Study on Purification Technology of High-salt Nitrogenous Printing and Dyeing Wastewater

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Abstract. This paper reports the microbial nitrogen removal, flocculation and decolorization purification technology of high-salt nitrogenous printing and dyeing wastewater. The combined microbial flora was used to perform simultaneous nitrification and denitrification (SND) nitrogen removal for high-salt nitrogenous printing and dyeing wastewater. When the sodium acetate was the carbon source and C:N was set to 7.5:1, the concentration of NH₄⁺-N was reduced from the initial 2000.0 mg/L to 18.0 mg/L and the nitrogen removal rate was 99.1% and the nitrogen removal efficiency was 16.5 mg L⁻¹·h⁻¹ at 120h. Poly aluminum chloride (PAC) was the suitable flocculant. Under the optimized conditions that the dosage of PAC was 0.5 g/L and the flocculation time was 10 min, the flocculation rate reached 96.5%. Among the four decolorization methods of ozone, 84 disinfectant, hydrogen peroxide and chlorine dioxide, the decolorization effect of ozone oxidation was superior. When the production of ozone was 167 mg/min and the reaction time was 4 min, the decolorization rates all of neutral red, acid green and methyl orange could reach over 94.0%. This study provides theoretical and technical support for the purification of high-salt nitrogenous printing and dyeing wastewater.

1. Introduction
The main pollutants in high-salt nitrogenous printing and dyeing wastewater include high concentration of salt which seriously inhibited microbial activity and resulted in low efficiency of traditional biological treatment[1], high concentration of ammonia nitrogen produced by using a large amount of urea as an auxiliary in the printing process, particles with a small particle size that are difficult to separate, and dyes and dyeing aids with chromospheres groups. The comprehensive treatment of this type of wastewater has become an urgent problem to be solved[2]. At present, the commonly used techniques for nitrogen removal include: air stripping, break point chlorination and biological methods. The air stripping method is relatively affected by temperature and has strict requirements of pH and high energy consumption. Break point chlorination has high requirements for the storage and use of liquid chlorine and by-product causes secondary pollution. In the process of biological nitrogen removal, the high salt environment inhibits the growth of microorganisms and even kills microorganisms[3]. The flocculants commonly used include organic flocculants and inorganic flocculants. Organic polymer flocculants have good purification effect and wide range of pH, but their prices are relatively expensive. Traditional inorganic flocculants are highly corrosive to equipment and the rate of polymerization is slow and the floc is small. Inorganic polymer flocculants are more effective than traditional flocculants and are less expensive than organic polymer flocculants.
Therefore, it has a tendency to become mainstream flocculants[4]. The common decolorization technology of dyeing wastewater is chemical flocculation, but this method has poor decolorization effect on reactive dyes and water-soluble dyes, and even has no effect[5].

In this paper, the high-salt nitrogenous simulated printing and dyeing wastewater was treated from the three key technologies, which include nitrogen removal, flocculation and decolorization, to provide theoretical and technical support for the treatment of such wastewater.

2. Materials and methods

2.1. Materials

Strains: strains with nitrogen removal function isolated and screened in our laboratory included Bacillus sp. Y01, Bacillus sp. Y03, Bacillus sp. Y06, Bacillus sp. Y10, Bacillus sp. Y21, Pseudomonas sp. J07, Pseudomonas sp. J09, Geotrichum sp. B09, Halomonas sp. B05, Halomonas sp. H02.

LB medium (g/L): peptone 10, yeast powder 5, NaCl 5 (30), pH 7.2, sterilized at 121 °C 20 min.

Strengthening medium (g/L): glucose 20, ammonium sulfate 4, yeast powder 1, K2HPO4:3H2O 9, KH2PO4 3, MgSO4:7H2O 0.1, NaCl 30, trace element 2 mL (trace elements: EDTA-2Na 63.7, ZnSO4 2.2, CaCl2 5.5, MnCl2-4H2O 5.1, FeSO4-7H2O 5, Na2MO2:2H2O 1.1, CuSO4·5H2O 1.6), trace element filtration sterilization (0.22 μm pore size, Millipore Express, USA).

Sludge: aeration tank sludge was from a sewage treatment plant in Dalian. High-salt nitrogenous simulated printing and dyeing wastewater (it was referred to as simulated wastewater hereinafter) (g/L): N element 2000 mg/L (ammonium sulfate), sodium acetate (concentration determined by experimental conditions), NaCl 30, dye (neutral red, acid green, methyl orange) 25 mg/L, turbidity 353 NTU (the particulate matter was derived from a high-salt nitrogenous printing and dyeing wastewater of a factory).

2.2. Methods

2.2.1. Activated sludge strengthening method. The nitrogen removal strains were activated by LB medium for 24 h and were centrifuged to remove the supernatant. Then they were added to the strengthening medium which the sludge sedimentation rate was 25.0% and was shaken at 120 rpm and 30 °C for 9 days.

2.2.2. Nitrogen removal methods. The settings and conditions of nitrogen removal methods were shown in table 1.

| Nitrogen removal methods | Organic carbon source | Training methods |
|--------------------------|-----------------------|------------------|
| Synchronous aerobic heterotrophy | Add to | Shaker oxygen supply |
| Synchronous aerobic self-support | Do not add | Anaerobic culture |
| Synchronous anaerobic heterotrophy | Add to | Shaker oxygen supply |
| Synchronous anaerobic self-support | Do not add | Anaerobic culture |

Note: The N element of simulated wastewater was 2000.0 mg/L and the organic carbon was sodium acetate (C:N=5:1). Oxygen was supplied in shaker at 120 rpm, 30 °C. Anaerobic culture: AG015 closed anaerobic tank, 30 °C.

2.2.3. Determination methods of inorganic nitrogen. Total inorganic nitrogen (TN) included ammonia nitrogen (NH4+ -N), nitrite nitrogen (NO2- -N) and nitrate nitrogen (NO3- -N). The rate of nitrogen removal was defined as the percentage of reduced TN in the nitrogen removal system as a percentage of TN. Nitrogen removal rate = (TNo-TNt)/TN0×100%. NT0 was the TN at the initial stage of nitrogen removal, and TNt was the TN at a certain moment in the nitrogen removal process. The concentration of NH4+ -N was determined by the Nessler’s reagent method[6]. The concentration of NO2- -N was...
determined by the diazotization-coupling reaction method[6]. The concentration of NO$_3^-$-N was determined by zinc cadmium reduction method[7].

2.2.4. Flocculation method[8]. A certain amount of flocculants solution (5% poly aluminum ferric chloride (PAFC), 5% poly ferric sulfate (SPFS) and 5% poly aluminum chloride (PAC)) was added to the beaker containing 1000 mL of nitrogen removal simulated wastewater. After fully stirring, it was allowed to stand for 20 min, and the supernatant was taken to measure the absorbance. The calculation method was flocculation rate = (B-A)/B×100%. A and B were the absorbance of the test group and blank group at 600 nm, respectively.

2.2.5. Decolorization method[9]. Ozone (the specification ozone generator is 10 g/h) was introduced in a beaker with 1000 mL of simulated wastewater for 10 min at room temperature. And the supernatant was taken to measure the absorbance each 1 min. The calculation method was decolorization rate = (A$_0$-A$_i$)/A$_0$×100%. A$_0$ and A$_i$ were the absorbance at the maximum absorption peak at the initial and t min of the simulated wastewater, respectively.

3. Results and discussions

3.1. Microbial flora enhanced activated sludge to nitrogen removal in simulated wastewater

3.1.1. Effects of different nitrogen removal methods on nitrogen removal efficiency. Firstly, the nitrogen removal efficiency of activated sludge, which was strengthened as method 2.2.1, was investigated. According to method 2.2.2, the nitrogen removal methods were set to synchronous aerobic heterotrophic, synchronous aerobic autotrophic, synchronous anaerobic heterotrophic and synchronous anaerobic autotrophic and the pH was controlled at 7~8. The results were shown in table 2. The activated sludge was denitrified only under heterotrophic conditions. The aerobic heterotrophic condition had the highest nitrogen removal rate that was 91.7% and the nitrogen removal efficiency was 19.1 mg·L$^{-1}$·h$^{-1}$ at 96 h. The optimal nitrogen removal method for the activated sludge was simultaneous nitrification and denitrification (SND) nitrogen removal.

| Nitrogen removal methods                      | Initial total inorganic nitrogen (mg/L) | Residual total inorganic nitrogen (mg/L) | Nitrogen removal rate (%) | Nitrogen removal efficiency (mg·L$^{-1}$·h$^{-1}$) |
|-----------------------------------------------|----------------------------------------|----------------------------------------|---------------------------|---------------------------------|
| Synchronous aerobic heterotrophy              | 2000.0                                 | 167.0±13.0                             | 91.7±0.7                  | 19.1                            |
| Synchronous aerobic self-support              | 2000.0                                 | 2064.0±12.0                            | -                        | -                               |
| Synchronous anaerobic heterotrophy            | 2000.0                                 | 1905.0±9.0                             | 4.8±0.5                   | 1.0                             |
| Synchronous anaerobic self-support            | 2000.0                                 | 2236.0±10.0                            | -                        | -                               |

Note: “.” indicated that no nitrogen removal had been detected.

3.1.2. Optimization of the conditions of SND nitrogen removal. The effects of different C/N on the nitrogen removal rate were investigated. The C/N was set to 2.5:1, 5:1, 7.5:1 and 10:1. According to the method 2.2.2 to perform SND nitrogen removal, the nitrogen removal rates at 120 h were shown in figure 1. The optimized C/N was 7.5:1 and the nitrogen concentration of the simulated wastewater was reduced from the 2000.0 mg/L to 18.0 mg/L. The nitrogen removal rate was 99.1% and the nitrogen
removal efficiency was 16.5 mg·L⁻¹·h⁻¹. When the C/N was 10:1, the nitrogen removal rate was no longer increased.

\[
\text{Nitrogen removal rate } = 16.5 \text{ mg·L}^{-1} \cdot \text{h}^{-1}.
\]

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\text{When the C/N was 10:1, the nitrogen removal rate was no longer increased.}
\]

![Figure 1. Effects of different C/N on nitrogen removal result.](image)

**Figure 1.** Effects of different C/N on nitrogen removal result.

Note: The N element of simulated wastewater was 2000.0 mg/L and the organic carbon was sodium acetate. The time of nitrogen removal was 120 h in the shaker at 120 rpm, 30 °C. The pH was controlled at 7~8.

In summary, the best method of nitrogen removal was SND nitrogen removal for strengthened activated sludge and the optimized C/N was 7.5:1. Under such conditions, the nitrogen concentration of the simulated wastewater was reduced from the 2000.0 mg/L to 18.0 mg/L. The nitrogen removal rate was 99.1% and the nitrogen removal efficiency was 16.5 mg·L⁻¹·h⁻¹ at 120 h.

### 3.2. Flocculation purification on simulated wastewater

#### 3.2.1. Type and dosage of flocculants

According to method 2.2.4, the effects of type and dosage of flocculants in simulated wastewater were investigated. The types of flocculants included PAC, PAFC and SPFS. The dosages were set to 0 g/L, 0.3 g/L, 0.5 g/L, 0.8 g/L, 1.0 g/L and 1.3 g/L. The flocculation time was 20 min. The results were shown in figure 2. The flocculation effect of PAC was the best and the flocculation rate was 95.2% at 0.5 g/L.

![Figure 2. Flocculation rate of PAC, PAFC, and SPFS.](image)

**Figure 2.** Flocculation rate of PAC, PAFC, and SPFS.

#### 3.2.2. Flocculation time

The effects of flocculation time on simulated wastewater were investigated. The flocculants included PAC, PAFC and SPFS. The dosages were set to 0.5 g/L, 0.8 g/L and 0.8 g/L. The time was set to 0 min, 5 min, 10 min, 15 min and 20 min, respectively. The results were shown in figure 3. The flocculation rates of PAC, PAFC and SPFS reached 91.8%, 87.5% and 79.8% at 5 min, respectively. When time was not less than 10 min, the flocculation rate was basically no longer increased.
5

Figure 2. Effects of dosages on flocculation result.
Note: The flocculation time was 20 min at room temperature.

Figure 3. Effects of flocculation time on flocculation result.
Note: The dosages of PAC, PAFC and SPFS were set to 0.5 g/L, 0.8 g/L and 0.8 g/L, respectively, at room temperature.

In summary, the suitable flocculant was PAC. When the dosage was 0.5 g/L and the flocculation time was 10 min, the flocculation rate reached 96.5%.

3.3. Decolorization on simulated wastewater
Firstly, ozone, 84 disinfectant, hydrogen peroxide and chlorine dioxide were used to decolorize the simulated wastewater, respectively. The results were shown in figure 4. The decolorization effects were ozone > 84 disinfectant > hydrogen peroxide > chlorine dioxide. Although 84 disinfectant and ozone had similar decolorization effects, ozone decolorization time was relatively short and had no secondary pollution. Therefore, ozone was selected to decolorize the simulated wastewater.

According to method 2.2.5 to do decolorization by ozone, the concentrations all of neutral red, acid green and methyl orange were 25 mg/L and the results were shown in figure 5. The decolorization rate reached 94.0% when ozone was introduced for 4 min. Although the decolorization rate could reach 99.0% or more, the decolorization rate did not change much with time after 4 min.

Figure 4. Effects of different decolorants on decolorization result.
Note: The decolorization time was 30 min at room temperature.

Figure 5. Effects of time on decolorization result.
Note: The concentrations all of neutral red, acid green and methyl orange were 25 mg/L and the measured wavelengths were 525 nm, 610 nm and 445 nm, respectively.

Used the spectrophotometer to scan the absorbance at the range of 300~700 nm and the spectrum of the simulated wastewater before and after ozone decolorization were shown in figure 6. The characteristic absorption peak disappeared, indicating that the chromospheres were completely
oxidized by ozone. The wastewater was nearly completely discolored.

Figure 6. Spectrum of simulated wastewater before and after decolorization. Note: (a), (b) and (c) showed the spectrum of neutral red, acid green and methyl orange before and after decolorization, respectively.

4. Conclusion
The best method of nitrogen removal for strengthened activated sludge was SND nitrogen removal and the optimized C/N was 7.5:1. Under such conditions, the concentration of NH$_4^+$-N was reduced from the 2000.0 mg/L to 18.0 mg/L and nitrogen removal rate was 99.1% and the nitrogen removal efficiency was 16.5 mg·L$^{-1}$·h$^{-1}$ at 120 h. PAC was the suitable flocculant. When the dosage of PAC was 0.5 g/L and the flocculation time was 10 min, the flocculation rate reached 96.5%. Among the four decolorization methods of ozone, 84 disinfectant, hydrogen peroxide and chlorine dioxide, the decolorization effect of ozone oxidation was superior. When the production of ozone was 167 mg/min and the reaction time was 4 min, the decolorization rates all of neutral red, acid green and methyl orange could reach over 94.0%.

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