Research on Treatment Technology of High Ammonia Nitrogen Wastewater from Shale Refinery

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Abstract. This article describes the nature and hazards of shale refining high ammonia nitrogen wastewater, and summarizes the characteristics of various treatment technologies for shale refining high ammonia nitrogen wastewater. Methods for treating ammonia-containing nitrogen include chemical precipitation and the like. This article reviews the research status and development trend of shale refining high-ammonia wastewater treatment technology.

1. Introduction
In recent years, the treatment of shale refining wastewater with high ammonia nitrogen has attracted widespread attention from the society. High concentration of ammonia nitrogen is the key to restrict the treatment of shale refining wastewater. For this reason, scholars at home and abroad have conducted a lot of research. Oil shale will produce a large amount of high ammonia nitrogen wastewater in the refining process. Because ammonia nitrogen is not conducive to sewage reuse, it needs advanced treatment. Humans drinking wastewater containing high ammonia nitrogen will cause great harm to human health. Therefore, taking efficient measures to treat ammonia nitrogen wastewater to reduce its environmental pollution has attracted widespread attention from scholars at home and abroad. The current treatment methods for wastewater containing ammonia nitrogen include stripping method, precipitation method, anaerobic ammonia oxidation technology. This article reviews the treatment technology of shale refining wastewater with high ammonia nitrogen, and summarizes the development direction of the treatment technology, which is of great significance to the reuse of shale refining wastewater.

2. Chemical treatment method
2.1. Chemical precipitation
The chemical precipitation method is to add magnesium salt and phosphate agent to ammonia-containing wastewater to form magnesium ammonium phosphate precipitation (MAP) with low solubility and crystal water at room temperature, commonly known as struvite [1-3]. The magnesium ammonium phosphate method began in the 1960s and gradually developed. In the past 20 years, this method has been widely used [4]. Due to the high ammonia nitrogen content in shale oil refinery wastewater, it cannot be directly treated by biochemical methods. If the wastewater is diluted and treated, the wastewater treatment volume will be increased. The struvite method does not need to dilute the wastewater and can be directly treated with chemicals. At the same time, the struvite
precipitates can be used as fertilizer or feed, and can also be used as flame-retardant materials or refractory materials to realize resource utilization. Magnesium ammonium phosphate precipitation method is feasible to treat ammonia nitrogen in shale oil refinery wastewater. This method has the advantages of simple operation, rapid response, no secondary pollution, etc., but the amount of medicament is large and the treatment cost is high. The processing cost can be reduced by optimizing the process, developing low-cost agents, and studying the crystal growth mechanism, so that it can be applied on a large scale.

2.2. Folding point chlorination
Breakpoint chlorination method [5] is to pass excess Cl₂ into the wastewater, and the ammonia nitrogen is oxidized to nitrogen and removed from the wastewater. Breakpoint chlorination method has the advantages of short reaction time, less equipment required and not affected by temperature, but other pollutants in the wastewater will react with Cl₂ to form more difficult-to-treat substances, causing secondary pollution, and the amount of chlorination is also difficult control. Therefore, this method is not suitable for the treatment of high-concentration ammonia nitrogen wastewater, which requires a relatively high cost. The wastewater after chlorine treatment needs to be neutralized with alkali before it can be discharged, which in turn increases the amount of chemicals used. Studies have shown that sodium hydroxide or soda lime is generally added to supplement the alkalinity when neutralizing wastewater.

2.3. Catalytic wet air oxidation method
Catalytic wet air oxidation requires high temperature, high pressure, and the presence of catalysts to completely oxidize ammonia nitrogen in wastewater. This method requires higher equipment requirements, more expensive catalysts, and higher investment.

3. Physicochemical method treatment methods

3.1. Blow off method
The removal of ammonia nitrogen by stripping method is a gas-phase mass transfer process. Under alkaline conditions, NH₄⁺ in the wastewater is gradually transformed into NH₃, the wastewater is fully contacted with steam, and the ammonia is stripped and transferred to the gas phase, reducing the concentration of ammonia nitrogen in the wastewater [6]. The factors that affect the blow-off efficiency include temperature, pressure, pH, etc., and various factors need to be adjusted appropriately to achieve a higher treatment efficiency. The temperature has a great influence on the blow-off efficiency, and the water temperature needs to be increased appropriately. The removal rate of ammonia nitrogen increases with the increase of pH value. When the pH reaches 12, the removal rate of ammonia nitrogen reaches the highest. For high ammonia nitrogen shale oil refinery wastewater, the stripping method can be used for treatment, the removal effect is better, and the ammonia nitrogen can be recovered at the same time, but the wastewater after the stripping method needs to be neutralized before it can be discharged, which increases the subsequent treatment cost.

3.2. Steam stripping method
Steam stripping is a better method for ammonia removal and has been widely used in the pretreatment of shale oil refinery wastewater biological denitrification process. Due to the large amount of steam consumed during steam denitrification, the process is more complicated. If the ammonia nitrogen in the wastewater is completely removed by the stripping method, it is uneconomical and technically difficult to achieve.

3.3. Ion exchange process
When the ion exchange method adsorbs ammonia nitrogen in shale oil refinery wastewater, the amount of adsorbent used is large, and frequent regeneration is required. Dilute ammonia is not easy to
recycle, not only the cost is high, but the waste liquid generated during the regeneration process may also cause secondary pollution.

### 3.4. Membrane absorption method
Absorption method for ammonia removal has the advantages of convenient operation and maintenance, small equipment footprint, high ammonia removal rate and recovery rate, no secondary pollution, suitable for the treatment of high-concentration ammonia nitrogen wastewater, and the effluent ammonia nitrogen concentration can be controlled according to needs. But there are also problems such as membrane fouling and membrane performance degradation.

### 4. Biochemical treatment methods
The iron-carbon micro-electrolysis method is a new type of wastewater denitrification treatment technology, which is the result of the joint action of electricity and biofilm, and the cost can be reduced by about 40%. The factors that affect the iron-carbon micro-electrolysis denitrification technology include: pH, iron-carbon ratio, reaction time, etc. The ferric hydroxide and ferrous hydroxide produced after the reaction are high-efficiency flocculants, which can absorb suspended solids in shale oil refinery wastewater and reduce the color. The iron-carbon micro-electrolysis method can also degrade toxic pollutants in shale oil refinery wastewater while treating ammonia nitrogen, and further improve the quality of the effluent.

### 5. Biological methods
Biological method is not suitable for the treatment of high-concentration ammonia nitrogen wastewater [7], and the treatment effect is poor. It can be treated by chemical method or physicochemical method first, and then treated by biological method. The principle of biological treatment of ammonia nitrogen wastewater is that ammonia nitrogen is first converted into nitrate nitrogen or nitrite nitrogen through nitrification under aerobic conditions, and then nitrate nitrogen is reduced to nitrogen through denitrification under anoxic conditions and escapes from the wastewater out. The conversion of ammonia nitrogen is shown in Figure 1. Biological nitrogen removal technology has the advantages of simple operation, economical efficiency, convenient management and low operating cost. Biological nitrogen removal processes include: A²/O, SBR, MBR[8], ANAMMOX, IMO, ICEAS, CASS, etc.

![Figure 1. Extraction and dephenolization process.](image)

6. Wastewater treatment technology comparison

| Method classification | principle | Main technology | Advantage | Disadvantage | Applicable water quality |
|-----------------------|-----------|-----------------|-----------|--------------|-------------------------|
| Chemical method       | Precipitation, oxidation | MAP, CWAO, breaking point chlorination method | Fast response, Simple operation | Higher cost | High concentration ammonia nitrogen wastewater |
| Physicochemical method| Phase balance | Blow off method, Steam stripping method, Ion exchange method, Membrane absorption method | Simple process | Have secondary pollution | Medium and high concentration ammonia nitrogen wastewater |
| Biochemical treatment methods | Denitrification | Iron-carbon micro-electrolysis | More economical | Higher technology | Medium and high concentration ammonia nitrogen wastewater |
|-------------------------------|----------------|-----------------------------|----------------|-----------------|--------------------------------------------------------|
| Biological method             | Nitrification, denitrification | $\text{A}^2\text{O}$, SBR, MBR, CASS, ANAMMOX, IMO, ICEAS | No secondary pollution, More economical | Need to add carbon source | Medium and low concentration ammonia nitrogen wastewater |

7. Conclusion

The high ammonia nitrogen content in shale oil refinery wastewater limits the treatment of shale oil refinery wastewater. Shale oil refinery wastewater is not suitable for biological treatment, and physical and chemical treatment is better. The physical and chemical method for removing ammonia nitrogen has the advantages of easy operation, wide application range and high treatment efficiency. At present, the research on high-efficiency ammonia nitrogen wastewater treatment technology to achieve the discharge of wastewater is of great significance to the reuse of shale oil refinery wastewater.

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