Treatment of Candied Fruit Wastewater by Adsorption Oxidation Combined Process

Mengxiang Zeng

Xiamen University of Technology, Xiamen, 361024, China
E-mail: zengmx@xmut.edu.cn

Abstract. In this experiment, we applied a combined process of adsorption and oxidation for the treatment of candied fruit production wastewater. The influence of the pH value and dosage of the Fenton reagent on the treatment effect were investigated. The impact of regeneration temperature, power, and time on the efficacy of the regeneration of adsorbents were examined by ultrasonic wave. The results revealed that at pH 4, the removal rate of COD was 81.74% at a dosage of FeSO$_4$ 7H$_2$O of 7 g/L and 40 mL/L of H$_2$O$_2$. The maximum regeneration rate of the adsorbent 90.73%, reached at a temperature of 35 °C, ultrasonic power of 200 W, and 10 min.

1. Introduction
Over the recent years, the processing industry of candied fruits has been becoming increasingly more developed, and there are more and more kinds of preserves are produced. The processing technology of candied fruits production must be pickled. The pickling is a heavy pollution process. The high concentration of Cl$^-$ discharged from the sauce makes it difficult to deal with the wastewater effectively. The pH value of candied fruit wastewater is low, salinity is high, the molecular weight of organic pollutants is large, and osmotic pressure is high, which seriously affects the treatment of sewage [1].

At present, the treatment of high-salt wastewater is performed mainly through the following methods: electrolysis, incineration, biological membrane purification, salt-adapted biological treatment technology and ozonation oxidation-biological method, etc.[2] Research work has made progress, but technical issues still . In this paper, we used activated carbon adsorption to pretreat preserved waste water. Meanwhile, the advanced oxidation technology of Fenton was introduced, and the ultrasonic method was employed to recycle the adsorbed activated carbon. Our findings provide a reference for solving the serious issues associated with the pollution of candied fruit wastewater.

2. Experimental part

2.1. Reagents and instruments

2.1.1 Experimental reagents
The experimental reagents were all analytically pure. The activated carbon particles were produced by Tianjin Guangfu Technology Co., Ltd., sodium hydroxide, concentrated sulfuric acid, potassium dichromate, and silver sulfate were produced from Xiqiao Chemical Industry Co., Ltd. and ferrous ammonium sulfate was produced from Guangdong Huaguang Chemical Factory Co., Ltd, phenanthroline, silver nitrate, hydrogen peroxide, ferrous sulfate heptahydrate was produced by Shanghai Sinopharm Group Chemical Reagent Co., Ltd.
2.1.2 Experimental instruments
Electronic balance produced in Fuzhou Hua Zhi Scientific Instrument Co., Ltd. (Fuzhou, Fujian, China). The pH-meter and the spectrophotometer produced in Shanghai Spectral Instrument Co., Ltd. (Shanghai, China). COD digestion instrument, Super constant temperature water bath, Magnetic stirrer, ultrasonic cleaner, Suction filter and Oven were produced in Qingdao Hong Hai environmental protection equipment Co., Ltd. (Qingdao, Shandong, China).

2.1.3 Experimental water sample
The water sample was collected from a candied fruit processing plant in Quanzhou (Fujian, China). The water sample solution contained suspended fruit and vegetable matter. The water was acidic, with obvious pungent sourness and a pH value of 3.5. The COD value was 5,800 mg/L, the concentration of total phosphorus was 1.813 mg/L, and that of total nitrogen was 28.1 mg/L.

2.2 Experimental steps and methods

2.2.1 Experimental treatment of candied fruit wastewater by Fenton oxidation
The effects of the initial pH value, dosage of the Fenton reagent, and the reaction time on the influence of the treatment of candied fruit wastewater by oxidation were investigated.

2.2.2 Study on ultrasonic regeneration of activated carbon particles
The effects of regeneration temperature, regeneration power, regeneration time, and regeneration times on regeneration of activated carbon particles were examined.

3. Experimental results and discussion

3.1 Experiment on the treatment of candied fruit wastewater by Fenton oxidation

3.1.1 Effect of initial pH on Fenton oxidation treatment of candied fruit wastewater
The pH values of the wastewater were adjusted to 2, 3, 4, 5, and 6, respectively. The concentrations of the fixed FeSO4·7H2O solid amount was 6 g/L, and that of the 30% H2O2 solution was 30 mL/L. Further, the COD value was measured, and the COD was calculated as 5,800 mg/L. The COD removal rate by the Fenton oxidation treatment at different initial pH values is depicted in Figure 1.

![Figure 1](image-url)

**Figure 1.** Effect of the pH value on the removal rate of COD.
As can be seen from Figure 1, with the increase of the pH value from 2 to 6, the removal rate of COD showed a trend of increasing first and then decreased. At a pH value of 4, the COD removal rate of the solution reached its maximum (78.33%), because at low pH, the following reaction occurs: Fe3++ H2O2→ Fe2++H++HO2-. As can be seen, the balance of the left side of the equation is not conducive to the production of Fe2+. When the pH increases, the same left movement according to the reaction of Fe2++ H2O2→ ·OH+ Fe3++ OH- is not conducive to the production of hydroxyl radicals, so the pH is high or low will reduce the removal of COD, so the optimum pH for this experiment is 4.

3.1.2 Effect of FeSO4·7H2O solid dosage on Fenton oxidation treatment of candied fruit wastewater
Fixed mass fraction of 30% H2O2 solution 30mL/L, Fixed pH is 4, and accurately weigh FeSO4·7H2O solid dosage 5.0 g/L, 6.0 g/L, 7.0 g/L, 8.0 g/L, 9.0 g/L, 10.0 g/L, and 11.0 g/L, the final determination of COD value, calculation of different FeSO4·7H2O solid dosage of Fenton oxidation COD removal rate, the results shown in Figure 2.

![Figure 2](image_url)

**Figure 2.** Effect of FeSO4·7H2O dosage on the removal rate of COD

As can be observed in Figure 2, at a dosage of FeSO4·7H2O of 7 g/L, the removal rate of COD was up to 80.63%. With the increase of the dosage of FeSO4·7H2O, the removal rate of COD decreased slightly and then tended to stabilize. The reason for the analysis may be that when the Fe2+ is excessive, the H2O2 will be oxidized to Fe3+ while the H2O2 is consumed, and the removal rate of COD is slightly decreased. Therefore, according to the experimental data, the optimal FeSO4·7H2O dosage established in this experiment was 7 g/L.

3.1.3 Effect of H2O2 dosage on Fenton oxidation treatment of candied fruit wastewater
Fixed the dosage of FeSO4. 7H2O is 7 g/L, adding 30% H2O2 solution 10 mL/L, 20 mL/L, 30 mL/L, 40 mL/L, 50 mL/L, 60 mL/L, and 70 mL/L respectively. At the beginning, a stirring time of 60 min was used, followed by measurements of the COD values was measured at the end of the reaction. According to the original water COD was 5,800 mg/L, the COD removal rate of Fenton oxidation treatment under different H2O2 dosage was calculated. The result shown in Figure 3.
Figure 3. Effect of the amount of H$_2$O$_2$ added on the removal rate of COD.

H$_2$O$_2$ was utilized as an oxidant for the Fenton oxidation. We found that the removal rate of COD increased significantly with the rise of H$_2$O$_2$ dose, and the removal rate of 10 mol/L was 64.32%, whereas that of 40 mol/L was 81.25% (Figure 3). When 40 mol/L was reached, the excess of H$_2$O$_2$ can not decompose more hydroxyl radicals, instead of oxidizing Fe$_2^+$ to Fe$_3^+$ at the beginning of the reaction, which not only inhibits the generation of hydroxyl radicals, but also consumes the amount of H$_2$O$_2$. Therefore, the concentration of H$_2$O$_2$ of 40 mol/L in this experiment was the optimal dosage, resulting in the maximum removal rate of 81.85%.

3.1.4 Effect of the reaction time on Fenton oxidation treatment of candied fruit wastewater

Figure 4. Effect of the reaction time on the removal rate of COD.
The fixed amount of solid FeSO$_4$. 7H$_2$O was 7 g/L and 30% H$_2$O$_2$ solution 30 mL/L. The stirring time was 5 min, 10 min, 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, 120 min, respectively. The COD value was determined at the end of the reaction. According to the COD of the raw water (5,800 mg/L), the COD removal rates realized by the Fenton oxidation treatment at different reaction times were calculated (Figure 4).

In Figure 4, it can be seen that within the time interval 0–15 min, the reaction was rapid, and the removal rate of COD increased to 78.36%. Then, with the prolongation of the reaction time, the removal rate rose more slowly. The maximum removal rate at 45 min was 81.74%, and the reaction time is prolonged, and the COD removal rate is slightly decreased, but the amplitude is not significant. It is possible to analyze the cause of the high concentration of Fe$^{2+}$ and H$_2$O$_2$ and the fastest rate of generating hydroxyl radicals, which may be due to the formation of a new possibility COD when the free radicals are more complex in the oxidizing water, increasing the COD value in the water and reducing the removal rate. Therefore, the best reaction time of this experiment was 45 min and the removal rate achieved 81.74%.

3.2 Study on ultrasonic regeneration of activated carbon particles

The regeneration of activated carbon plays an important role in industrial production. Therefore, it is necessary to explore the effects of temperature, power, and time on the regeneration of activated carbon particles [3].

3.2.1 Effect of temperature on the regeneration of activated carbon particles

In our experiment, the ultrasonic power was set at 200 W, and the ultrasonic time was 6 min. The activated carbon was regenerated at different temperatures, and the COD value was finally determined. The regeneration performance was determined by comparing the COD removal rate before and after regeneration. The results are illustrated in Figure 5.

![Figure 5. Influence of the temperature on the regeneration rate.](image-url)
the excessive temperature also increased the steam pressure of the bubbles in the water, thus affecting the regeneration effect. Therefore, the regeneration temperature of this experiment was set to 35 °C, leading to a maximum regeneration rate of 90.61%.

3.2.2 Effect of the power used on the regeneration of activated carbon particles

The ultrasonic temperature was set at 35 °C, and the ultrasonic time was 6 min. The activated carbons were regenerated under different power conditions, and the COD values were finally determined. The regeneration performance was determined by comparing the COD removal rate before and after regeneration. The results are presented in Figure 6.

![Figure 6. Influence of the power on the regeneration rate.](image)

As illustrated in Figure 6, the regeneration rates at levels of the power of 160 W, 200 W, 240 W, 280 W, and 320 W were 85.09%, 90.71%, 90.63% and 90.58%, respectively. When the power reached 200 W, it further increased exerted insignificant effects on the regeneration efficacy. The reason for this phenomenon may be that the power increased in a certain range, and the rise in the ultrasonic strength was beneficial to the desorption. Nonetheless, the excessive power may damage the structure of the activated carbon itself. The best activated carbon power was 200 W, and the regeneration rate was 90.71%.

3.2.3 Effect of time on the regeneration of activated carbon particles

![Figure 7. Effect of reaction time on regeneration rate](image)
The ultrasonic temperature was set to 35 °C and the power to 200 W. The carbon was activated at different times, followed by determination of the COD value. The regeneration performance was determined by comparing the COD removal rates before and after regeneration (Figure 7). The results in Figure 7, display regeneration rates of 43.86%, 90.51%, 92.18%, 90.13%, and 89.23% at 2 min, 6 min, 10 min, 14 min, and 18 min, respectively. When the reaction time was 10 min, the regeneration rate reached its maximum (92.18%). However, the further increase on the reaction time led to less obvious effects, and even to a slight decrease. Analyze the reason, It is may be that the long time of the ultrasonic wave causes the activated carbon to break, and the internal space structure of the activated carbon is broken to a certain extent, so that the adsorption performance is weakened. Therefore, the optimal regeneration time established in this experiment was 10 min, and the respective maximum removal rate was 92.18%.

3.2.4 Effect of the regeneration times on the regeneration efficacy of activated carbon particles
The effect of choosing the best regeneration conditions on the number of regenerations of activated charcoal was investigated. The temperature was 35 °C, the power was 200 W, and the time was 10 min. The regeneration adsorption effect is shown in Figure 8.

![Figure 8. Effect of regeneration times on regeneration rate.](image)

As shown in Figure 8, as the number of regeneration increases, the regenerative effect of the first three times is not changed, and there was a clear downward trend at the fourth time. From the 90% to 70%. The reason may be that the high pressure shock wave is produced with the increase of the number of regeneration times, which makes the surface of the activated carbon rise. High pressure increases and decomposes by heat, which changes the performance of activated carbon.

4. Conclusions
(1). The COD concentration of the candied fruit was reduced from 5,803.581 mg/L to 1,059.73 mg/L, and the removal rate was 81.74% when pH = 4, FeSO4 / 7H2O was 7 g/L, 40 mol/L of H2O2, and a reaction time of Fenton oxidation of 45 min were used as reaction conditions.
(2). In the experiment of ultrasonic regeneration of activated carbon, the obtained temperature was 35°C, the power was 200W, the time was 10 minutes, and the regeneration frequency was more than 90% within three times.

5. References
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Lead author: Mengxiang Zeng (1982.11-) male, Post-Graduate, the main research direction is environmental engineering and water pollution control. zengmx@xmut.edu.cn
Corresponding author: Mengxiang Zeng (1982.11-) male, Post-Graduate, the main research direction is environmental engineering and water pollution control. zengmx@xmut.edu.cn