Kinetics Analysis of Dicamba Degradation using O_3-Fly Ash Combined Process at Different pH values

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Abstract. Decamba degradation using ozone-fly ash combined process has been studied in laboratory. The effect of pH value on dicamba degradation was investigated. Kinetic analysis was carried out. The experimental results show that pH value has a significant influence on dicamba degaration. The increase of pH value promotes dicamba degradation. Degradation rate constant (*k*) is obtained using pseudo-first-order kinetics to fit the concentration of dicamba. Along with pH value increases, *k* value first increases rapidly, and then increases slow, after that it tends to be steady. High pH value can promote the generation of hydroxyl radicals, enhance the dissociation of dicamba in aqueous solution, and neutralize acidic materials produced during the degradation of dicamba using O_3-fly ash combined process. Collected from different positions of one thermal power plant, finer fly ash has better promotion performance than coarser fly ash on improving ozonation process. The relationship of *k* value and pH value can be fitted well using exponential decay model.

Introduction

Fly ash is a kind of solid waste generated from coal-fired power plants. The output of fly ash is very large and will be increasing in the future. If no effective disposal, fly ash can cause water pollution, soil pollution and air pollution. Many researchers have been trying to find ways to recycle fly ash and solve the disposal problem of fly ash. Yao et al. reviewed the applications of coal fly ash [1]. They mentioned that about 20% of fly ash generated is being used in concrete production. Other uses include road base construction, soil amendment, zeolite synthesis, and use as fillers in polymers. Wee reviewed the availability and the potential of the carbon dioxide capture and storage (CCS) technology using coal fly ash [2]. However, fly ash will be an inconvenient environmental problem if not be beneficially used.

Recently, advanced oxidation processes (AOPs) have aroused more and more interest. Among them, ozonation has been widely used in disinfection of drinking water and deep treatment of water pollution. There are also a growing number of studies reported that the combination of ozonation with other techniques such as O_3-UV [3], O_3-US [4], catalytic ozonation [5] and O_3-H_2O_2 [6, 7] can significantly improve the degradation efficiency. In our previous study [8], the effectiveness of the combined technology of O_3 and fly ash was proved. In this paper, dicamba continues to be model pollutant degraded by O_3-fly ash combined process. Dicamba(3,6-Dichloro-2-methoxybenzoic acid) is used in pastures, cultivated land, lawn, urban green space, and so on. It will cause soil pollution and water pollution during the process of production and application. Dicamba has been detected as a pollutant in water reservoirs or estuarine waters[9]. The control of dicamba contamination in water has been an urgent question required more efforts. In this paper, pH value of aqueous solution, as an important factor, was changed to investigate the effect of pH value on dicamba degradation, and kinetics analysis was carried out .

Experimental Part

The model pollutant used in laboratory was dicamba(Purity>95%, purchased from Shanghai Yuanye Bio-Technology Co., Ltd.). Two kinds of fly ash used in this study were taken from a certain power plant of Hebei province. Fly ash collected from electric field I of Electrostatic Precipitator(ESP) was named No.1 fly ash. Fly ash collected from electric field II and III of ESP was named No.2 fly ash. From the result of screening, No.2 fly ash is finer than No.1 fly ash. pH value of solution was adjusted using sulfuric acid solution or sodium hydroxide solution.

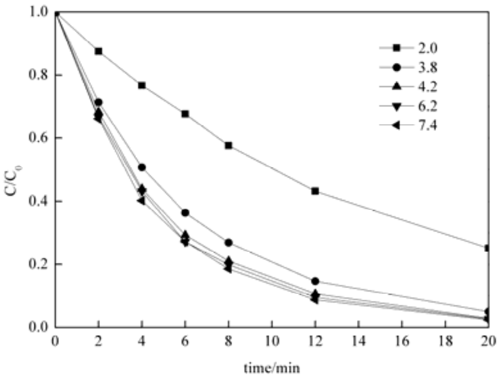
The experimental system consisted of a bubble contactor, an ozone generator and some pipes. The reactor was placed in a temperature-controlled water bath. Mixed gas of ozone and oxygen was produce by the ozone generator(3S-A5, Beijing Tonglin High-tech Technology Co., Ltd. China) using pure oxygen source as feed gas. The reaction solutions were prepared with deionized water. The solution volume in reactor was 900 mL. A certain amount of fly ash was added into the reaction solution and mixed well before gas introducing. The mixed gas was fed into reactor after being adjusted to desirable gas flow rate using rotameter. Samples were withdrawn from the reactor periodically, filtered through 0.22 μm filter membrane, and then analyzed using HPLC.

If there is no particular declaration, the experimental conditions were as follows: the dosage of fly ash was 1.0 g in O_3-No.1 fly ash system, 0.5 g in O_3-No.2 fly ash system; the ozone production ratio was 70%; the gas flow was $1L\cdot min^{-1}$; the temperature was 20 ^oC; the initial concentration of dicamba was $100\ mg\cdot L^{-1}$.

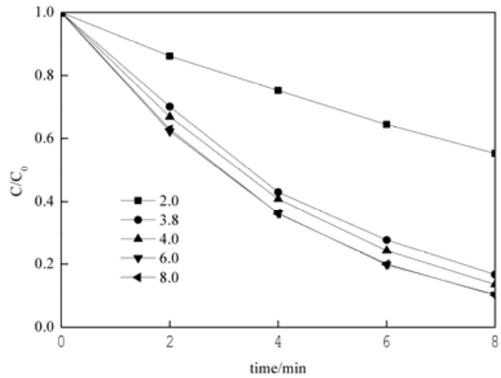
The concentration of dicamba was determined by HPLC (LUMTECH, Lumiere Tech. Ltd. China). The mobile phase was a mixture of methanol and water (volume ratio of 65:35) (pH value was adjusted using phosphoric acid). The flow rate of mobile phase was $1\ mL\cdot min^{-1}$. The injection volume was 20 μL, and the detection wavelength was 230 nm.

Results and Discussions

There are many influence factors during ozone-fly ash combined process, such as temperature, pH value, and so on. Fig. 1 shows the concentration trend of dicamba during ozone-fly ash combined process at different pH values.



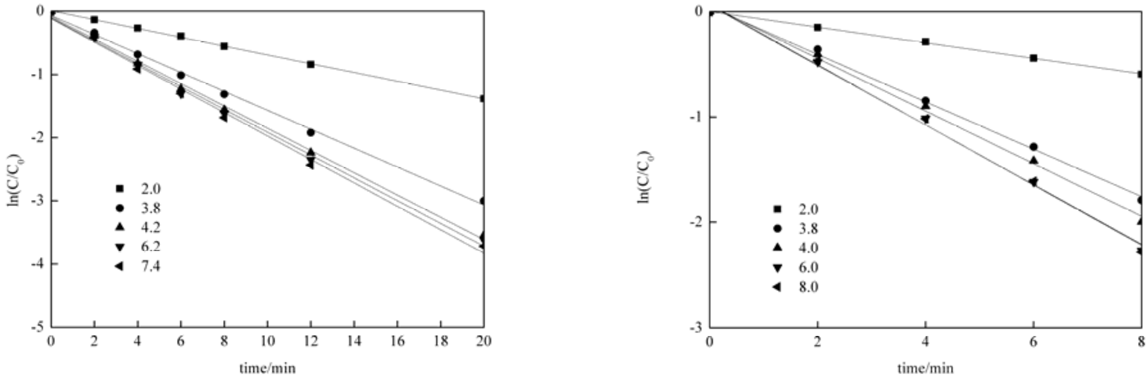
(a) O_3-No.1 fly ash system



(b) O_3-No.2 fly ash system

Fig. 1 Concentration trend of dicamba during process at different pH values

From Fig. 1, it can be seen that pH value have a large effect on dicamba degradation. Both in O_3-No.1 fly ash system or in O_3-No.2 fly ash system, dicamba removal increases with the increase of pH value. In the pH range less than 3.8, the change of pH value has a more significant effect on dicamba removal; but when pH value increases to a certain degree, the effect of pH value becomes weakened. Dicamba degradation was proved to be in accord with pseudo-first-order kinetics[10]. Fig. 2 shows that there is a good linear between $\ln(C/C_0)$ and time(t) in O_3-No.1 fly ash system or in O_3-No.2 fly ash system. The slope of line is the pseudo-first-order rate constant(k). Fig. 3 shows the relationship of k value and pH value in O_3-No.1 fly ash system and in O_3-No.2 fly ash system.



(a) O_3-No.1 fly ash system (b) O_3-No.2 fly ash system

Fig. 2 Graph of $\ln(C/C_0)$ vs. time at different pH values

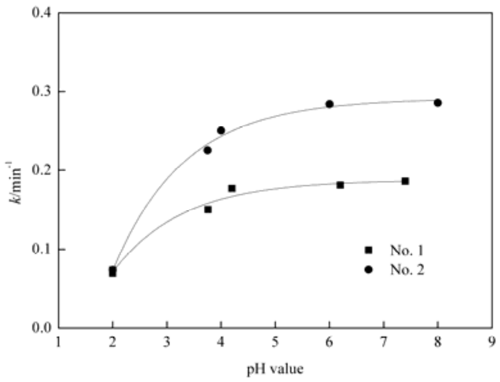


Fig. 3 Graph of k vs. pH value

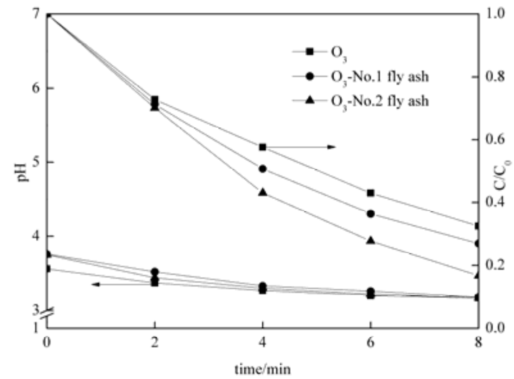


Fig. 4 Variation of pH value in reaction solution

Along with pH value increases, k value first increases rapidly, and then the increasing trend is gradually slow down, until to a certain value. Either in O_3-No.1 fly ash system or in O_3-No.2 fly ash system, k value increases with pH value increases. When pH value is 2.0, k values of the two systems are basically the same. At this pH value, there are more acidic substances in aqueous solution, the acidic substances can inhibit ozone decomposition to generate hydroxyl radicals. At that conditions, direct oxidation of ozone molecule plays dominant role in dicamba degradation. Considering that the promotion of fly ash on ozonation is mainly to promote ozone decomposition to produce more hydroxyl radicals, hence, the promoting effect of fly ash is no longer functioning at this conditions. In the pH range of more than 2.0, k values of O_3-No.2 fly ash system is larger than that of O_3-No.1 fly ash system. During degradation process of dicamba, pH value of solution plays its role from three aspects. Firstly, high pH value promotes decomposition of ozone to generate more hydroxyl radicals. The chain reaction of O_3 decomposition to generate hydroxyl radicals is initiated by hydroxyl ions in pure water. The higher pH value, the more concentration of hydroxyl ions present in aqueous solution, and the more hydroxyl radicals are produced. Secondly, solution alkalinity neutralizes acidic materials produced during dicamba degradation. From Fig.4, it can be seen that pH value of solution shows a trend of slow downward as the reaction is carried out, which indicate that acidic materials is produced during the reaction process. The lower the initial pH value is, the more acidic substances is present in aqueous solution, which inhibits the degradation direction accompanying with acidic materials production. When the initial pH value is relatively high, there are more hydroxyl ions to neutralize the acidic intermediates, promotes reaction, enhances degradation rates. Thirdly, pH value affects the dissociation species of organics in aqueous solution. Dicamba dissolved in water can be dissociated to ionic and non-ionic species. The ionic species is more easily degraded than the non-ionic species. The rate constant of ionic species degradation is bigger than the non-ionic species. High pH value promotes the dissociation of dicamba and thereby promotes degradation. When pH value rises to a certain value, however, more and more hydroxyl radicals are produced with the increase of pH value. As a consequence, the chances of collision of hydroxyl radicals becomes increasing. The quenching of hydroxyl radicals leads to that the promotion effect of pH value becomes less apparent. In conclusion, the effect of pH value on dicamba degradation is a comprehensive process. Exponential decay equations can be used to simulate well the relationship of *k* value with pH value：

O_3-No.1 fly ash system: k=0.19-0.55exp(-pH/1.29) (R^2=0.98) (1)

O_3-No.2 fly ash system: k=0.29-0.99exp(-pH/1.32) (R^2=0.99) (2)

Conclusion

During degradation of dicamba using O_3-fly ash combined process, pH value is a significant influence factor. With the increase of pH value, dicamba degradation is promoted. Along with the pH value increases, pseudo-first-order degradation rate constant (*k*) first increases rapidly, and then increases slowly, finally tends to be a certain level. At nearly same pH value, the finer fly ash has more obvious promotion on than relative coarse fly ash. High pH value can promote ozone decomposition to generate more hydroxyl radicals, neutralize acid intermediates produced during the degradation process and promote the dissociation of organics in aqueous solution to bring about more ionic species.

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References

[1] Z. T. Yao, X. S. Ji, P. K. Sarker, J. H. Tang, L. Q. Ge, M. S. Xia, Y. Q. Xi. A comprehensive review on the applications of coal fly ash[J], Earth-Science Reviews. 2015, 141: 105-121.

[2] J. H. Wee. A review on carbon dioxide capture and storage technology using coal fly ash[J]. Applied Energy, 2013, 106: 143-151.

[3] W. Zhao, Q. Liao, J. Zhang, Y. Yang, J. Dai, D. Zhao. Oxidation of Cationic Red X-GRL by ozonation combined with UV radiation in aqueous solution: degradation, kinetics, and modeling[J]. Chemical Engineering Journal, 2011, 171: 628-639.

[4] Z. He, L. Lin, S. Song, M. Xia, et al. Mineralization of C.I. Reactive Blue 19 by ozonation combined with sonolysis[J]. Separation and Purification Technology, 2008, 62: 376-381.

[5] L. Yuan, J. Shen, Z. Chen, Y. Liu. Pumice-catalyzed ozonation degradation of p-chloronitrobenzene in aqueous solution[J]. Applied Catalysis B: Environmental, 2012, 117-118: 414-419.

[6] L.Chen, Y.Quan. Effect of coexisting substances on degradation of 2,4-D in O_3/H_2O_2 process(I) 2,4-D degradation kinetics[J]. CIESC Journal, 2011, 62:2920-2925(in Chinese).

[7] L.Chen, Y.Quan. Effect of coexisting substances on degradation of 2,4-D in O_3/H_2O_2 process(II) Kinetics analysis of chlorine and hydrogen peroxide[J]. CIESC Journal, 2011, 62: 2926-2931.

[8] L. Chen, Y.Y. Wang. Degradation of Dicamba in Aqueous Solution Using Ozonation Assisted by Fly Ash[C]. 2015 International Conference on Electrical Engineering and Mechanical Automation (ICEEMA 2015), Wuhan.

[9] D.B. Donald, A.J. Cessna, E. Sverko, N.E. Glozier. Pesticides in surface drinking water supplies of the northern Great Plains[J], Environ. Health Perspect. 2007, 115: 1183-1191.

[10] L. Chen. Influence Factor of Dicamba Degradation Using O_3-FA Process in Aqueous Solution[C]. 2015 International Conference on Electrical Engineering and Mechanical Automation (ICEEMA 2015), Wuhan. .