Contrast Experiment on Advanced Treatment of Pharmaceutical and Paper-making Wastewater through Cinder Fenton-like Process

Jia Xiaofeng[1,2], *Chen Xiaoyu*[2], and *Mai Wenning*[3]

[1]Luohe Yinge Industrial Group Co., Ltd,462003, Luohe, Henan, China
[2]Zhengzhou University of Aeronautics,450000, Zhengzhou, China
[3]Zhengzhou University of Aeronautics,450000, Zhengzhou, China

Abstract. The Fenton-like process of catalyzing H_2O_2 with Fe^{2+} and cinder is adopted to subject pharmaceutical and paper-making wastewater to advanced treatment. The influence of each factor is determined using orthogonal experiment and single factor test. The optimal combination of influencing factors is $0.3mmol \cdot L^{-1}$ of $FeSO_4 \cdot 7H_2O$, $[H_2O_2]:[Fe^{2+}]=8:1$ and $10g \cdot L^{-1}$ of pyrites cinder. The reaction time in pharmaceutical wastewater and paper-making wastewater is 30min and 60min respectively, testifying to the fact that the reaction in pharmaceutical wastewater is faster than that in paper-making wastewater and the lower utilization rate of cinder in pharmaceutical wastewater. Under the optimal reaction condition, the COD removal rate of these two kinds of wastewater can reach as high as 65% and 72%. Characterized by simple operation and requiring less reagent dosage, this method does not have to regulate the pH of flooding water and allows the repeated usage of cinder.

1 Introduction

Fenton reaction[1] refers to the production of hydroxyl radical with strong oxidizing property by catalyzing H_2O_2 with Fe^{2+} that is used to oxidize and degrade contaminants. Despite its strong oxidizability, Fenton's reagent first requires the addition of acid and then alkali to adjust the pH to neutral. The complicated operation and frequent adjustment of pH will increase the operational costs and investment costs of infrastructure equipment[2].

With Fe content of 30~55% and Si, Ca, Mg, Mn, Cu and Zn, pyrites cinder refers to the waste residue from the production of sulfuric acid with pyrite[3]. Recent researches show that the pyrites cinder is highly active in catalyzing [4-5]the oxidation of H_2O_2 and effective in forming the new Fenton-like reaction with surface catalysis as the mechanism, which testifies to good treatment of Acid Red B, phenol and many other actual industrial wastewater.

The wastewater from a pharmaceutical company and a paper-making company in Henan are all subjected to the traditional anaerobic and aerobic treatment. The pharmaceutical wastewater, with complicated components, high concentration, high toxicity, dark color and strong smell, hardly degradable substances and inhibitory drugs[6-7], is difficult to be treated. With the implementation of *Discharge Standard of Water Pollutants for Pharmaceutical Industry Fermentation Products Category* (GB21903-2008), the single secondary biological treatment cannot satisfy the requirements. Characterized by high chromaticity and poor biodegradability, the paper-making wastewater usually contains chlorinated aromatic compounds[10] as a result of the usage of decolorizer, thus bringing harm to environment and human health[11]. For these reasons, it is a must to subject both the pharmaceutical and paper-making wastewater to advanced treatment. Under the condition of not regulating pH, the experiment of treating the secondary effluent from pharmaceutical and paper-making wastewater with H_2O_2 under the catalysis of pyrites cinder shows that there is no obvious decrease of COD. Therefore, the author intends to adopt the Fenton-like process of catalyzing H_2O_2 with pyrites cinder and Fe^{2+} to study the feasibility of the advanced treatment of pharmaceutical and paper-making wastewater.

2 Materials and methods

2.1 Test water quality

The water is from the aerobic treatment secondary effluent of a pharmaceutical and a paper-making company in Henan, whose quality is presented in Table 1.

Table 1. Water quality of secondary effluent

Item	ρ (CODcr)/ (mg·L^{-1})	ρ (BOD5)/ (mg·L^{-1})	ρ (SS)/ (mg·L^{-1})	pH

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*Corresponding author: 191826850@qq.com

Pharmaceutical Wastewater	100~150	12~16	40~60	7.5~8.0
Paper-making Wastewater	240~270	20~40	30~50	7.5~8.5

For easier comparison, the paper-making wastewater is diluted with equal amount of water during experiment.

2.2 Experimental method

1000 mL wastewater, together with pyrites cinder and a certain amount of $FeSO_4 \cdot 7H_2O$ and H_2O_2(30%) is added to the 1000 mL beaker for reaction. After 20min of aeration and 30min of static settlement, the supernate is taken to test its COD.

2.3 Analysis item and methods

pH: glass electrode method; COD: potassium dichromate method; BOD: standard dilution method; SS: 103~105℃ oven drying and weighing method[12].

3 Results and analysis

3.1 Orthogonal test

The four controllable parameters, namely, amount of pyrites cinder, $[H_2O_2]:[Fe^{2+}]$, dosage of $FeSO_4 \cdot 7H_2O$ and reaction time, are used as the influencing factor of orthogonal test. Three representative levels of each influencing factor is chosen and presented in Table 2.

Table 2. Influencing factor and level of orthogonal test

Level	Influencing Factor			
	Cinder Amount/(A) (g·L⁻¹)	(B) [H₂O₂]:[Fe²⁺]	n(Fe²⁺) /(C) (mmol·L⁻¹)	Reaction Time /(D) (min)
1	5	4:1	0.1	20
2	15	8:1	0.2	60
3	30	12:1	0.3	120

According to the determined factor, level and the L9(3⁴) orthogonal table, the experiment is carried out with COD removal rate as the standard of evaluation, as shown in Table 3. The size of influencing factor determined through range is shown in Table 4.

Table 3. Orthogonal text results

Test No.	A	B	C	D	Removal Rate of COD in Pharmaceutical Wastewater%	Removal Rate of COD in Paper-making Wastewater%
1	5	4:1	0.1	20	18.6	25.7
2	5	8:1	0.2	60	57.3	67.5
3	5	12:1	0.3	120	61.1	70.2
4	15	4:1	0.2	120	39.2	43.7
5	15	8:1	0.3	20	64.7	68.6
6	15	12:1	0.1	60	42.6	54.7
7	30	4:1	0.3	60	48.3	44.3
8	30	8:1	0.1	120	41.8	48.7
9	30	12:1	0.2	20	55.3	63.5

It is shown in Table 3 and 4 that the influence of each influencing factor of pharmaceutical wastewater in descending order is C>B>D>A; the optimal combination is $A_2B_2C_3D_1$, which means the dosage of pyrites cinder of 15g·L⁻¹, dosage of $FeSO_4 \cdot 7H_2O$ of 0.3mmol·L⁻¹, $[H_2O_2]:[Fe^{2+}]$ (molar ratio) of 8:1 and reaction time of 20min. The influence of each influencing factor of pharmaceutical wastewater in descending order is B>C>A>D. The optimal combination is $A_1B_3C_3D_3$, which means the dosage of pyrites cinder of 5g·L⁻¹, dosage of $FeSO_4 \cdot 7H_2O$ of 0.3mmol·L⁻¹, $[H_2O_2]:[Fe^{2+}]$ (molar ratio) of 12:1 and reaction time of 120min. It shows that the degrading effect in pharmaceutical wastewater under the catalysis of H_2O_2 with cinder and Fe^{2+} is worse than that in paper-making wastewater; however, it takes longer time to treat the paper-making wastewater because cinder can obviously adsorb the chromaticity of paper-making wastewater. However, complete degradation is very slow.

Table 4. Range Analysis(a)

Analysis Item	Pharmaceutical Wastewater			
	A	B	C	D
K1	45.67	35.37	34.33	46.2
K2	48.83	54.6	50.6	49.4
K3	48.47	53	58.03	49.53
Range R	3.16	19.23	23.7	3.33

Table 4. Range Analysis(b)

Analysis Item	Paper-making Wastewater			
	A	B	C	D
K1	54.47	37.9	42.03	52.6
K2	55.67	61.6	58.23	54.5
K3	52.17	61.8	61.03	54.2
Range R	3.5	23.9	19	1.9

3.2 Single factor analysis

The single factor analysis is carried out by controlling the best level determined by orthogonal test.

3.2.1 Influence of molar ratio of $[H_2O_2]:[Fe^{2+}]$

To compare the treatment effect in the two different wastewater under the same condition, 10g pyrites cinder and 0.3mmol $FeSO_4 \cdot 7H_2O$ are added for 60min of reaction in order to study the influence of different H_2O_2 dosage on the removal rate of COD in these two different wastewater. The experimental results are shown in Fig. 1.
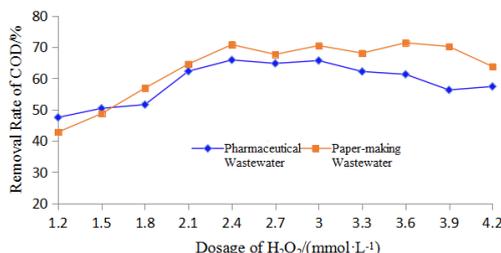

Fig. 1 The influence of H_2O_2 dosage on COD removal effect

Fig. 1 shows that along with the increasing dosage of H_2O_2, the removal rate of COD in pharmaceutical wastewater first increases significantly and then slowly, resulting in the decrease in the removal rate of COD. At lower dosage of H_2O_2, the production rate of OH· along with the increase in the initial concentration, thus significantly increasing the removal rate of COD. At higher dosage of H_2O_2, OH· will be captured by H_2O_2 and Fe^{2+} as it is produced at very fast rate. The ineffective decomposition of H_2O_2 is accelerated with Fe^{2+} oxidized into Fe^{3+}, which impedes catalysis and gives rise to the unobvious removal effect of COD. With excessive dosage of H_2O_2, Fe^{2+} will soon be oxidized into Fe^{3+} at the beginning of reaction. The excessive H_2O_2 will also soon be broken into H2O and O_2 and compete with organic matters for OH· and other free radicals, thus reducing the removal rate of COD. However, the COD removal rate in paper-making wastewater at the later stage decreases insignificantly because the cinder, with good adsorption effect, can thoroughly utilize the iron in the iron in the cinder. An overall consideration of the treatment requirements of wastewater and the important impact of H_2O_2 dosage on operation costs shows that 2.4mmol H_2O_2 can apply to these two wastewater; in other words, the molar ratio of $[H_2O_2]:[Fe^{2+}]$ should be 8:1.

3.2.2 The influence of the dosage of FeSO₄·7H₂O

Under the condition of dosage of cinder of 10g, $[H_2O_2]:[Fe^{2+}]$ of 8:1 and reaction time of 60 min, the dosage of $FeSO_4 \cdot 7H_2O$ is adjusted. The influence of the dosage of $FeSO_4 \cdot 7H_2O$ on COD removal rate is shown in Fig. 2.

Fig. 2 shows that COD removal rate rises along with the increase of Fe^{2+} dosage. Fe^{2+} is the essential condition for the production of hydroxyl radical. Under the catalysis of Fe^{2+}, the following reactions will take place[13-14]:
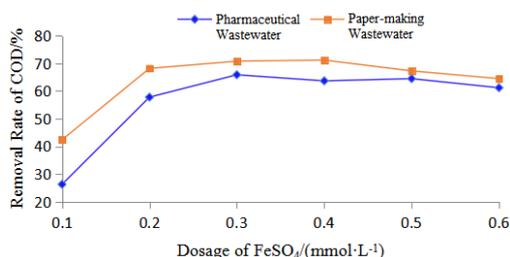
$$Fe^{2+}+H_2O_2 \rightarrow OH^-+\cdot OH+Fe^{3+} \quad (1)$$

$$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+H^++\cdot O_2H \quad (2)$$

$$RH+\cdot OH \rightarrow R\cdot+H_2O \quad (3)$$

$$R\cdot+H_2O_2 \rightarrow ROH+\cdot OH \quad (4)$$

$$Fe^{2+}+\cdot OH \rightarrow OH^-+Fe^{3+} \quad (5)$$
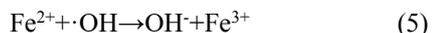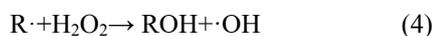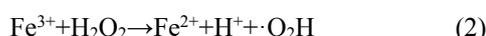

Fig. 2 The influence of $FeSO_4$ dosage on COD removal effect

Higher $[Fe^{2+}]$ content will promote the reaction in equation (1) and the high production rate of hydroxyl radicals. After the reaction, the Fe^{3+} produced is possessed of flocculation, which can remove some of

COD after precipitation and filtration. However, the too high dosage of Fe^{2+} will also promote the reaction in equation (5) without significantly increasing the removal of COD. As a result, there will also be an increase in the dosage expense and sludge quantity, which will cause secondary pollution. For this reason, the dosage of $FeSO_4 \cdot 7H_2O$ is determined as 0.3mmol·L^{-1}.

3.2.3 The influence of dosage of pyrites cinder

Under the condition of the dosage of $FeSO_4 \cdot 7H_2O$ of 0.3mmol, $[H_2O_2]:[Fe^{2+}]$ of 8:1 and reaction time of 60min, the dosage of pyrites cinder is regulated, whose impact on COD removal rate is shown in Fig. 3.
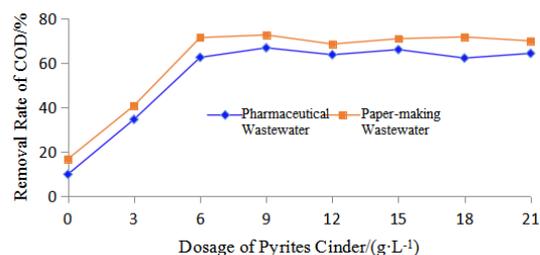

Fig. 3 The influence of dosage of pyrites cinder on COD removal effect

Fig. 3 shows that at lower content of cinder, the COD removal rate rises along with the increase in cinder dosage. After the dosage reaches a certain amount, there is a limited increase in COD removal rate. However, due to its large volume in the reactor and large pressure drop, the power expenses increase. Comparison shows that the optimal dosage of cinder in these two different wastewater is determined as 10g·L^{-1}.

3.2.4 The influence of reaction time

Under the condition of the dosage of $FeSO_4 \cdot 7H_2O$ of 0.3mmol, 10g pyrites cinder and $[H_2O_2]:[Fe^{2+}]$ of 8:1, the influence of different reaction time on COD removal effect is investigated with experimental results shown in Fig. 4.
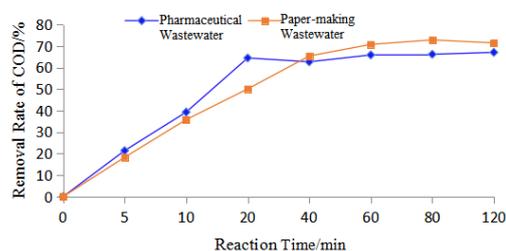

Fig. 4 The influence of reaction time on COD removal effect

It is presented in Fig. 4 that the pharmaceutical wastewater reacts faster than the paper-making wastewater. The COD removal rate basically reaches the highest after 20min in pharmaceutical wastewater and 60min in paper-making wastewater. As the reaction time prolongs, there is no obvious change in removal rate because at the beginning of the reaction, the large amount of H_2O_2 reacts with Fe^{2+} to produce abundant OH·, which immediately attacks organic matters and oxidizes the unreacted Fe^{2+}. As a result, at the beginning of the reaction, the degradation velocity of COD is very

high. As the reaction continues, H_2O_2 and Fe^{2+} are gradually consumed. Although Fe^{3+} can still be reduced to Fe^{2+}, this reduction reaction is carried out at a lower rate. In this process, Fe^{3+} might be hydrolyzed, which will reduce the degradation rate of organic matters. For these reasons, the best reaction time of pharmaceutical wastewater is determined as 30min while that of paper-making wastewater as 60min.

3.2.5 Reutilization experiment of pyrites cinder.

The single factor experiment is conducted under the optimal condition, namely, dosage of $FeSO_4 \cdot 7H_2O$ of 0.3mmol, 10g pyrites cinder, $[H_2O_2]:[Fe^{2+}]$ of 8:1, 30min reaction in pharmaceutical wastewater and 60min reaction in paper-making wastewater. After each experiment, the wastewater is discarded and the cinder saved to investigate the influence of times of pyrites cinder usage on the COD removal rate in the wastewater with the results shown in Fig. 5.
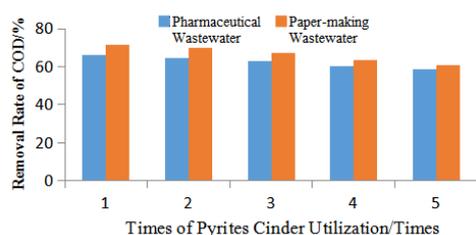

Fig. 5 The influence of the times of pyrites cinder utilization on COD removal rate

It can be seen from Fig. 5 that along with the increase of utilization times, the catalytic effect of cinder reduces but in an insignificant way. After five times, the COD removal rate in these two paper-making wastewater still remains at 60%, a fact indicating that the various elements in the cinder are basically not consumed but catalyze H_2O_2 together with Fe^{2+}. This expands the pH range of Fenton and reduces the dosage of Fe^{2+} and H_2O_2.

4 Conclusions

Through orthogonal test, the influence of each factor is presented in descending order as: pharmaceutical wastewater: $FeSO_4 \cdot 7H_2O$ dosage> $[H_2O_2]$:$[Fe^{2+}]$>reaction time>cinder dosage; paper-making wastewater: $[H_2O_2]$: $[Fe^{2+}]$> $FeSO_4 \cdot 7H_2O$ dosage>cinder dosage>reaction time. It shows that the utilization effect of cinder in pharmaceutical wastewater is less satisfactory than that in paper-making wastewater.

The optimal condition for the advanced treatment of pharmaceutical wastewater and paper-making wastewater by catalyzing H_2O_2 with cinder and Fe^{2+} is the dosage of pyrites cinder of $10g \cdot L^{-1}$, the dosage of $FeSO_4 \cdot 7H_2O$ of $0.3mmol \cdot L^{-1}$, $[H_2O_2]:[Fe^{2+}]$ of 8:1, the reaction time of pharmaceutical wastewater of 30min and reaction time of paper-making wastewater of 60min. Under the optimal condition, the removal rate of COD in pharmaceutical wastetwater and paper-making wastewater can reach 65% and 72% respectively. This method does not require the regulation of the pH of

inflow or high dosage of reagents, which testifies to the simple operation.

The cinder still possesses certain concerted catalysis capacity even after five times of reutilization with a COD removal rate in the two wastewater of more than 60%.

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