream was introduced into the self-designed bubbling reactor. The bubbler was a glass aeration head, which could generate bubbles with 5–10 μm in diameter. The solution pH was adjusted to the designated value with 10% (v/v) $HClO_4$ solution. A given amount of $FeSO_4$ solution was introduced before the H_2O_2 solution was added. The time upon the H_2O_2 added was set as the reaction start time. Meanwhile, in order to ensure the continuous oxidation methane with hydroxyl radicals generated by Fenton reagent, the mixed gas from bubbling reactor was extracted and pressurized back into the reactor by using a high-accuracy mine explosion-proof pump. All the experiments were carried out at 25 ± 1 °C.

The gaseous methane concentration was determined *via* online analysis by using Agilent gas chromatograph (6890). According to the standard curve of concentration, the value of $\Delta C/C_0$ was calculated and indicated the decomposition efficiency. The measurements were repeated three times for each degradation reaction, and the experimental error was found to be within ±3%.

3. Results and discussion

3.1. Methane oxidation mechanism

Fenton process is an Advanced Oxidation Process (AOP) known for more than a century and considered an effective method for wastewater treatment and indoor air purification (Pignatello et al., 2006; Kajitvichyanukul et al., 2008). Fenton's reaction (combination of H_2O_2 and Fe^{2+}) has been demonstrated to rapidly degrade many organic compounds *via* hydroxyl radicals (${}^{\cdot}OH$), due to the strong reactivity (second-order rate constants of 10^7–10^{10} M^{-1} S^{-1}) (Hoigne and Bader, 1975). The Fenton's reaction generally occurs in acidic medium at initial pH 2–4 and involves the steps shown in Eqs. (1)–(8).

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\cdot}OH + OH^- + Fe^{3+} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^{\cdot} \tag{2}$$

$$Fe^{3+} + HOO^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \tag{3}$$

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^- \tag{4}$$

$${}^{\cdot}OH + H_2O_2 \rightarrow H_2O + HOO^{\cdot} \tag{5}$$

$$Fe^{2+} + HOO^{\cdot} \rightarrow HOO^- + Fe^{3+} \tag{6}$$

$${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2 \tag{7}$$

$${}^{\cdot}OH + \text{organic} \rightarrow \text{products} + CO_2 + H_2O \tag{8}$$

$$\text{reductant} + H_2O_2 \rightarrow O_2 + \text{products} \tag{9}$$

During Fenton reaction, hydrogen peroxide is catalyzed by ferrous ion to produce hydroxyl radical, which can degrade almost all the

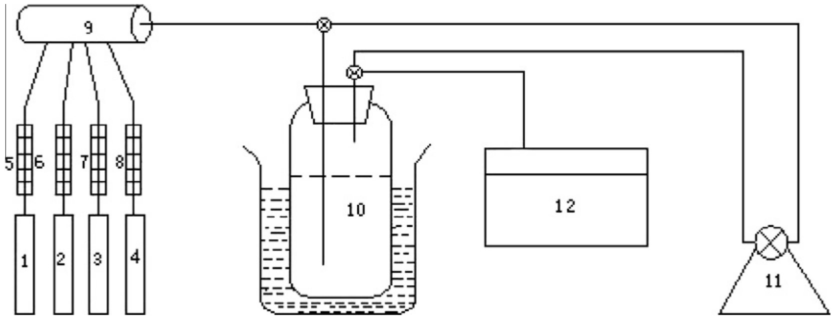

Fig. 1. Schematic diagram of the experimental setup. 1 – Methane cylinder; 2 – O_2 cylinder; 3 – N_2 cylinder; 4 – CO_2 cylinder; 5, 6, 7, 8 – rotameter; 9 – gas mixer; 10 – bubbling reactor; 11 – vacuum pump; 12 – GC.

organic substrates. However, the rate constant of reaction (1) is around 63 $M^{-1} S^{-1}$ (Kang et al., 2002), while the rate of reaction (2) is only 0.01–0.02 $M^{-1} S^{-1}$ (Martinez et al., 2003). This indicates that ferrous ions are consumed more rapidly than they are produced. The hydroxyl radicals can degrade organic compounds through reaction (8) and hydrogen peroxide can also react with Fe^{3+} *via* reaction (2).

3.2. Methane degradation by various processes

Control experiments were carried out to verify whether methane can be degraded by hydrogen peroxide only, ferrous ion only, or Fenton process. The experimental results indicated that hydrogen peroxide only and ferrous ion only can remove methane about 3% and 2%, respectively. However, Fenton process can degrade 24% of methane when using 1.50 mM ferrous ion and 100 mM hydrogen peroxide at pH 2.5, as shown in Fig. 2. Obviously, methane degradation during the experiments could be attributed to hydroxyl radical oxidation *via* Fenton reaction, which makes the Fenton process much more efficient than the others.

The intent of this study was to explore the application of hydroxyl radical oxidation through Fenton process to degrade coal-mine methane. Therefore, the parameters affecting the methane degradation by Fenton process, such as the H_2O_2 concentration, dosage of $FeSO_4$ and the initial pH values, were evaluated respectively.

3.3. Effects of hydrogen peroxide concentration

Hydrogen peroxide plays the role of an oxidizing agent in the Fenton reaction. Usually it has been observed that the degradation percentage of the pollutant increases with an increase in the concentration of hydrogen peroxide (Lin et al., 1999). It is the precursor in generating the hydroxyl radicals in the combination with Fe^{2+} as shown in Eq. (1). Moreover, hydrogen peroxide can also react with Fe^{3+} to regenerate Fe^{2+} as illustrated in Eq. (2). Nevertheless, in the presence of excess amount of hydrogen peroxide, oxidation reaction can be limited by the generation of O_2 instead of hydroxyl radicals and inhibited due to H_2O_2 consuming hydroxyl radicals as shown in Eqs. (9) and (5), respectively.

To study the effects of H_2O_2 concentration on the hydroxyl radical oxidation for the degradation of methane, 2.00 mM Fe^{2+} at pH 2.5 was fixed as the initial condition, while H_2O_2 concentrations were varied as 5, 10, 20, 30, 50, 80, 100 and 120 mM. The degradation of methane was shown in Fig. 3. The results indicated that increasing the initial H_2O_2 concentration from 5 to 100 mM can enhance methane removal. When an initial H_2O_2 concentration of 5 mM was added, 7% degradation of methane was achieved. Increasing the initial H_2O_2 concentration up to 100 mM could degrade 25% of methane. The increase in methane removal efficiency was due to the presence of higher concentration of H_2O_2, forming more hydroxyl radicals when reacted with Fe^{2+}. However, decreasing methane degradation efficiency was observed at 120 mM of H_2O_2 concentration. The methane removal efficiency was decreased from 25% to 23% when hydrogen peroxide concentration increased from 100 to 120 mM. This decrease was probably due to the competition of oxidative intermediates with methane on hydroxyl radicals. The higher concentration of H_2O_2 might have favoured the side reaction that scavenged the $^{\cdot}OH$ to form hydroperoxyl radicals *via* reaction (5), which has a rate constant of about $(1.2–4.5) \times 10^7$ $M^{-1} S^{-1}$ (Sun et al., 2007; Watts and Teel, 2005).

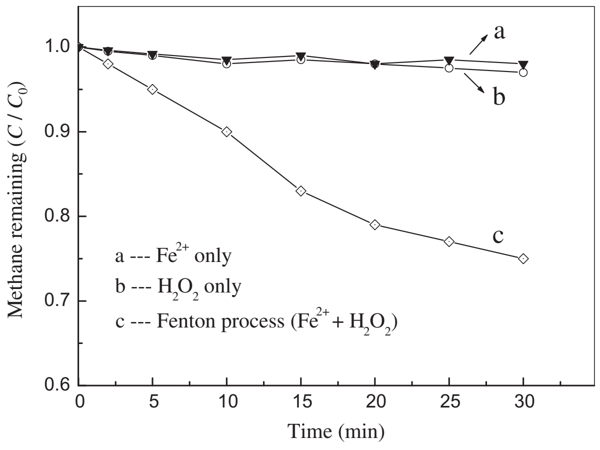

Fig. 2. Methane removal efficiency by various methods. Experimental conditions: 1.50 mM Fe^{2+}, 100 mM H_2O_2, pH 2.5, T = 25 °C.

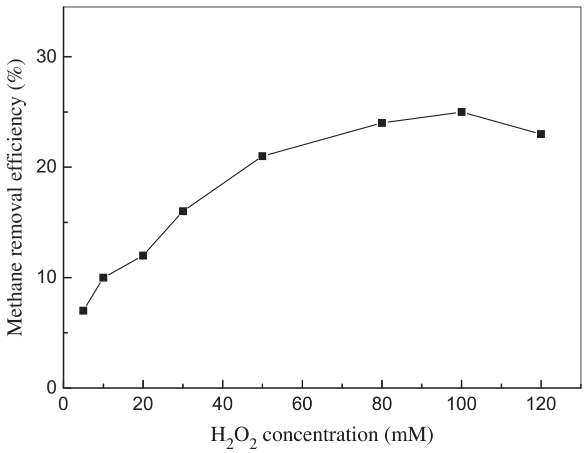

Fig. 3. Effects of H_2O_2 concentration on methane removal efficiency by hydroxyl radical oxidation *via* Fenton reagent. Experimental conditions: 2.00 mM Fe^{2+}, pH 2.5, T = 25 °C.

3.4. Effects of ferrous ion concentration

Ferrous ion acts as catalyst in the Fenton process. Catalyst concentration increases the oxidation rate because iron activates the hydrogen peroxide to form hydroxyl radicals (Mijangos et al., 2006). However, ferrous ion can also be scavenger of hydroxyl radicals as shown in Eq. (4) (Pignatello, 1992). In the excess amounts of ferrous ion, it can react with hydrogen radicals. Then, the hydroxyl radicals in the system will decrease and the organic degradation will also reduce.

To evaluate the effect of ferrous ion, the experiments were conducted on various amounts of ferrous ion as shown in Fig. 4. It can be seen from Fig. 4 that increasing the Fe^{2+} concentration from 0.25 to 2.00 mM enhanced the methane removal efficiencies. The removal of methane increased from 6%, 15%, 22%, 24% to 25% when ferrous ions were applied from 0.25, 0.50, 1.00, 1.50, to 2.00 mM, respectively. The increase in methane removal efficiency can be explained by the rate constant of reaction (1) being 63 $M^{-1} S^{-1}$, while that for reaction (2) is only 0.01 $M^{-1} S^{-1}$ (Martinez et al., 2003). This means that ferrous ions are consumed faster than they are generated. Accordingly, increasing the Fe^{2+} concentration promoted the hydroxyl radical formation through reaction (1) and enhanced the methane removal *via* reaction (8). However, the methane removal decreased to 22% when Fe^{2+} concentration was increased to 2.50 mM. It might be due to the side reaction between ferrous ions and hydroxyl radicals through reaction (4), which has a high rate constant of 3.2×10^8 $M^{-1} S^{-1}$ (Kang et al., 2002). That is, some

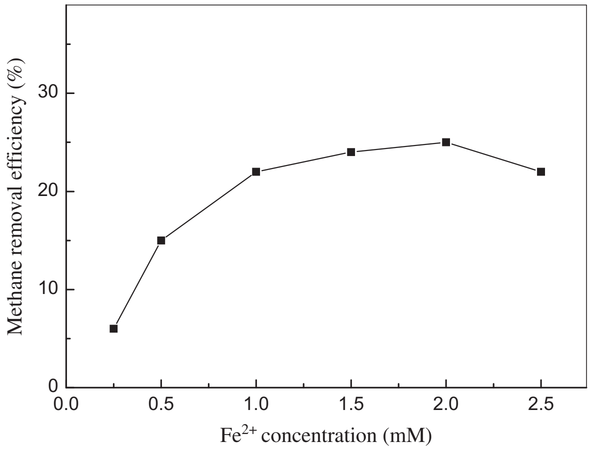

Fig. 4. Effects of ferrous ion concentration on methane removal efficiency by hydroxyl radical oxidation through Fenton reaction. Experimental conditions: 100 mM H_2O_2, pH 2.5, $T = 25$ °C.

available ferrous ion, which did not yet undergo reaction (1), firstly reacted with the produced hydroxyl radicals owing to the competitive oxidation (Eq. (4)). Thus, the concentration of the hydroxyl radicals that could react with the organic pollutants was reduced. Moreover, it may be due to the formation of iron complexes *via* reaction (6). From the study, the optimum initial ferrous ion concentration for degradation of methane was 2.00 mM.

3.5. Effects of initial pH

According to literature, it was frequently reported that the catalytic decomposition of H_2O_2 with ferrous ion (Fenton reaction) can lead to very high efficiency in acid conditions (Lindsey and Tarr, 2000; Zimbron and Reardon, 2005). Walling and Johnson (1975) have reported that pH should be in the range 3–5 to reach maximum organic removal efficiency. Similarly, Wolfgang et al. (2006) have also reported that in high acid conditions (pH < 3) protons can function as scavengers for hydroxyl radicals; however, at low acid medium (pH > 5), the regeneration of Fe^{2+} catalyst becomes difficult because of $Fe(OH)_3$ precipitation.

To examine the influence of initial pH on the efficiency of methane degradation, a set of experiments at initial pH from 1 to 5 was carried out, keeping Fe^{2+} and H_2O_2 doses fixed to 2.00 mM and 80 mM, respectively. Fig. 5 represents the degradation efficiency for methane at different initial pH. The highest methane removal efficiency (24%) was found at pH 2.5. As pH was increased from 2.5 to 5, the degradation efficiency decreased from 24% to 10%. The lowest efficiency was obtained at pH 5, proving that $Fe(OH)_3$ precipitation made the regeneration of Fe^{2+} ions more difficult and consequently limited the formation of hydroxyl radicals. At pH 2 the efficiency of methane removal was lower than that at pH 2.5, which suggested that the scavenging effect of protons toward hydroxyl radicals started to be more important at high acidic conditions. Hence, the optimum initial pH for decomposing methane with hydroxyl radicals generated by Fenton reagent in the present study was pH 2.5.

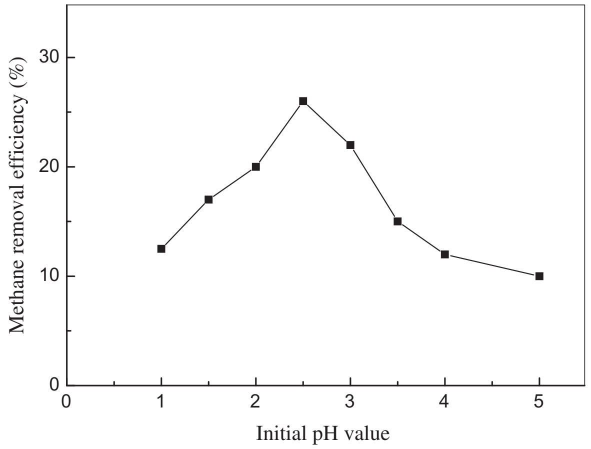

Fig. 5. Effects of initial pH value on methane degradation efficiency by hydroxyl radical oxidation *via* Fenton process. Experimental conditions: 2.00 mM Fe^{2+}, 80 mM H_2O_2, $T = 25$ °C.

Moreover, the effects of varying the flow rate and different components of simulated coal-mine gas on the methane degradation efficiency are under study.

4. Conclusions

In brief, the hydroxyl radical oxidation through Fenton process is effectively used to decompose methane. H_2O_2 concentration, dosage of Fe^{2+}, and initial solution pH value are the primary factors, which influence the removal efficiency of methane. About 25% of methane was degraded under the optimized experimental conditions of 100 mM H_2O_2, 2.00 mM Fe^{2+}, and initial pH value of 2.5 after 30 min. The hydroxyl radical oxidation *via* Fenton process can be a feasible and effective technology for actual coal-mine methane treatment.

Acknowledgements

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References

Chen, Dongke, Lu, Wang, Jin, Longzhe, Xia, Chungu, Jian, Zhang, 2006. The preliminary research on coal-bed gas degradation by microorganism. Journal of China Coal Society 31 (5), 607–609 (in Chinese).

Hoigne, J., Bader, H., 1975. Ozonation of water: role of hydroxyl radicals as ozonizing intermediates. Science 190, 782–784.

Hou, Chentao, Wang, Shengquan, Nie, Wenjie, Zeng, Shejiao, 2008. Preliminary study on application of microorganism technique for coal mine gas control. Mining Safety & Environmental Protection 35 (2), 11–23 (in Chinese).

Kajitvichyanukul, P., Lu, M.C., Jamroensan, A., 2008. Formaldehyde degradation in the presence of methanol by photo-Fenton process. Journal of Environmental Management 86, 545–553.

Kang, N., Lee, D.S., Yoon, J., 2002. Kinetic modeling of Fenton oxidation of Phenol and Monochlorophenols. Chemosphere 47, 915–924.

Lin, S.H., Lin, C.M., Leu, H.G., 1999. Operating characteristics and kinetic studies of surfactant wastewater treatment by Fenton oxidation. Water Research 33 (7), 1735–1741.

Lindsey, M.E., Tarr, M.A., 2000. Quantification of hydroxyl radical during Fenton oxidation following a single addition of iron and peroxide. Chemosphere 41, 409–417.

Liu, Dong, Zhang, Pengyi, Wang, Junwei, 2006. Photocatalytic degradation of methane under irradiation of vacuum ultraviolet light. China Environmental Science 26 (6), 653–656 (in Chinese).

Martinez, N., Fernandez, J., Segura, X., Ferrer, A., 2003. Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent. Journal of Hazardous Materials B101, 315–322.

Mijangos, F., Varona, F., Villota, N., 2006. Changes in solution color during phenol oxidation by Fenton reagent. Environmental Science and Technology 40 (17), 5538–5543.

Nyman, G., Clary, D.C., 1994. Quantum scattering calculations on the $HO + CH_4 \rightarrow H_2O + CH_3$ reaction. Journal of Chemical Physics 101 (7), 5756–5771.

Pignatello, J.J., 1992. Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environmental Science and Technology 26, 944–951.

Pignatello, J.J., Oliveros, E., Mackay, A., 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Critical Reviews in Environmental Science and Technology 36, 1–84.

Sun, Jianhui, Sun, Shengpeng, Fan, Maohong, Guo, Huiqin, Qiao, Liping, Sun, Ruixia, 2007. A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process. Journal of Hazardous Materials 148, 172–177.

United Nations Environment Program, 2001. Climate Change 2001. Trace Gases: Current Observations, Trends, and Budgets.

Walling, C., Johnson, R.A., 1975. Fenton's reagent. V. Hydroxylation and side chain cleavage of aromatics. Journal of the American Chemical Society 97, 363–367.

Watts, R., Teel, A., 2005. Chemistry of modified Fenton's reagent (catalyzed H_2O_2 propagations-CHP) for in situ soil and groundwater remediation. Journal of Environmental Engineering 131, 614–629.

Wolfgang, A.S., Ernst, S., Hans-Jurgen, H., Ulrich, W., 2006. Hydroxyl radical scavenging reactivity of proton pump inhibitors. Biochemical Pharmacology 71, 1337–1341.

Zhang, Tiegang, 2001. Comprehensive Control Technology of Coal-mine Gas. Coal Industry Press, Beijing (in Chinese).

Zimbron, J.A., Reardon, K.F., 2005. Hydroxyl free radical reactivity toward aqueous chlorinated phenols. Water Research 39, 865–869.