Optimization of operating parameters of biological denitrification for coking wastewater treatment

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Abstract. Biological denitrification is a traditional method for treating coking wastewater. Based on the theory of stage-feed water in biological denitrification process, the calculation method of stage-feed water distribution in coking wastewater treatment was discussed. As 100t/h incoming water, 30% incoming water for carbon supplemented source could meet the carbon source requirements. Further, response surface method was used to optimize the refluxes of nitrifying solution and sludge. When the nitrifying solution reflux and sludge reflux is between 51-105% and between 113-175% respectively in the process window controls, the total nitrogen could be controlled below 50mg/L. The research results can be used for reference in the practical application of the segmented inlet water process in biological denitrification for coking wastewater treatment.

1. Introduction

High concentration toxic compounds containing in coking wastewater need to be treated before discharging into environment [1]. According to the characteristics of coking wastewater quality and the requirements for environmental protection, many kinds of methods for coking wastewater treatment were developed, such as electrochemical oxidation by using Ti/RuO₂–IrO₂ electrodes [2] and adsorption by lignite activated coke and coal tar-derived activated carbon [3]. Biological denitrification process is widely used in treating coking wastewater, but the external carbon addition determines the economic cost and treating effect [4]. Reasonably allocated the flow rate of segmented water inlet AO process in three different ways was discussed [5]. The internal circulation control strategy from the utilization efficiency of carbon source was obtained and the fuzzy controller model of the internal circulation strategy model was established, which can effectively improve the management level of sewage plant [6]. The effects of various parameters of segmented inlet water AO process on the removal effect from the carbon nitrogen ratio in raw water and sludge reflux ratio was studied [7]. In this paper, the water inflow in two stages was calculate to replace part of the carbon source supplement in the second stage for the biological denitration method (anaerobic/ anoxic/ oxic/ oxic (A2/O2)), and a reasonable reflux ratio of nitrifying solution and sludge were studied by the response surface method.
2. Research methods
In biological denitration method (anaerobic/ anoxic/oxic/oxic (A2/O2)) for treating coking wastewater, the calculation of the distribution for raw water ratio is the key to overall process effect and the carbon source added. Therefore, how to match the water inflow in two stages to replace the carbon source supplement in the second stage is important to the staged water inflow process. In this paper, a coking wastewater in a company is taken as an example, by combining the quality characteristics of raw water and the segmented inlet process, the optimal flow distribution is determined by calculating the relationship between carbon source consumption and total nitrogen. When the COD of raw water is about 3000mg/L, if the high COD of raw water is used as carbon source supplement, the demand for carbon source in the second stage can be completely or partially replaced. In this way, the second stage of anoxic A2 will receive two parts of wastewater, one is the wastewater after the first stage of A/O treatment, and the other is part of raw water as a carbon source. Divided raw water into two sections A/O according to the calculated proportion makes full use of raw water as carbon source. In addition, to ensuring the treatment effect of the denitrification process, the problem of insufficient carbon source in the second stage is also solved. In this way, the two stages continuous A/O process is optimized by stage water inlet A/O process, as shown in figure 1. The efficiency of denitrification was also determined by the optimal reflux ratio of nitrifying solution and sludge, which was studied by the response surface method.

![Figure 1. The stages water inlet A/O process](image)

3. Results and discussion

3.1 Calculation of section inlet water
In the design process, the system needs to be considered of how to effectively completely match the water quality and water quantity for different wastewater. Namely, there is a very closely and relatively complex relationship between supply and demand for how to match the content of nitrogen and COD with the carbon source needed by denitrification in the second stage of anoxic pool (A2) for the mix of the first section of the A/O outlet water with the allocated water of raw segmented water [8].

If the allocation of segmented water is too large, the nitrifying load of the secondary aerobic tank will be too high, which will result in the substandard for ammonia nitrogen and total nitrogen from the secondary sedimentation tank. If the allocation of segmented water is insufficient, the supplemented carbon source for the second-stage anoxic pool will be insufficient. The theoretical calculation is as follows.

3.1.1 Calculation of carbon source for A2 needed. The carbon source for A2 needed composed the following two parts:

1) carbon source needed by nitrifying consumption of raw water. When nitrate nitrogen in raw water is 250 mg/L, the COD of available carbon source is about 1250mg/L.

2) The total amount of carbon source of nitrate and nitrite for O1 outlet water. According to the measurement data, the total value of nitrogen content is about 80 ~ 100mg/L, that is, the needed CODcr of available carbon source is:

\[(80-100\text{mg/L}) \times 5=400-500\text{mg/L}.\]

Considering that available carbon source for O1 effluent is insufficient, so the carbon source in this part is not considered as available carbon source.
3.1.2 Calculation of water allocation for A2.

(1) If the carbon source is supplemented according to 10% ratio (100t/h of incoming water), and its own denitrification and degradation consume 1250mg/L, the carbon source supplemented by A2 water is:

\[(3000 - 1250) \text{mg/L} \times 10 \text{t/h} \times 24 \text{h} \div 1000 = 420 \text{kg}\]

The total amount of available COD needed for nitrification by O1 water is:

\[(400 \sim 500 \text{mg/L}) \times 90 \text{t/h} \times 24 \text{h} \div 1000 = (864 \sim 1080) \text{kg} > 420 \text{kg}\]

The result is considering that all the supplementary carbon sources are utilized. In fact, all the supplementary carbon sources cannot be utilized, so the carbon sources are insufficient.

(2) If the carbon source is supplemented according to 20% ratio (100t/h of incoming water), and its own denitrification and degradation consume 1250mg/L, the carbon source supplemented by A2 water is:

\[(3000 - 1250) \text{mg/L} \times 20 \text{t/h} \times 24 \text{h} \div 1000 = 597 \text{kg}\]

The total amount of available COD needed for nitrification by O1 water is:

\[(400 \sim 500 \text{mg/L}) \times 80 \text{t/h} \times 24 \text{h} \div 1000 = (768 \sim 960) \text{kg} > 597 \text{kg}\]

Even if all the supplementary carbon sources are utilized, the carbon source is also insufficient.

(3) If the carbon source is supplemented according to 30% ratio (100t/h of incoming water), and its own denitrification and degradation consume 1250mg/L, the carbon source supplemented by A2 water is:

\[(3000 - 1250) \text{mg/L} \times 30 \text{t/h} \times 24 \text{h} \div 1000 = 1260 \text{kg}\]

The total amount of available COD needed for nitrification by O1 water is:

\[(400 \sim 500) \text{mg/L} \times 70 \text{t/h} \times 24 \text{h} \div 1000 = (672 \sim 840) \text{kg} < 1260 \text{kg}\]

According to the calculation result, the carbon sources meet the requirements.

Summary: CODcr supplemented with raw water cannot be utilized by all microorganisms. If only about 60-80% of CODcr can be utilized by microorganisms, the effective carbon source supplemented with 30% of water ratio is 756~1008kg, which can basically meet the carbon source required for the denitrification in section A2.

3.1.3 Check for volume load of nitrification. When the ammonia nitrogen in the raw water is about 80mg/L, the ammonia nitrogen from the O1 pool is 10mg/L, and the water allocation is 30%, the effective capacity of the O2 pool is 2376m³, the nitrifying volume load of the O2 pool is checked (The amount of ammonia nitrogen required per cubic meter per day in the O2 pool) as follow:

\[(80 \text{mg/L} \times 30 \text{t/h} \times 1 \text{m}^3/\text{t} \times 24 \text{h} + 10 \text{mg/L} \times 70 \text{t/h} \times 1 \text{m}^3/\text{t} \times 24 \text{h}) \div 2376 \text{m}^3 = 30 \text{mg/L} = 0.03 \text{kg}\]

The calculation result can meet the requirements.

There is a certain deviation between the theoretical calculation and the actual operation, and the influencing factors are also diversity. At present, the water allocation ratio of the second stage A/O in the actual operation is the most reasonable at 20-30%.

From the above, it can be seen that the nitrifying liquid reflux is set at the end of both A/O aerobic segments to supplement the demand for nitrate nitrogen in the anoxic segment A and ensure the total nitrogen to reach the standard. Meanwhile, in order to ensure the activity of bacteria in the anoxic segment, sludge reflux pipes should be set in the secondary sedimentation tank after the subsection A/O treatment to meet the demand for sludge in the anoxic segment.

3.2 Study on reflexes of nitrifying solution and sludge

According to the conventional design, the nitrifying solution reflux is set to 0-300% [9] and the reflux of sludge is set to 100-200% [10]. The adjustment range is large and the field control is difficult. In order to better guide the field practice, the optimal reflux ratio in the above range is determined
through DOE experiment. In this study, the operation sequence design was carried out according to the data of the influence of different reflux ratios on total nitrogen removal, as shown in table 1.

| Standard sequence | Operation sequence | Point type | Nitrifying liquid reflux | Sludge reflux | Ammonia nitrogen |
|-------------------|-------------------|------------|--------------------------|----------------|-----------------|
| 1                 | 1                 | 1          | 21.967                   | 71.967         | 111.4           |
| 2                 | 2                 | 1          | 128.033                  | 71.967         | 108.3           |
| 3                 | 3                 | 1          | 21.967                   | 178.033        | 105.7           |
| 4                 | 4                 | 1          | -0.000                   | 178.033        | 78.3            |
| 5                 | 5                 | -1         | 150.000                  | 125.000        | 125.1           |
| 6                 | 6                 | -1         | 75.000                   | 125.000        | 114.9           |
| 7                 | 7                 | -1         | 75.000                   | 50.000         | 105.1           |
| 8                 | 8                 | -1         | 75.000                   | 200.000        | 40.2            |
| 9                 | 9                 | 0          | 75.000                   | 125.000        | 30.5            |
| 10                | 10                | 0          | 75.000                   | 125.000        | 34.2            |
| 11                | 11                | 0          | 75.000                   | 125.000        | 44.8            |
| 12                | 12                | 0          | 75.000                   | 125.000        | 40.1            |
| 13                | 13                | 0          | 75.000                   | 125.000        | 44.1            |

In the simulation calculation by using Minitab software, it was found in the experiments of two kinds of reflux: the influence of nitrifying liquid reflux and sludge reflux on total nitrogen in effluent was significant (because P<0.05), and the central point was significant (P<0.05) (as shown in table 2).

| Project          | Effect | Coefficient | Coefficient standard error | T    | P    |
|------------------|--------|-------------|---------------------------|------|------|
| Constant         | 54.38  | 1.060       | 51.31                     | 0.000|
| Nitrifying liquid reflux | -18.55 | -9.27 | 1.060 | -8.75 | 0.001 |
| Sludge reflux    | -43.95 | -21.97      | 1.060                     | -20.73 | 0.000 |
| Nitrifying liquid reflux * Sludge reflux | 2.95 | 1.48 | 1.060 | 1.39 | 0.236 |
| Ct Pt             | 7.13   | 1.422       | -5.02                     | 0.007|

In order to determine the relationship between the above factors, response surface analysis is required to create a two-factor response surface design. The level of nitrifying liquid return flow is 0 and 150%, and the level of sludge return flow is 50 and 200%, respectively. The results are shown in table 3.

| Project          | Coefficient | Coefficient standard error | T    | P    |
|------------------|-------------|---------------------------|------|------|
| Constant         | 36.74       | 4.313                     | 8.519| 0.000|
| Nitrifying liquid reflux | -5.616 | 3.410 | -1.647 | 0.001 |
| Sludge reflux    | -15.935     | 3.410                     | -4.674| 0.002|
| Nitrifying liquid reflux * Sludge reflux | 42.780 | 3.656 | 11.700 | 0.000 |
| Sludge reflux * Sludge reflux | 19.105 | 3.656 | 5.225 | 0.001 |

S=9.64372      PRESS=2840.83
R-Sa=95.64%    R-Sq (Predict)=87.34%   R-Sq (Adjust)=93.46%
According to response surface analysis, the P value of "nitrifying liquid reflux * sludge reflux" was > 0.05, R-Sq = 96.50% was significantly different from R-Sq (prediction) = 79.32%. After one times deletion, the P value was < 0.05, and R-Sq = 95.64% was close to R-Sq (prediction) = 87.34% (as shown in table 3). The residual normality is good and the model is reliable, as shown in figure 2.

Contour map analysis was used to obtain the optimal process control range. According to the contour map (as shown in figure 3).

Figure 2. Second analysis of response surface after deletion.

Figure 3. Contour map of ammonia nitrogen, nitrifying solution reflux and sludge reflux.

As shown in Figure 3, the process window should control the nitrifying solution reflux between 51-105% and sludge reflux between 113-175% for controlling the total nitrogen below 50mg/L.

4. Result
In the case of ensure the best effect of biological denitrification, the operating cost in the external carbon source can be reduced by reasonable water allocation. In this paper, the optimal flow ratio is determined by the relationship between the COD and ammonia nitrogen contents in raw water and the water distribution. The best removal effect of total nitrogen was determined by refluxes of nitrifying solution sludge calculated by Minitab software. The results can be used for reference in the water distribution for A/O process.

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