

LPWCO method for the treatment of high concentrated organic wastewater

Yang Run-chang, Shu Ming-jun

Department of Environmental Engineering, Xiangtan University, Xiangtan 411105, China

Zhou Shu-tian

Department of Environmental Engineering, Xiangtan University, Xiangtan 411105, China

Abstract—Based on wet air oxidation (WAO) and Fenton reagent, this paper raised a new low pressure wet catalytic oxidation (LPWCO) which requires low pressure for the treatment of highly concentrated and refractory organic wastewater. Compared with general wet air oxidation, the pressure of the treatment (0.1—0.6MPa) is only one of tens to percentage of latter (3.5—10MPa). In addition, its temperature is no more than 180°C. Compared with Fenton reagent, while H_2O_2/COD (weight ratio) is less than 1.2, the removal of COD in the treatment is over twenty percents more than Fenton's even the value of COD is more than 14000mg/L. In this paper, the effect factor of COD removal and the mechanism of this treatment were studied.

The existence of synergistic effect (catalytic oxidation and carbonization) for COD removal in H_2SO_4 -Fenton reagent system under the condition of applied pressure and heating (0.1—0.6MPa, 104—165°C) was verified. The best condition of this disposal are as follows: H_2O_2/COD (weight ratio) = 0.2—1.0, Fe^{2+} 0.6×10^{-3} mol, H_2SO_4 0.5mol, $COD > 1 \times 10^4$ mg/L, the operating pressure is 0.1—0.6MPa and temperature is 104—165°C. This method suits to dispose the high-concentrated refractory wastewater, especially to the wastewater containing H_2SO_4 produced in the manufacture of pesticide, dyestuff and petrochemical works.

Keywords: wet oxidation; Fenton reagent; catalytic oxidation; organic wastewater treatment.

1 Introduction

Many industries (such as pesticide, paper making and dyestuff) may drain off highly concentrated, inbiodegraded, and even pernicious organic wastewater. Technologies of this water's disposition have been positively developed in home or abroad. In all those technologies, wet air oxidation developed by Zimpro in USA had been successfully applied in the disposition of city sewage sludge, paper black liquor, and sewage of petrochemical engineering. About more than 300 pieces of equipment are used all over the world. However, this kind of technology needs high pressure and temperature. What's more, it's expensive. In China, the research of this method has been under way since 1980's. However until now, there is no an intact set of industrial equipment. Since 1960's, when Eisenhower first used Fenton reagent in the disposing of the sewage contained phenol and the water contained alkyl benzene's people paid more attention to the

* Corresponding author

study of the Fenton reagent's use in disposing of wastewater. Fenton reagents especially useful to inbiodegraded wastewater or the wastewater that cannot be disposed by general chemical oxidation process. Yet this technology is expensive. The higher the oxidation removal ratio of organic is, the bigger $[H_2O_2]/[organic]$ required. So this method is hard to be used widely to highly concentrated organic wastewater(Wan, 1994; Wang, 1995).

Based on two ways described above, this article probes into a new way to deal with highly concentrated inbiodegraded organic wastewater. This new way is low pressure wet catalytic oxidation(LPWCO). LPWCO mainly utilizes the cooperation between Fenton reagent and sulfuric acid. Under low temperature and pressure, the cooperation let the organic in wastewater be disposed by wet catalytic oxidized and carbonization, which can promote the industrial process of wet oxidation.

2 Experimental method

2.1 Devices and reagents

Stainless steel reactor ($< 1.6\text{MPa}$); wastewater containing phenol that compounded by chemically pure phenol; 98% sulfuric acid; 30% H_2O_2 and $FeSO_4 \cdot 7H_2O$ are all chemically pure.

2.2 Experimental method

The experiment of this study first goes on with high concentrated phenol, then with high concentrated dyestuff and pesticide. The process of the experiment are: put some certain concentrated phenol, sulfuric acid, $FeSO_4$ and H_2O_2 into reactor first, then let volume of reactants be $1/2$ — $1/3$ of reactor's (required reaction inliquor phase) by distilled water, and then seal up the reactor, heat to increase pressure and temperature. After reaction, cool down and take the sample to analysis.

3 Experimental results and discussion

3.1 The effects of $[H_2O_2]$

Take certain amount of wastewater, containing phenol ($[phenol] = 6000\text{mg/L}$, $[COD] = 14350\text{mg/L}$), as an sample, add H_2SO_4 ($[H_2SO_4] = 0.939\text{mol}$), $FeSO_4 \cdot 7H_2O$ ($[Fe^{2+}] = 0.00121\text{mol}$), and different amount of H_2O_2 in the sample. Under 0.6MPa , 165°C , let the reaction react for an hour. Then take out some sample to analysis. Illustrate the results in Fig.1.

In Fig.1 comparing the dots: a, b, c, and d, the cooperation of H_2SO_4 and Fenton reagent can be displayed clearly when pressurized and heated. Dot c displays that, by using Fenton reagent, the removal of COD is 56%. Dot b displays the rest is 60% when pressurized and

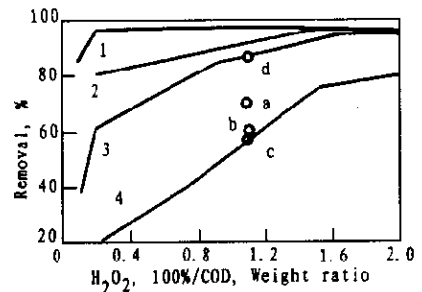


Fig.1 Relationship between H_2O_2/COD and removal of COD and phenol
1. LPWCO removal of phenol; 2. Fenton removal of phenol; 3. LPWCO removal of COD; 4. Fenton removal of COD

heated. Under the same conditions as dot a displays the rate is 70% when using H_2SO_4 . Dot d is 85% by using $\text{H}_2\text{SO}_4 + \text{Fenton}$ reagent. Based on the comparison above, it's obvious that the cooperation is not a simple addition.

3.2 The effects of $[\text{Fe}^{2+}]$

Conditions of experiment are the same as 3.1. Fix the concentration of $[\text{H}_2\text{O}_2]$ in water sample on 0.49mol, $\text{H}_2\text{O}_2/\text{COD}$ is 1.15. Only change the concentration of Fe^{2+} . The results are shown in Fig. 2.

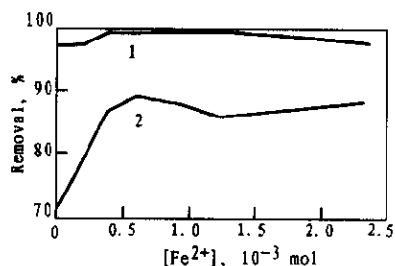
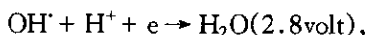
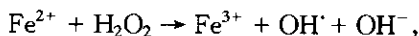


Fig.2 Relationship between $[\text{Fe}^{2+}]$ and removal of COD and phenol
1. removal of phenol; 2. removal of COD

Just as Fig.2's describing, in LPWCO, the concentration of Fe^{2+} does not influence phenol's removal much. The H_2O_2 is a strong oxidizing agent itself. When heating; pressing and putting H_2SO_4 in H_2O_2 can destroy the hydroxyl in phenol easily. Even not put Fe^{2+} in wastewater, the removal rate of phenol can be as high as 98%. However, the concentration of Fe^{2+} affects the removal rate of COD much more. If there is no Fe^{2+} , the cooperation between H_2O_2 and H_2SO_4 can reduce 70% of COD, with $[\text{Fe}^{2+}]$ increasing to $0.6 \times 10^{-3} \text{ mol}$, the removal rate increases 20%. After this, when $[\text{Fe}^{2+}]$ increasing more, it does not influence the removal rate

much, which indicates that under this condition Fe^{2+} has catalytic effect. Fe^{2+} can decompose H_2O_2 to OH^\cdot catalytically. The electrode voltage of OH^\cdot is much higher than H_2O_2 (Fraser, 1984).



So, H_2O_2 in Fenton reagent has higher oxidation ability than single and can remove more COD. So, H_2O_2 in Fenton has more oxidized ability than single H_2O_2 and it can remove more COD.

Before and after reaction, Fe^{2+} in sample can be analysis by atomic absorption spectrophotometer. The result indicates that the total amount Fe^{2+} does not change. This study also analysis the black sediment in sample and does not find Fe^{2+} . It states once again that the Fe^{2+} in LPWCO is just a catalysis.

3.3 Influence of H_2SO_4

Experimental condition is basically the same as above, $[\text{Fe}^{2+}]$ is fixed on $0.604 \times 10^{-3} \text{ mol}$. Put in different amount H_2SO_4 and go on LPWCO experiment date results in Fig. 3.

Fig. 3 indicating, if not put in H_2SO_4 , under the same pressure and temperature, the removal rate of COD by Fenton reagent is 64.4% (under normal temperature is 56%). When put in H_2SO_4 because of H_2SO_4 's dehydrogenating, polymerizing and carbonizing actions, the removal rate of COD is higher according to increasing. But these defects can only be useful to big molecule, these is no effect. So, when H_2SO_4 's increases beyond a certain limit, if $\text{H}_2\text{O}_2/\text{COD}$ is fixed, the

removal rate of COD can increase not.

SO_4^{2-} in water sample before and after experiment is catalytic analysis by barium-chloride test. The results show that the total amount of SO_4^{2-} did not change, which indicates that H_2SO_4 is also a catalytic in the reaction.

3.4 The influence of temperature and pressure

Take a certain amount of water sample whose concentration is different phenol, and fix $[\text{H}_2\text{SO}_4]$ on 0.563mol (that is 5.4%), $[\text{Fe}^{2+}]$ in 0.604×10^{-3} mol, $[\text{H}_2\text{O}_2]$ in 0.491 mol, heat to different pressure and temperature. After reaction, cool down and take the sample to analysis.

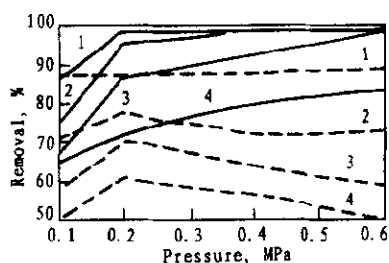


Fig. 4 Relationship between pressure (temperature) and removal of COD and phenol

----- phenol removal; ——— COD removal

1. COD = 14350mg/L, $\text{H}_2\text{O}_2/\text{COD} = 1.16$, $\text{H}_2\text{SO}_4/\text{COD} = 3.43$

2. COD = 35870mg/L, $\text{H}_2\text{O}_2/\text{COD} = 0.481$, $\text{H}_2\text{SO}_4/\text{COD} = 1.53$

3. COD = 71750mg/L, $\text{H}_2\text{O}_2/\text{COD} = 0.231$, $\text{H}_2\text{SO}_4/\text{COD} = 0.76$

4. COD = 107600mg/L, $\text{H}_2\text{O}_2/\text{COD} = 0.155$, $\text{H}_2\text{SO}_4/\text{COD} = 0.51$

cheap biochemistry methods.

Compared with WAO, though consuming more H_2O_2 , but the operating pressure of this technology is only ten percent of WAO's. Thus, the investment of equipment is reduced greatly, and the operation condition is much more moderated, which are good to realize the industrialize.

4 The experiment of dyestuff and pesticide wastewater

Compound different high concentrated dyestuff, pesticide and phloroglucinol wastewater that are indegraded. According to 3.4, fix the pressure and do the experiment ($[\text{H}_2\text{SO}_4]$ on 0.563 mol, $[\text{Fe}^{2+}]$ of 0.604×10^{-3} mol, $[\text{H}_2\text{O}_2]/[\text{COD}] = 1.15$, 0.6MPa, 165°C, 1 hour). The

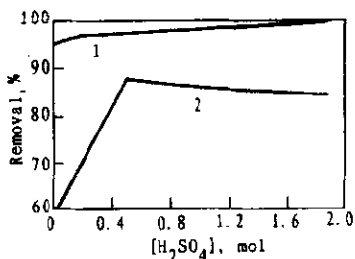


Fig. 3 Relationship between $[\text{H}_2\text{SO}_4]$ and removal of COD and phenol
1. removal of phenol; 2. removal of COD

From Fig. 4, we can see that pressure (temperature) does not influence the removal rate so much, which indicates that in this reacted scope. Pressure (temperature) is not the decisive factor in LPWCO.

3.5 Discussion

Compared with Fenton reagent, LPWCO can remove about 40 percent of COD when $\text{H}_2\text{O}_2/\text{COD}$ is 0.2—0.8. Thus, to high concentrated poisonous organic effluent, LPWCO can be used as anticipation, then use biochemistry as a further step. The compasion of those two steps is an effectively, practically disposal technology. In this technology, LPWCO can degrade most poisonous organic and remove most parts of which avoids the high consumption of H_2O_2 in Fenton. The rest COD is mainly small molecule, and organic which can be degraded easily, such as formic acid, acetic acid and propionic acid, which can be removed by using the

results are shown in Table 1 and Fig. 5.

Table 1 The results of the experiment of dyestuff and pesticide wastewater

	Water sample concentration, mg/L	Before reaction of COD, mg/L	After reaction of COD, mg/L	Removal of COD, %
Reactive brilliant				
red	5.0	3450	720.6	79.1
Mettles blue	5.0	5158	1269	75.4
Dodecyl sodium sulfate	10.0	21400	5154	76.0
Methamidophos	11.0	9418	1643	82.6

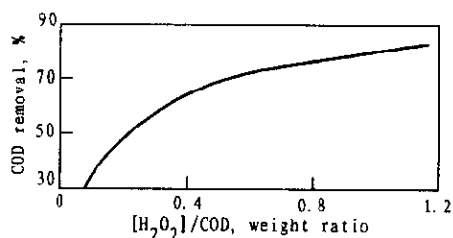


Fig.5 Relationship between $[H_2O_2]$ and removal of phloroglucinol COD

Just as the results show, the effect using LPWCO to dispose the high-concentrated, indegradated organic wastewater is good. This method can suit many kinds of pollution.

5 Conclusion

The synergistic effect of catalytic oxidation and carbonization of COD removal in H_2SO_4 -Fenton system under the condition of increasing pressure and heat was existence. This method suits to dispose the high-concentrated wastewater, especially to the wastewater containing H_2SO_4 produced in the manufacture of pesticided, dyestuff and petrochemical engineering.

The better conditions of the disposal are as follows: H_2O_2/COD (weigh ratio) = 0.4—0.8, $[Fe^{2+}] = 0.6 \times 10^{-3} \text{ mol}$, $[H_2SO_4] = 0.5 \text{ mol}$, $COD > 1 \times 10^4 \text{ mg/L}$, the operating pressure is 0.2—0.6MPa, temperature is 120—165°C.

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