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Two-stage synergistic oxidation treatment of neomycin sulfate wastewater by potassium ferrate and hydrogen peroxide

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ABSTRACT

This study proposed a two-stage oxidation process of combining potassium ferrate and hydrogen peroxide to reduce the amount of potassium ferrate and further improve the treatment effect of neomycin sulfate wastewater. Compared with the K_2FeO_4 single oxidation process and the H_2O_2 single oxidation process, the K_2FeO_4 + H_2O_2 two-stage oxidation process had a higher chemical oxygen demand (COD) removal rate than the sum of the two single oxidation processes, showing a certain synergy. In addition, H_2O_2 dosage, system acidity, reaction temperature and reaction time did not affect this conclusion. In the first stage, the optimized processing parameters are the dosage of K_2FeO_4 7 g/L, pH value 4, reaction time 40 min and temperature 40°C. In the latter stage, the appropriate dosage of H_2O_2 is 20 mL/L, pH value is 3, the reaction time is 50 min and the reaction temperature is 40°C as same as the first stage, the COD removal rate of neomycin sulfate wastewater is 96.83%, showing a good treatment effect and obvious synergistic effect.

Keywords: Neomycin sulfate wastewater; Potassium ferrate; Hydrogen peroxide; Fenton-like oxidation; Synergistic effect

1. Introduction

Because of their effective treatment for many infectious diseases, antibiotics are widely used in the field of medicine, which makes more and more antibiotic pollutants continue to enter the water body. Some antibiotics such as neomycin sulfate, ciprofloxacin, enrofloxacin, amoxicillin and ampicillin are considered to be refractory organic compounds because they can kill the microorganisms, so it is almost impossible to use conventional biological methods to remove them from wastewater [1–4].

Advanced oxidation processes (AOPs) can produce highly active hydroxyl radicals, which can effectively remove recalcitrant organic compounds [5,6]. Common AOPs include Fenton oxidation [7–10], ozone oxidation [11,12] and photooxidation [13]. Although these AOPs can remove recalcitrant organic compounds, they more or less have some disadvantages, such as complicated operation, poor universality and excessively high cost, etc. Recently, as an emerging AOP, potassium ferrate has attracted great attention because of its better stability, easy preparation and wide application in wastewater treatment than sodium ferrate [14]. Potassium ferrate is a hexavalent compound of iron, and iron exists in the form of tetrahedral structure FeO_4^{2-} [15]. It can effectively degrade organic matter through electron transfer and oxygen transfer mechanisms [16–19]. Under acidic (pH < 6.5) and alkaline (pH = 8~10) conditions, its redox potentials are +2.20 V and +0.72 V, respectively. In addition, potassium ferrate also has the functions of flocculation, disinfection, and deodorization. Although potassium ferrate has the ability to treat recalcitrant organic compounds, the high usage required to effectively degrade recalcitrant organic compounds will undoubtedly lead to a high cost in the current condition. Therefore, how to reduce the usage of potassium ferrate and improve the effect of wastewater treatment is a key issue for the large-scale

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application of ferrate(VI) oxidation technology. Some additives and assisted means, such as hydroxylamine [20], MgO nanoparticles [21] and UV radiation [22] were introduced to improve the ferrate(VI) oxidation process. Although these methods improved the treatment effect of wastewater by different procedures, the usage of ferrate(VI) could not be significantly reduced.

From the mechanism of organic matter oxidized by ferrate(VI), ferric ions are generated after the oxidation-reduction reaction between potassium ferrate and an organic compound. At this point, if a proper amount of hydrogen peroxide is added to the solution, the ferric ions will cause the formation of Fenton-like reagents by catalyzing hydrogen peroxide and continue to oxidize deeply, thus forming the combination of two advanced oxidation processes, then the wastewater treatment effect will be improved significantly.

Therefore, the purpose of this study is to investigate the potential of combining potassium ferrate and hydrogen peroxide to remove neomycin sulfate as much as possible. Considering the performance of the combined process for the removal of neomycin sulfate, it is necessary to investigate the differences in the removal of neomycin sulfate in the following three processes of potassium ferrate oxidation, hydrogen peroxide oxidation and Fenton-like oxidation after potassium ferrate oxidation, which the synergistic effect is an exit or not can be found.

2. Materials and methods

2.1. Main materials

Potassium ferrate (AR), hydrogen peroxide solution (30%, AR) and neomycin sulfate (USP grade) were all purchased from Shanghai Maclean Biochemical Technology Co., Ltd., (Shanghai). MnO_2(AR) was purchased from Sinopharm Chemical Reagent Co., Ltd., (China). All the reagents, unless specifically stated, were not be purified before use.

Take a certain amount of neomycin sulfate and dissolve it in deionized water to prepare the simulated neomycin sulfate wastewater which chemical oxygen demand (COD) value is 363.959 mg/L according to the actual wastewater information from a local pharmaceutical factory.

2.2. Experimental methods

A 250 mL beaker was filled with 100 mL of simulated wastewater of neomycin sulfate. The experiment was divided into two stages, potassium ferrate oxidation was performed first, and then Fe^{3+} generated by potassium ferrate was used to catalyze H_2O_2 for latter Fenton-like oxidation. Initially, the pH of the wastewater solution was adjusted to 4 with 0.2 mol/L NaOH solution and 0.1 mol/L H_2SO_4 solution and placed in an electric heating constant temperature water bath which temperature was kept at 40°C and added a certain amount of potassium ferrate solid reacted for 40 min. Then, adjusted the pH and temperature of the reaction solution, added a certain amount of 30% H_2O_2 solution, after a certain time of reaction, adjusted the pH of the wastewater solution between 8 and 10, decomposed the residual H_2O_2 by adding a certain amount of MnO_2 and blew off O_2 by nitrogen flow. After 10 min, drew 5 mL wastewater sample with a syringe and filtered it with a 0.45 mm pore size organic filter, and then absorbed 2 mL of the filtrate to measure the COD value in a multifunctional integrated water quality analyzer (EF-903, Hefei Enfan Instrument Equipment Co., Ltd., China) [23]. The comparative experiments of potassium ferrate alone oxidation and hydrogen peroxide alone oxidation were carried according to the two-stage oxidation process.

3. Results and discussion

3.1. Treatment of neomycin sulfate wastewater by three oxidation processes

The treatment of neomycin sulfate wastewater by three processes of potassium ferrate and hydrogen peroxide two-stage oxidation, potassium ferrate single oxidation, and hydrogen peroxide single oxidation was all studied. In addition, the influences of dosage of K_2FeO_4 and H_2O_2, pH value, reaction time and reaction temperature on the oxidation treatment experiment were discussed systematically.

3.1.1. Influence of dosage of K_2FeO_4

In our previous study, the optimal conditions for the oxidation treatment of neomycin sulfate wastewater by potassium ferrate were obtained, they were pH value 4, reaction temperature 40°C and reaction time 40 min. Therefore, for the potassium ferrate and hydrogen peroxide two-stage oxidation experiment, the optimal reaction conditions were adopted in the first stage of the potassium ferrate oxidation treatment. The influence of the dosage of K_2FeO_4 on the oxidation treatment effects of the two-stage oxidation processes is shown in Fig. 1.

It can be seen from Fig. 1 that when the concentration of neomycin sulfate is constant, as the dosage of K_2FeO_4 increases, the COD removal rate of neomycin sulfate wastewater increases, after reaching the maximum value of 96.83%, it is basically stable. This is because at the beginning, as the dosage of K_2FeO_4 increases, the probability of collision between FeO_4^{2-} and the reducing substances in the wastewater gradually increases, thereby increasing the COD removal rate. In addition, the increase in the dosage of K_2FeO_4 also increases the concentration of Fe^{3+} in the solution, and the excess Fe^{3+} will react quickly with H_2O_2 to generate more iron salt compounds. After the iron salt compounds are decomposed, hydroxyl radicals will be generated, which will react with reducing substances in the wastewater. The COD removal rate of wastewater increases continuously until the oxidation treatment of neomycin sulfate wastewater tends to be completed [24]. So, in the two-stage oxidation process, the parameters in the first stage are designed as the dosage of K_2FeO_4 7 g/L, pH value 4, reaction temperature 40°C and reaction time 40 min. We mainly discuss the process of Fenton-like oxidation in the latter stage.

3.1.2. Influence of dosage of H_2O_2

H_2O_2 is the oxidant of the latter-stage process. The influences of the dosage of H_2O_2 on the oxidation treatment effect of the three processes were studied and are demonstrated in Fig. 2.

It can be seen from Fig. 2 that as the dosage of H_2O_2 increases, the COD removal rate of neomycin sulfate wastewater increases first and decreases after reaching the maximum value for the two-stage oxidation process of K_2FeO_4 + H_2O_2. It is because at the beginning, as the dosage of H_2O_2 increases, H_2O_2 will react with the Fe^{3+} originated from the first stage to generate more and more iron salt compounds. After the iron salt compounds are decomposed, hydroxyl radicals will be generated and react with pollutants in the wastewater to make the COD removal rate increase. Later, when the dosage of H_2O_2 is too much, the excessive H_2O_2 will react with hydroxyl radicals at certain extent, which causes the loss of strong oxidizing groups, resulting in a decrease of COD removal rate. For the H_2O_2 single oxidation process, the COD removal rate of wastewater increases first and then decreases with the increase of H_2O_2 dosage. This is because at the beginning, the dosage of H_2O_2 increases, the collision probability of molecular collision between H_2O_2 and reducing substances in wastewater also gradually increases, so the reaction efficiency increases.

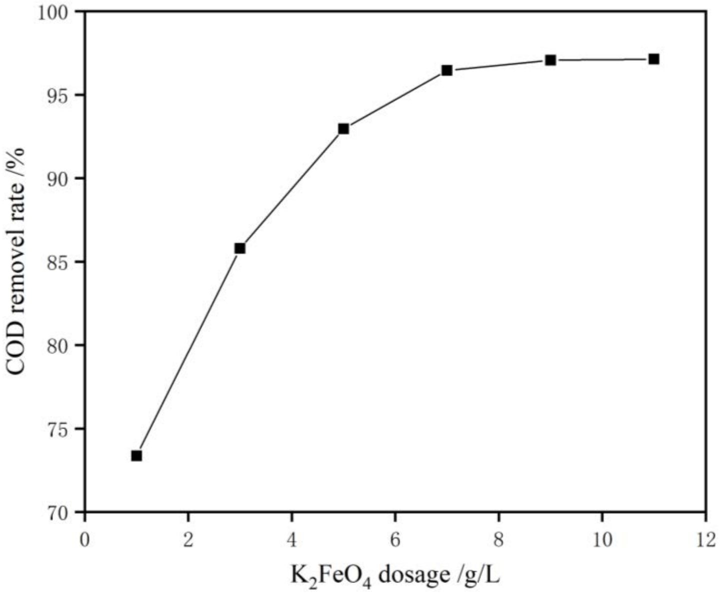

Fig. 1. Influence of dosages of K_2FeO_4 on the removal rate of COD in the two-stage oxidation process.
Note: a dosage of H_2O_2 20 mL/L; reaction temperature 40°C; reaction time 40 min; pH value 3 in the latter stage.

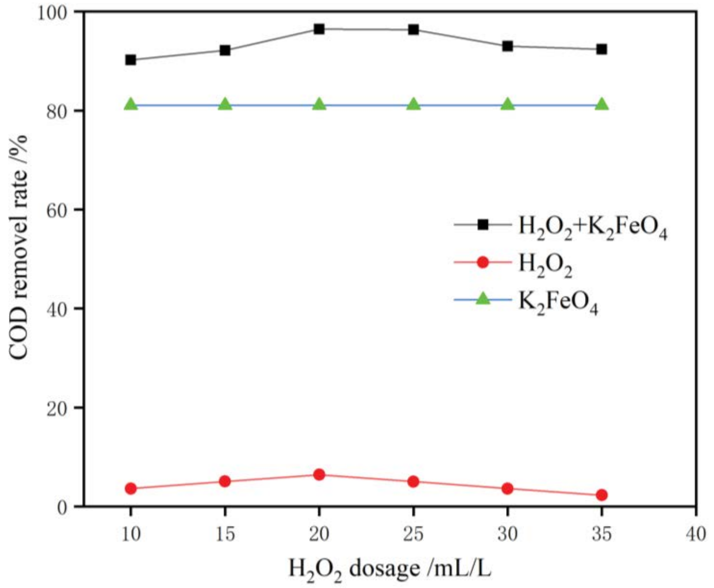

Fig. 2. Results of COD removal rate with different H_2O_2 dosages in the three oxidation processes.
Note: reaction temperature 40°C; reaction time 40 min; pH value 3 in the latter stage.

Later, when the dosage of H_2O_2 is too much, the unreacted H_2O_2 will show reducibility unnaturally and make the COD removal rate decrease. As for the K_2FeO_4 single oxidation process, due to the K_2FeO_4 has been exhausted in the first stage and no H_2O_2 was added in the latter stage, the COD removal rate of wastewater remains unchanged at the level of 81.01%.

3.1.3. Influence of pH value

About the influence of pH value on the oxidation treatment effect of the three processes, it can be seen from Fig. 3. For the two-stage oxidation process of K_2FeO_4 + H_2O_2, with the pH value increases, the COD removal rate increases first and decreases after reaching the maximum value. The reason is under strongly acidic conditions, the Fenton-like reaction is restricted, and only a small part of the trivalent iron salt compounds are decomposed to generate hydroxyl radicals, and the rest all decompose to generate OH^-, which leads to a low removal rate of COD. On the other hand, if the pH value is too high, Fe^{3+} can generate $Fe(OH)_3$ precipitation partly, the reduction in the amount of Fe^{3+} will inhibit the generation of hydroxyl radicals, and $Fe(OH)_3$ has also catalytic decomposition effect on H_2O_2, which leads to decrease in COD removal rate [25]. For the H_2O_2 single oxidation process, the COD removal rate of wastewater also increases first and then decreases with the increase of pH value. This is because when the pH value is too low, H_2O_2 and H^+ form $H_3O_2^+$, which enhances the stability of H_2O_2 but reduces its oxidation ability, resulting in a lower removal rate of COD. When the pH value increases over 4, the reaction activity of H_2O_2 is too low, resulting in a decrease in the COD removal rate. For the K_2FeO_4 single oxidation process, since the potassium ferrate had been almost completely reacted in the first stage, adjusting the pH value of the solution has no effect on the experiment. Therefore, the COD removal rate of the wastewater remains unchanged.

3.1.4. Influence of the reaction temperature

The stability and activity of oxidants are heavily dependent on temperature, so reaction temperature has a great influence on the oxidation treatment effect of the three processes and the results are shown in Fig. 4. For the K_2FeO_4 + H_2O_2 two-stage oxidation process, in the beginning, the COD removal rate gradually increases as the reaction temperature increases. When the reaction temperature is 40°C, the COD removal rate reaches the maximum value of 96.46%, then the COD removal rate begins to decrease. This is mainly because H_2O_2 is unstable in an aqueous solution. When the temperature is lower than 40°C, the reaction temperature rises, the decomposition rate of H_2O_2 increases, but the molecular movement rate also increases, and the increase of molecular movement rate is greater than the increase of decomposition rate, ultimately showing as COD removal rate increases. But when the temperature is higher than 40°C, the increase of decomposition rate is greater than the increase of molecular movement rate, which is manifested as the decrease in COD removal rate. Therefore, when the reaction temperature is 40°C, the COD removal rate of neomycin sulfate wastewater is the highest. Fortunately, the optimal temperature is the same as that in the first stage, so it is energy efficient and easy to operate for the two-stage oxidation. For the H_2O_2 single oxidation process, the COD removal rate changes and the reasons are the same as above. For the K_2FeO_4 single oxidation process, K_2FeO_4 has been exhausted at the first stage, so the COD removal rate of wastewater remains unchanged.

3.1.5. Influence of the reaction time

About the influence of the latter stage reaction time on the oxidation treatment effects of the three processes, it can be seen from Fig. 5 that for the K_2FeO_4 + H_2O_2 two-stage oxidation process, the COD removal rate gradually increases to

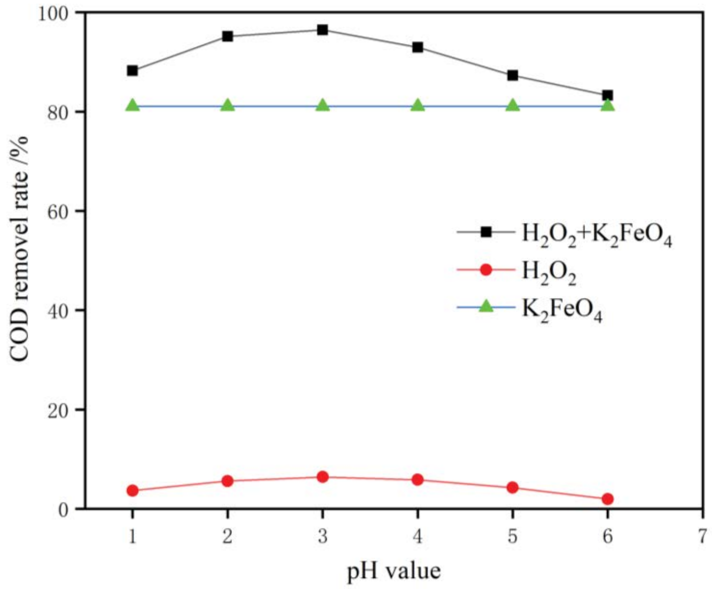

Fig. 3. Results of COD removal rate with different pH values in the latter stage oxidation process.
Note: a dosage of H_2O_2 20 mL/L; reaction temperature 40°C; reaction time 40 min.

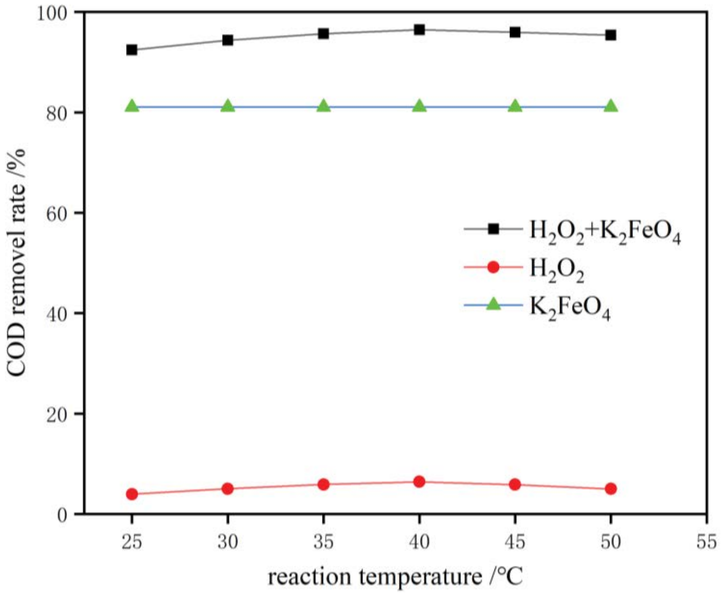

Fig. 4. Results of COD removal rate with different temperatures in the latter stage oxidation process.
Note: a dosage of H_2O_2 20 mL/L; reaction time 40 min; the pH value 3.

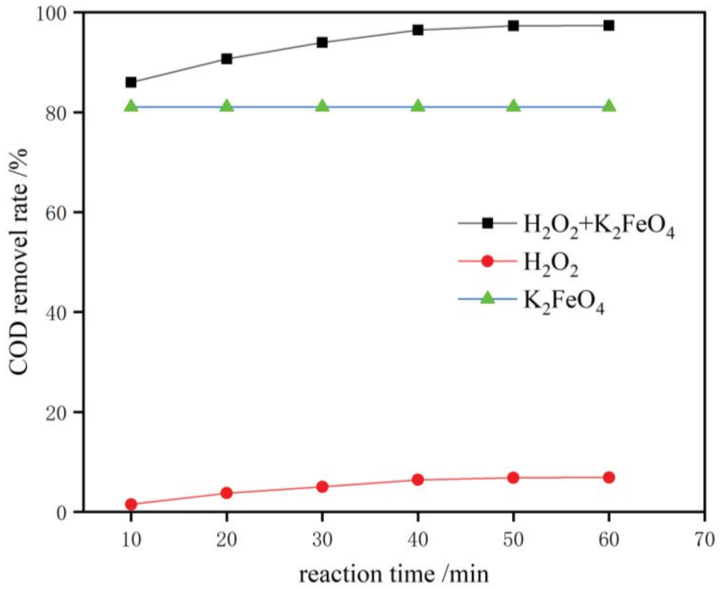

Fig. 5. Results of COD removal rate with different reaction time in the latter stage oxidation process.
Note: a dosage of H_2O_2 20 mL/L; reaction time 40 min; the pH value 3.

the maximum value as the reaction time increases, and then keeps almost unchanged. This is because at the beginning, the higher the H_2O_2 concentration, the faster the Fenton-like reaction rate, so the COD removal rate increases rapidly. When the reaction is almost completed, the COD removal rate is basically constant. For the H_2O_2 single oxidation process, the change in the removal rate of wastewater COD is the same as above. For the K_2FeO_4 single oxidation process, since the potassium ferrate reaction is almost completed in the first stage, extending the reaction time at the latter stage will not have any effect on the experiment. Therefore, the COD removal rate of the wastewater remains unchanged.

From the above single factor analysis results, it can be seen that the K_2FeO_4 + H_2O_2 two-stage oxidation process has a higher COD removal rate for wastewater than the sum of the H_2O_2 single oxidation process and the K_2FeO_4 single oxidation process, showing a good synergy. The reason is ferrate(VI) can be reduced to Fe^{3+} in the first stage, which provides a kind of effective catalyst for the latter stage and promotes the oxidative ability of hydrogen peroxide significantly. The influence factors of dosage of H_2O_2, pH value, reaction temperature and reaction time at the latter stage do not affect this conclusion, which indicates that the two-stage oxidation process of K_2FeO_4 + H_2O_2 exhibits a more significant and stable synergistic effect, which has greater application and promotion value.

3.2. Determination of the optimal process conditions for the two-stage synergistic oxidation

On the basis of the above single factor experiment, three factors of H_2O_2 dosage (factor *A*), pH value (factor *B*), and reaction time (factor *C*) in the latter stage were selected as the factors of the orthogonal experiment, and the COD removal rate of neomycin sulfate wastewater was used as the evaluation index. The designed three levels of the reaction factors are shown in Table 1.

According to the $L_9(3^3)$ orthogonal experiment model, nine experiments were carried out and results were shown in Table 2.

According to the results in Table 2, the influence order of the three factors is $R(A) > R(C) > R(B)$. It shows that the dosage of H_2O_2 has the largest effect on the two-stage synergistic oxidation treatment of neomycin sulfate wastewater and should be gained especially attention. In addition, the removal rate of COD is not sensitive to the pH value, which will reduce the operation difficult in practice. The best factors combination is $A_2B_2C_3$, the corresponding removal rate of COD is 96.83%. According to this result, three parallel experiments are carried under the optimal conditions of K_2FeO_4 dosage 7 g/L, pH value 4, temperature 40°C and reaction time 40 min in the first stage, the dosage of H_2O_2 20 mL/L, pH value 3, temperature 40°C and reaction time 50 min, the average removal rate of COD is about 96.28%, which demonstrates the optimal process is reliable.

Table 1
Designed levels of the reaction factors

Level	*A* (mL/L)	*B*	*C* (min)
1	15	2	30
2	20	3	40
3	25	4	50

Table 2
Results and analysis of designed $L_9(3^3)$ orthogonal experiments

No	*A*	*B*	*C*	Removal rate of COD (%)
1	1	1	1	86.43
2	1	2	2	92.35
3	1	3	3	89.26
4	2	1	2	94.28
5	2	2	3	96.83
6	2	3	1	90.48
7	3	1	3	95.87
8	3	2	1	93.78
9	3	3	2	92.68
K_1	268.04	276.58	270.69	
K_2	281.59	282.96	279.31	
K_3	282.33	272.42	281.96	
R	14.29	10.54	11.27	

4. Conclusion

This study provides effective two-stage oxidation of potassium ferrate and hydrogen peroxide for the treatment of neomycin sulfate wastewater. The results show that there has a certain synergistic effect. The optimal process conditions for the two-stage synergistic oxidation of potassium ferrate and hydrogen peroxide were obtained through an orthogonal experiment. Under these conditions, the COD removal rate of neomycin sulfate wastewater was 96.83%.

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