Treatment of Penicillin Wastewater by Sequencing Batch Reactor

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Abstract. During the treatment of penicillin wastewater, facultative and aerobic bacteria in intermittent aeration can effectively degrade the organic matter in the wastewater without physical and chemical pretreatment of $SO_4^{2-}$ and DTAB. When the highest COD concentration of the influent is 12 000 mg/L, the load is 8 kgCOD/(m³·d), and the maximum impact load is 13 kg COD/(m³·d), COD removal rate can reach over 87%. The foam produced by DTAB in penicillin wastewater will not affect the normal operation of the SBR treatment plant. The foam can disappear in the aeration process, and eventually the DTAB can achieve more than 97% removal rate. Therefore, sequencing batch reactor is an ideal way to treat penicillin wastewater.

1. Introduction
Through the exploration of relevant scientific research institutions, it is agreed that $SO_4^{2-}$ and dodecyl trimethyl ammonium bromide (hereafter referred to as DTAB) in penicillin wastewater severely inhibit the normal metabolism of anaerobic organisms. No matter it is removed by physicochemical method or biological method, its cost is an insupportable burden on practical engineering. The purpose of this project is to provide an ideal way for the treatment of high concentration penicillin wastewater through the experimental study of SBR method. Sequencing batch reactor (SBR) is also known as batch activated sludge process, which is a biological treatment process with intermittent operation. Since the 1970s, Irvine of Natra Dame University in the United States has studied the basic operation characteristics of SBR method in the laboratory. Later, this technology was mainly used in biological nitrogen and phosphorus removal of urban sewage [1]. In this project, SBR process is used to treat penicillin wastewater with high concentration, high volume load and low energy consumption.

The process flow of water treatment adopted in this test is shown in Figure 1. The size of the aeration sedimentation tank is $A \times B \times H=400 \times 250 \times 440$ mm, the effective volume is 25 L, the superelevation is 190 mm, the waste water distribution bucket is 10 L, and it is stirred mechanically. Both water influent and effluent are siphons. Z-0.025/6 type air compressor is used for aeration, and the exhaust volume is 0.025 m³/min.
Figure 1. The process flow of water treatment

The wastewater is from the actual production wastewater of Jiangxi pharmaceutical factory in China, and the quality of the original wastewater is shown in the table 1.

Table 1. The quality of the original wastewater

| Water quality index       | Index value | Water quality index     | Index value |
|---------------------------|-------------|-------------------------|-------------|
| CODcr (mg/L)              | 16000–20000 | NH$_3$N (mg/L)          | 130–148     |
| BOD$_5$ (mg/L)            | 9000–11000  | pH value                | 4–5         |
| Residual penicillin (mg/L)| 36–44       | SO$_4^{2-}$ (mg/L)      | 6500–7500   |
| SS (mg/L)                 | 600–700     | DTAB (mg/L)             | 1500–1700   |

2. Test Condition and Discussion

2.1. Domestication of Activated Sludge
The inoculated sludge was obtained from the mixed wastewater of oxytetracycline and gentamicin in the laboratory. 5 L small aeration tank was used for acclimation in the first 5 days. 1 g glucose and 100ml penicillin concentrated wastewater (COD=20 g/L) were added into the tank every day. Intermittent feeding and continuous aeration were carried out. Paramecium was the main microorganism with a small amount of legume. After 5 days, the aeration tank with an effective volume of 25 L was used for continuous domestication. From August 15 to 16, 4 g glucose was added into the tank every day, 400 mL concentrated wastewater (COD=20 g/L), 5 g glucose and 500 mL concentrated wastewater (COD=20 g/L) was added into the tank every day from August 15 to 16. At this time, the microorganism was still dominated by Paramecium, and the COD volumetric loading was 0.6 COD/(m$^3$·d). From August 21 to 23, we increased COD volumetric loading to 1 kg COD/(m$^3$·d). On August 23, microscopic examination found that Paramecium was all dead, no other indicator appeared, and the first domestication failed. Analysis of the failure reasons: the waste water added from August 21-23 was the waste water at the bottom of the 200 L waste water bucket, with a large amount of salt precipitated. It can be seen from the naked eye that the waste water is turbid. It was estimated that too much salt in the sediment causes the active sludge poisoning.
The second domestication started on August 24, when all the original sludge was poured out and replaced with new sludge. The inoculated sludge is still from the activated sludge of oxytetracycline and small scale oxygen test. The acclimation process was carried out smoothly. In 17 days, the COD volumetric loading reached 1 kg COD/(m$^3$·d), the microorganism was active and the sludge concentration was 3000 mg/L. From the domestication process, it was preliminarily judged that SBR process was feasible for penicillin wastewater.

2.2. Exploratory Test

2.2.1. pH value problem. Generally speaking, the pH value of aerobic treatment should be lower than 6.5 [2], and the pH value of effluent water is slightly lower than that of influent water. However, when the pH value of influent water is only 5.5, the degradation of organic matter is not affected, and the pH value of effluent water rises to 8.2. This is different from the conventional aerobic method. According to the relevant data, when the pH of the conventional aerobic method is lower than 6.5, it will affect the sludge settling performance, while the intermittent activated sludge can greatly improve the sludge settling performance. Therefore, when the pH value of the influent water is 5.5, the treatment effect is not affected. On the contrary, when the pH value is low, due to the presence of fungi, it is beneficial to improve the purification efficiency of the activated sludge. Therefore, we consider that the pH value of influent water is as low as possible, but the pH value of effluent water is more than 7. The test results are shown in Table 3. It can be seen that the latter is better than the former. In terms of limitation of test time, we did only 24 hours for a cycle and 12 hours for a cycle as a comparative test. This is a very important question. There are different opinions on data at home and abroad. Or take a few hours as a cycle, or take 20 hours as a cycle. This is the pH value of influent at about 5.0.

| Date  | Water quantity (L/d) | COD cr (mg/L) | pH | Sludge concentration (g/L) | Mixture temperature (℃) | COD volumetric loading (kgCOD/m$^3$·d) |
|-------|----------------------|---------------|----|---------------------------|-------------------------|--------------------------------------|
|       |                      | Influent      | Effluent | Removal rate (%) | Influent | Effluent |                      |                        |                        |                         |
| 9.1   | 10                   | 3 000         | 305.84    | 89.8          | 3.4      | 7.1      | 3.06                  | 21.5                    | 1.2                    |
| 9.11  | 12.5                 | 3 000         | 274.9     | 90.8          | 3.4      | 7.1      | 3.06                  | 22                      | 1.5                    |
| 9.12  | 12.5                 | 3 000         | 332.86    | 88.9          | 3.4      | 7.1      | 3.06                  | 21.5                    | 1.5                    |
| 9.13  | 12.5                 | 3 000         | 332.86    | 88.9          | 3.4      | 7.1      | 3.06                  | 19                      | 1.5                    |
| 9.14  | 12.5                 | 3 000         | 257.05    | 91.4          | 3.4      | 7.1      | 3.06                  | 19                      | 1.5                    |
| 9.15  | 12.5                 | 3 000         | 246       | 91.8          | 3.4      | 7.1      | 4.15                  | 19                      | 1.5                    |
| 9.16  | 20                   | 2 500         | 305       | 87.8          | 5        | 7        | 4.15                  | 17.5                    | 2                      |
| 9.17  | 20                   | 2 500         | 277.55    | 88.9          | 5        | 7        | 4.15                  | 18                      | 2                      |
| 9.18  | 20                   | 2 500         | 272.11    | 89.1          | 5        | 7        | 4.15                  | 18.5                    | 2                      |
| 9.19  | 20                   | 2 500         | 272.11    | 89.1          | 5        | 7        | 4.15                  | 19                      | 2                      |
| 9.2   | 20                   | 3 125         | 321.09    | 89.7          | 3.4      | 7        | 4.15                  | 18                      | 2.5                    |
| 9.22  | 20                   | 3 125         | 315.6     | 89.9          | 3.4      | 7        | 4.15                  | 18                      | 2.5                    |
| 9.23  | 20                   | 3 125         | 390.6     | 87.5          | 3.4      | 7        | 4.15                  | 18                      | 2.5                    |
| 9.24  | 20                   | 3 125         | 408.16    | 86.9          | 3.4      | 7        | 4.15                  | 18.5                    | 2.5                    |

2.2.2. Selection of treatment cycle. How long is a cycle is a very important question. There are different opinions on data at home and abroad. Or take a few hours as a cycle, or take 20 hours as a cycle. This is related to wastewater quality and other factors. Due to the limitation of test conditions, especially the limitation of test time. We did only 24 hours for a cycle and 12 hours for a cycle as a comparative test. The test results are shown in Table 3. It can be seen that the latter is better than the former. In terms of energy conservation, the latter has twice as much idle time as the former in 24-hour operation. In addition,
the former COD removal rate is not higher than the latter. Therefore, this test decided to use 12 hours as a cycle.

### Table 3. Comparison table of processing cycle selection

| Date  | Influent COD (mg/L) | Effluent COD (mg/L) | Removal rate (%) | Influent pH | Effluent pH | Sludge concentration (mg/L) | Mixture temperature (℃) | Water quantity (l/d) | COD volumetric loading (kgCOD/m³·d) | Cycle (h) |
|-------|---------------------|---------------------|------------------|-------------|-------------|-----------------------------|-------------------------|-------------------|-------------------------------------|-----------|
| 9.11  | 3000                | 274.9               | 3.4              | 7.1         | 3.06        | 22                          | 12.5                    | 1.5               | 1.5                                 | 12        |
| 9.12  | 3000                | 332.86              | 3.4              | 7.1         | 4.15        | 19                           | 12.5                    | 1.5               | 1.5                                 |           |
| 9.13  | 3000                | 332.86              | 3.4              | 7.1         | 4.15        | 19                           | 12.5                    | 1.5               | 1.5                                 |           |
| 9.14  | 3000                | 257.05              | 9.14             | 7.1         | 4.15        | 19                           | 12.5                    | 1.5               | 1.5                                 |           |
| 9.15  | 3000                | 258                 | 9.14             | 7.1         | 4.15        | 19                           | 12.5                    | 1.5               | 1.5                                 |           |
| avg   | 3000                | 291.6               | 9.08             | 7.1         | 4.15        | 20.1                         | 12.5                    | 1.5               | 1.5                                 |           |
| 10.1  | 3000                | 483.4               | 83.9             | 5           | 7           | 5.48                         | 18~20                   | 10                | 1.5                                 |           |
| 10.2  | 3000                | 483.4               | 83.9             | 5           | 7           | 5.48                         | 18~20                   | 10                | 1.5                                 |           |
| 10.3  | 3000                | 483.4               | 83.9             | 5           | 7           | 5.48                         | 18~20                   | 10                | 1.5                                 |           |
| 10.4  | 3000                | 483.4               | 83.9             | 5           | 7           | 5.48                         | 18~20                   | 10                | 1.5                                 |           |
| 10.5  | 3800                | 514.1               | 86.5             | 5           | 7           | 5.48                         | 16                      | 10                | 1.5                                 |           |
| 10.6  | 3800                | 529.5               | 86               | 5           | 7           | 5.48                         | 16                      | 10                | 1.5                                 |           |
| 10.7  | 3800                | 565.5               | 85.1             | 5           | 7           | 5.48                         | 16                      | 10                | 1.5                                 |           |
| avg   | 3340                | 509.6               | 84.7             | 5           | 7           | 5.48                         | 17.7                    | 10                | 1.5                                 |           |

2.2.3. Temperature problems. The temperature requirement of SBR method is higher than that of conventional method. Generally, it is better to control the temperature above 18 °C, otherwise the treatment efficiency lower than 18 °C. During the 6 days from October 8 to 13, the COD volume load was controlled to 3 kg COD/ (m³·d), the temperature of the mixture was 16-17 °C, the sludge concentration was 5.6 g/L and the COD of the influent was 3800mg/L. After detection, it was found that the COD of effluent was 861.2-1280 mg/L, and the COD removal rate decreased to 66.3-77.3%.

2.3. Stable load operation test

During the test, the proportion of the nutrient feed is COD: N: P = 100:5:1. The nitrogen source is supplemented by adding urea (H₂NCONH₂) and the phosphorus source is supplemented by adding potassium dihydrogen phosphate (KH₂PO₄) or potassium dihydrogen phosphate (KH₂PO₄). From January 27 to February 22, 27 days of stable load operation. The test results are shown in Table 4. During this period, the highest COD concentration of influent water is 10772 mg/L, the lowest is 5850 mg/L, and the average COD concentration is 6970 mg/L. The highest COD concentration of effluent is 1162 mg/L, the lowest is 620mg/L, and the average COD concentration is 775 mg/L. The removal rate of COD is 86.2-91.4%, with an average of 88.9%. Sludge concentration (SS) is 11.16-14 g/L, volatile sludge concentration (VSS) is 9.72-11.62 g/L, and SS is 0.83-0.87 mg/L. The 30 minute sedimentation ratio is 34-54%, and the sludge index (SVI) is 29-41. COD volumetric loading is 5.85-10.77 kg COD / (m³·d), with an average is 6.97 kg COD/ (m³·d). Sludge load is 0.48-0.88 kg COD / (kgSS·d). Inflow DTAB is 453-834 mg/L, average is 540 mg/L. The DTAB of effluent is 8-15mg / L, with an average of 9 mg/L, so the results show that the removal rate of DTAB is more than 98%. The influent SO₄²⁻ is 2010-3700 mg/L, with an average of 2400 mg/L. The effluent concentration is the same as the influent.
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Table 4. Stable load operation test

| Date  | Water quantity (L/d) | COD (mg/L) | pH  | Sludge concentration (mg/L) | Mixture temperature (℃) | COD load distribution kgCOD/(m²·d) | Sludge concentration kgCOD/(kgSS·d) |
|-------|---------------------|------------|-----|-----------------------------|-------------------------|-----------------------------------|--------------------------------------|
| 1.27  | 20                  | 6500       | 660 | 89.8                        | 6.0 6.7                 | 12.27 10.25                       | 25 6.50 0.53                          |
| 1.28  | 20                  | 6500       | 655 | 89.9                        | 6.0 6.7                 | 12.27 10.25                       | 25 6.50 0.53                          |
| 1.29  | 20                  | 6500       | 700 | 89.2                        | 6.0 6.7                 | 12.27 10.25                       | 25 6.50 0.53                          |
| 1.30  | 20                  | 6200       | 730 | 88.2                        | 6.0 6.5                 | 12.27 10.25                       | 25 6.20 0.51                          |
| 1.31  | 20                  | 6900       | 620 | 91.0                        | 6.0 6.5                 | 12.27 10.25                       | 25 6.90 0.56                          |
| 2.1   | 20                  | 6100       | 720 | 88.2                        | 6.0 6.5                 | 12.27 10.25                       | 25 6.10 0.50                          |
| 2.2   | 20                  | 6800       | 780 | 88.5                        | 6.0 6.5                 | 12.80                            | 25 6.80 0.53                          |
| 2.3   | 20                  | 6700       | 760 | 88.6                        | 6.0 6.5                 | 12.90                            | 25 6.70 0.52                          |
| 2.4   | 20                  | 8370       | 765 | 90.6                        | 6.0 6.5                 | 13.52                            | 25 8.37 0.62                          |
| 2.5   | 20                  | 5920       | 745 | 87.4                        | 6.0 6.5                 | 11.16                            | 25 5.92 0.53                          |
| 2.6   | 20                  | 5920       | 640 | 89.2                        | 6.0 6.5                 | 11.16                            | 25 5.92 0.53                          |
| 2.7   | 20                  | 6600       | 655 | 89.1                        | 6.0 6.5                 | 11.16                            | 25 6.00 0.54                          |
| 2.8   | 20                  | 6150       | 660 | 89.3                        | 6.0 6.5                 | 12.54 11.00                       | 25 6.15 0.49                          |
| 2.9   | 20                  | 8100       | 930 | 88.5                        | 6.0 6.5                 | 12.46                            | 25 8.10 0.65                          |
| 2.10  | 20                  | 7273       | 917 | 87.4                        | 6.0 6.5                 | 12.46                            | 25 7.27 0.58                          |
| 2.11  | 20                  | 6780       | 903 | 86.7                        | 6.0 6.5                 | 12.46                            | 25 6.78 0.54                          |
| 2.12  | 20                  | 6500       | 755 | 88.4                        | 6.0 6.5                 | 12.46                            | 25 6.50 0.52                          |
| 2.13  | 20                  | 6500       | 691 | 89.4                        | 6.0 6.5                 | 12.46                            | 25 6.50 0.52                          |
| 2.14  | 20                  | 6313       | 833 | 86.8                        | 6.0 6.5                 | 12.46                            | 25 6.51 0.51                          |
| 2.15  | 20                  | 7581       | 782 | 89.7                        | 6.0 6.5                 | 12.46                            | 25 7.58 0.61                          |
| 2.16  | 20                  | 5850       | 810 | 86.2                        | 6.0 6.5                 | 11.68 9.72                       | 25 5.85 0.50                          |
| 2.17  | 20                  | 6500       | 780 | 88.0                        | 6.0 6.5                 | 11.68 9.72                       | 25 6.50 0.56                          |
| 2.18  | 20                  | 6680       | 760 | 88.6                        | 6.0 6.5                 | 14.00                            | 25 6.68 0.48                          |
| 2.19  | 20                  | 7490       | 722 | 90.4                        | 6.0 6.5                 | 12.19                            | 25 7.49 0.61                          |
| 2.20  | 20                  | 7490       | 645 | 91.4                        | 6.0 6.5                 | 12.19                            | 25 7.49 0.61                          |
| 2.21  | 20                  | 9834       | 1148| 88.3                        | 6.0 6.5                | 12.19                            | 25 9.83 0.81                          |
| 2.22  | 20                  | 10772      | 1162| 89.2                        | 6.0 6.5                | 12.19                            | 25 10.77 0.88                         |
| avg   | 20                  | 6970       | 775 | 88.9                        | 6.0 6.5                | 12.30                            | 25 6.97 0.57                          |

2.4. Destructive test

Due to the time limit, the stable operation time of the test for the load of 8-10 kg COD/(m³·d) was not long, immediately the load was increased to 14 kg COD/(m³·d), the removal rate was greatly reduced to 79% soon, and a large number of indicator organisms were dead. The destruction test had been carried out for two cycles, and then the load was reduced to resume operation. 24 hours later, the indicator organisms were active. It is feasible to analyze the stable operation of the load under the condition of 8-9 kg COD/(m³·d) from the test, and it is difficult to estimate the stable operation of the load over 10 kg COD/(m³·d). Whether it can run stably under high load condition remains to be verified in production.

2.5. Problem discussion

The main advantage of SBR process compared with physicochemical anaerobic process is that it does not need physical and chemical pretreatment [3]. Physicochemical treatment is not only a problem of high operating cost, but also a problem of complex operation and management in production and operation, and the treatment of sediment is difficult to solve. So why can SBR process achieve ideal treatment effect without physical and chemical treatment? The reason is that anaerobic digestion of wastewater can be divided into two stages in microorganism. In the first stage, the carbohydrate, fat, protein and other components in the waste water are firstly decomposed into low-level fatty acids, aldehydes, alcohols and other low-molecular organics under the enzyme action of acidogenic bacteria. The second stage is the low-level fatty acid produced by the enzyme of acidogenic bacteria, which is decomposed into methane and carbon dioxide under the action of methane bacteria. Acidogenic bacteria have the function of liquefying complex organic matter and strong anti-interference ability. However, methanogens are very sensitive to the change of salt and temperature in wastewater, and their proliferation rate is very slow. The most difficult problem in the anaerobic treatment of penicillin wastewater is the inhibition of SO²⁻, DATB to methanogens. SBR process only uses the first stage of anaerobic digestion to decompose the original difficult biochemical substances into organic substances that can be degraded, and then use aerobic bacteria and facultative bacteria to degrade it. Therefore, SBR is a biological treatment method with the synergistic effect of anaerobic and aerobic.
3. Technical characteristics and application scope of test results

3.1. Technical characteristics

3.1.1. It is not affected by the inhibitory substances in the wastewater. The wastewater does not need to be pretreated, the removal rate of DATB can be more than 97%, and $\text{SO}_4^{2-}$ has no inhibitory effect on facultative bacteria.

3.1.2. Impact load resistance. SBR reaction tank is designed for intermittent water inlet and intermittent discharge, which has the capacity of resistance to impact load of water capacity. Moreover, the sludge in SBR reactor has good activity (VSS: SS>0.8) and high concentration (sludge concentration is up to 8-12 g/L), so it has the ability to withstand the impact load of concentration. The results showed that the COD concentration of influent water increased from 8 g/L to 12 g/L in a short period of time, which had no significant effect on the treatment effect.

3.1.3. Good sludge performance. SBR reactor itself is a biological selector, high concentration of substrate in the influent is conducive to the rapid growth of non filamentous bacteria. According to the data, the content of RNA (deoxyribonucleic acid) in the sludge is 3-4 times higher than that in the conventional activated sludge process, and RNA determines the bacterial proliferation rate. Therefore, in the aeration tank of this experiment, the sludge has good activity and high concentration. Moreover, the sludge index was kept below 100, there was no filamentous growth and no sludge bulking. This is the key to keep the normal and stable operation of SBR system.

3.1.4. Low operating cost. SBR system does not need sludge reflux device (including sludge pump, sludge tank, etc.). Without aeration in idle time, the gradient of dissolved oxygen concentration in the aeration tank is large, and the utilization rate of oxygen is improved, which can save the power of the blower needed for aeration, so the operation cost is about 40% less than that of the conventional activated sludge method.

3.1.5. The sludge yield is low. SBR is operated under low oxygen or micro oxygen. According to the Monod equation, when the dissolved oxygen is less than 0.5 mg/L, the sludge yield is at least 25% lower than the dissolved oxygen more than 2 mg/L. The test shows that the sludge yield is 0.22 g dry sludge/(g COD).

3.2. Scope of application

SBR is a better technology to treat penicillin production wastewater, which is convenient in management and reliable in operation. Compared with the ordinary activated sludge process or anaerobic process, SBR has the advantages of high load, stability, impact resistance, etc., and has the advantages of low investment, less land occupation, low energy consumption, etc.

4. Conclusion

The SBR process overcomes the shortcomings of conventional aerobic process, such as high energy consumption, large dilution water, large floor area, high requirements for pretreatment and high operating cost. In practice, this method solves the problem of high concentration organic wastewater treatment which is seriously inhibited by anaerobic treatment, and the foam produced by DATB in waste water will not affect the normal operation of SBR treatment plant. Therefore, using SBR to treat penicillin wastewater has the advantages of low investment, low operation cost and easy construction, so it has great promotion value.

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