Study on two-stage air-recirculation ammonia stripping process for membrane concentrate in livestock and poultry breeding

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Abstract. Aiming at the problems of the subsequent treatment of the biogas liquid membrane concentrate and the large alkali consumption of the traditional stripping process, a two-stage closed-cycle ammonia stripping process was designed, and the two-stage air-recirculation ammonia stripping process was used to treat the biogas liquid membrane concentrate. Studies have shown that in the first stage of ammonia stripping, when the gas-liquid ratio is 3600, the pH of the membrane concentrate liquid after the closed loop treatment reaches the maximum value of 8.75, and the alkalinity is also reduced from the initial 8150 to 6615.After the primary stripping is completed, the pH of the membrane concentrate can be quickly increased by adding alkali to meet the normal ammonia stripping conditions for the secondary stripping tower. When the liquid ratio of the secondary stripping tower is 3600, the temperature is 40°C, and the CaO dosage is 25g/L, the removal rate of ammonia nitrogen is 86%. Adding a first-stage tower blowing off, the CaO dosage is reduced by 5g/L.

1 Introduction

In recent years, biogas projects have been widely used for the treatment of large-scale livestock and poultry farming manures, but at the same time, wastes such as biogas residues and liquids will also be generated. Biogas liquids can be used as good fertilizers for subsequent use. Due to the basic national conditions of Separation of planting and breeding, the biogas slurry in most farms cannot be effectively returned to the field. The biogas slurry membrane concentration technology has both separation and concentration methods, and is energy-saving, efficient and environmentally friendly. At present, there have been a lot of researches on biogas slurry nanofiltration, ultrafiltration and reverse osmosis [1-3]. Membrane concentration can remove COD well, but it cannot remove ammonia nitrogen efficiently.

For nitrogen reduction and recovery methods, mainly including physical methods, chemical methods, biological methods, etc. Among them, physical methods include reverse osmosis, distillation and other technologies; chemical methods include ion exchange, ammonia stripping, breaking point chlorination, incineration, catalytic cracking, electrodialysis, electrochemical treatment and other technologies; biological methods include algae cultivation, biological nitrification, and denitrification.[4]. The stripping method is the most commonly used physical method to treat ammonia nitrogen wastewater. It uses the difference between the concentration of volatile substances such as ammonia nitrogen contained in the wastewater and the corresponding equilibrium concentration in the gas phase. Under alkaline conditions, it is stripped with air or steam. Stripping makes the ammonia nitrogen and other volatile substances in the wastewater continuously transfer from the liquid phase to the gas phase, so as to achieve the purpose of removing ammonia nitrogen from the wastewater [5].

The stripping method has been studied in different fields due to its high ammonia nitrogen removal rate, low treatment cost, simple equipment system, etc. It has been widely used as the treatment of ammonia nitrogen wastewater such as landfill leachate, coking wastewater, livestock and poultry breeding wastewater,[6-10] Compared with other physical and chemical treatment methods, the stripping method does not require complicated equipment, has simple process, simple operation and relatively low operating cost, and is an efficient physical and chemical denitrification process. The main factors affecting ammonia stripping are air-liquid ratio, pH value, stripping time, temperature.[7]. Although the stripping method can effectively remove ammonia nitrogen, it consumes a large amount of alkali, and the stripping tower is prone to problems such as scaling and wall flow. Aiming at the above problems, this paper proposes a two-stage closed-cycle ammonia stripping system to study the effect of the system on the treatment of ammonia nitrogen in the liquid membrane concentrate of livestock and poultry breeding, and provide technical reference for the subsequent use of the process and the advanced treatment of the biogas slurry.

2 Experimental materials, devices and methods

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2.1 Experimental materials

The biogas slurry used in the experiment was taken from the anaerobic digestion liquid from a large-scale pig farm in Jiading District, Shanghai, which was concentrated and separated by ultrafiltration membrane. The test water quality indicators are shown in Table 1.

Table 1. Water quality index of biogas slurry in ammonia stripping experiment

Index	pH value	Alkalinity (mg·L^{-1})	COD (mg·L^{-1})	NH_4^+-N (mg·L^{-1})	TP (mg·L^{-1})
Biogas slurry	7.8	8150	4000～5000	600～700	100～120

2.2 Experimental device

The two-stage closed air-circulation system consists of a first-stage stripping tower, a second-stage stripping tower, a strong acid absorption tower and a strong alkali absorption tower. The material of the stripping tower is made of organic glass resistant to acid and alkali corrosion. The tower is 1.2m long and 100mm in diameter. The top of the tower is equipped with a spray head, the tower body is equipped with an exhaust port, the tower body and the liquid storage tank are sealed with flanges, the liquid collection tank adopts a cylindrical structure, a pressure relief valve is installed on the top, and a heater is installed inside. The packing layer adopts polyethylene hollow polyhedral sphere with a diameter of 25mm,the height of the packing layer is 1m. The CO_2 absorber and ammonia absorber are also made of plexiglass, the size is 20cm×20cm×30cm, and the cylindrical structure is still adopted. The inlet of the intake pipe is about 5cm away from the bottom of the reactor, and the top of the ammonia absorber is reversely installed to relieve pressure valve.

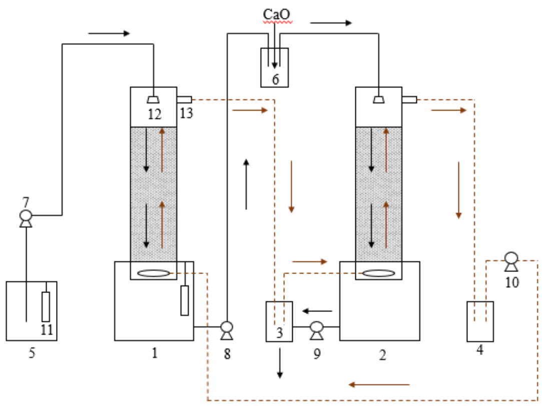

Fig. 1. Schematic diagram of two-stage air-recirculated stripping system.(1) First stage stripping tower; (2) Second stage stripping tower; (3) CO_2 absorber tank; (4) NH_3 absorber tank; (5) Liquid storage tank; (6) Mixing tank; (7) Biogas slurry peristaltic pump 1; (8) Biogas slurry peristaltic pump 2; (9) Biogas slurry peristaltic pump 3; (10) Air pump; (11) Heating rod; (12) Sprinkler; (13) Gas outlet

2.3 Experimental method

At the beginning of the experiment, the air is circulated according to the following process,the air is sprayed from the aeration port at the bottom of the first-stage stripping tower, flows from bottom to top, and then enters the CO_2 absorber from the air outlet to remove CO_2.Then follow the pipeline to the bottom of the secondary stripping tower, flow through the packing layer, and finally enter the ammonia absorber from the air outlet. After removing the ammonia from the gas, it will be sent back to the primary stripping tower by the air pump to form a closed loop system. At the beginning of stripping, the biogas slurry is pumped into the top of the first-stage tower through the liquid inlet tank, flows down through the top nozzle, and enters the liquid storage tank at the bottom of the stripping tower, and then is extracted by the peristaltic pump and sent to the agitator. Add alkaline agent to adjust the pH of the solution to 11, and then send it to the top of the secondary tower by a water pump, and flow down through the nozzle. After reaching the bottom of the tower, it is sent to the CO_2 absorber through a pipe.After absorbing the CO_2 in the exhaust gas from the first-stage tower, it is discharged out of the system.

2.3.1 Effects of temperature on the first stage stripping

There are various forms of carbonic acid compounds in livestock wastewater and effluent after anaerobic digestion,these carbonates are important factors in determining the pH value of these water quality systems, and make the water quality systems have buffer capacity for external acid and alkali.Carbonic acid mainly exists in four forms of CO_2, H_2CO_3, $HCO_3^-$and CO_3^{2-}[11]. In the process of stripping and aeration, the free CO_2 will be blown out first due to the low solubility of CO_2. When the concentration of dissolved CO_2 gradually decreases, The HCO_3^- and H^+ in the anaerobic digestion solution have the following ionization equilibrium formula:

$$HCO_3^- + H^+ = CO_2 + H_2O \tag{1}$$

The relationship between HCO_3^- and CO_2 can be drawn:

$$[HCO_3^-] = [CO_2] \times K_1 / [H^+] \tag{2}$$

The ionization constant K_1 is a fixed value. When the anaerobic digestion solution is stripping, the dissolved CO_2 concentration will continue to decrease, the equilibrium system will shift, and the HCO_3^- and hydrogen ions in the water will also continue to decrease.According to the equilibrium relationship of water ionization, OH^- ions continue to increase, and the pH value of the solution rises accordingly. Kim [12] et al. used the stripping process to remove CO_2 from the solution and increase the pH value of the anaerobic digestion solution of the sludge bed of the paper mill, so that the alkalinity of the anaerobic digestion solution was precipitated in the form of calcium carbonate. Therefore, the pretreatment by stripping can reduce the alkalinity of

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the anaerobic digestion solution, increase the pH, and reduce the amount of alkaline substances added in the ammonia stripping, which is beneficial in terms of economic costs and environmental ecology.

This experiment first explores the pretreatment effect of the first stage stripping tower on membrane concentration. The experimental device is shown in the Figure 2.

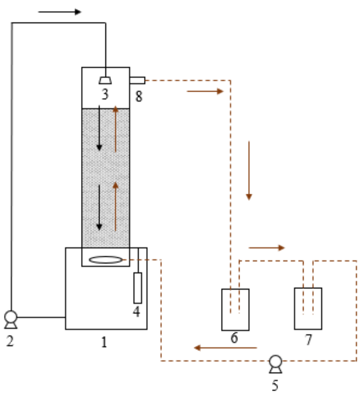

Fig.2 Schematic diagram of first stage air-recirculated stripping system. (1) Stripping tower; (2) Biogas slurry peristaltic pump (3) Sprinkler; (4) Heating rod; (5).Air pump (6) CO_2 absorber tank (7) NH_3 absorber tank; (8) Gas outlet;

Turn on the regulating valve switch, the system is in an open state, set three temperature gradients of 20, 30, and 40°C, adjust the flow rate of the diaphragm vacuum pump to 60L/min, and use a heating rod to heat 3 parts of 1L anaerobic digestion solution to 20, 30, 40 ℃ and then perform ammonia stripping, take samples from the liquid outlet according to different gas-liquid ratios to determine the ammonia nitrogen concentration, pH and alkalinity, and conduct three parallel tests. The optimum temperature of ammonia stripping was analyzed by the change curves of ammonia concentration, PH and alkalinity.

2.3.2 Effects of system status on the first-stage stripping

Turn off the regulating valve switch, and the system is in a closed loop state. According to the optimum temperature obtained before, set the diaphragm vacuum pump flow rate to 60L/min, and use a heating rod to heat 1L anaerobic digestion to the optimum temperature.The pH value and alkalinity of the anaerobic digestion solution are measured.

2.3.3 Effects of different doses of alkaline agent on the PH of the effluent from the first-stage tower

Take 3 parts of 1L effluent of first-stage tower and untreated membrane concentrate, and add 15, 20, 25g/L CaO respectively, and measure the variation of pH value after stirring and precipitation.

2.3.4 Treatment effect of the secondary tower on the effluent that has been added with alkali

When the dosage of CaO is 15g, 20g, 25g/L, the effect of the second-stage stripping on the removal of ammonia nitrogen and COD.

2.3.5 Test methods

Turn off the control valve switch to make the stripping system in a closed loop state,according to the optimum temperature obtained before, set the diaphragm vacuum pump flow rate to 60L/min, and use a heating rod to heat 1L anaerobic digestion liquid After reaching the most suitable temperature, blow off and measure the pH and alkalinity of the anaerobic digestion solution.

3 Experimental results and analysis

3.1 Effects of temperature on first-stage stripping

Variations of pH with air-liquid ratio and alkalinity at different temperatures are shown in Figure 3 and Figure 4. At the beginning of the experiment, due to the low pH and the greater alkalinity of the membrane concentrate, the increase in pH and the decrease in alkalinity have significant effects. As the air-liquid ratio increases, the curves of pH and alkalinity tend to stable. It is found from the figure that when the pH is greater than 8.3, the rate of change of the pH curve slows down, and the effect of the change of air-liquid ratio on the pH in the anaerobic digestion solution is significantly reduced, but the alkalinity curve does not change significantly after the pH exceeds 8.3. It may be because the alkalinity is mainly dominated by the first-order carbonic acid ionization balance, and the pH value of the anaerobic digestion liquid is the result of the combined effect of the air-liquid carbon dioxide balance, the acid-base balance in the liquid phase, and the dissolution balance between the solid and liquid phases. [13], making the buffering capacity of the solution strong. When the temperature is 20℃, whether it is pH or alkalinity, the range of change is much lower than the range of change under the other two temperature conditions. This is because the solubility of CO_2 will decrease as the temperature rises. The best temperature is above 20℃. When the air-liquid ratio was 3600, the pH of the treatment solution at 40°C increased from 7.8 to 8.63, and the alkalinity also decreased from the initial 8150 to 6745.

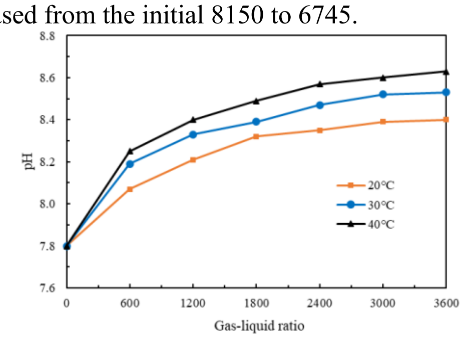

Fig. 3. Variations of pH with gas-liquid ratio at different temperatures

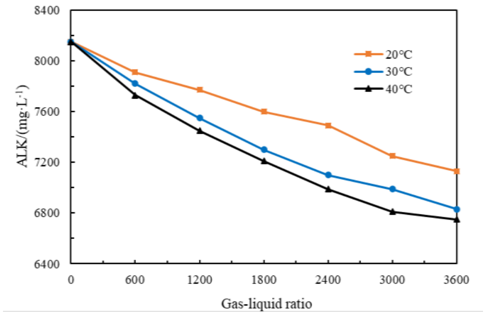

Fig. 4. Variations of alkalinity with gas-liquid ratio at different temperatures

Figure 5 shows the concentration change curve of ammonia nitrogen in the anaerobic digestion solution at different temperatures after the primary stripping treatment. In the absence of an alkali agent, the air-liquid ratio and temperature become the main factors affecting the removal of ammonia nitrogen. The ammonia nitrogen concentration keeps decreasing as the temperature rises and the air-liquid ratio increases. When the air-liquid ratio was 3600, the concentration of the anaerobic digestion solution under the three temperature conditions dropped from the original 671mg/L to 656, 636, and 592mg/L, and the removal rates were 2.2%, 5.2% and 11.8%.

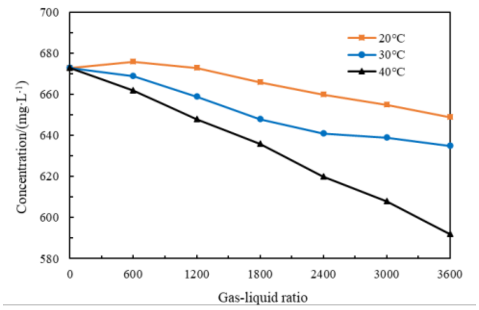

Fig. 5. Variations of ammonia nitrogen concentration with gas-liquid ratio at different temperatures

3.2 Effects of the state of the experimental device on the first-stage stripping

The content of CO_2 in the air is about 0.038%. Reducing the content of CO_2 can increase the partial pressure difference between the gas phase and the liquid phase of CO_2, and increase the mass transfer driving force of the free CO_2 in the solution to the gas phase.Thereby improving the stripping effect of the first stage tower[14].Figure 6 and 7 respectively show the treatment effects of the closed loop system on the pH and alkalinity in the anaerobic digestion solution. As the gas-liquid ratio increases,the closed loop system raises the membrane concentrate pH faster than the open loop system, and the gap between the two is increasing. When the gas-liquid ratio is 3600, the pH of the solution treated by the closed loop system reached 8.75,and the pH of the solution treated by the open loop system is 8.63.The alkalinity change range of the membrane concentrate treated by the closed loop system is also significantly greater than the alkalinity change range of the concentrated liquid processed by the open system. When the gas-liquid ratio is 3600,The alkalinity of the closed loop system decreased from the initial 8150mg/L to 6615mg/L,and the alkalinity of the open loop system decreased from the initial 8150mg/L to 6745mg/L.

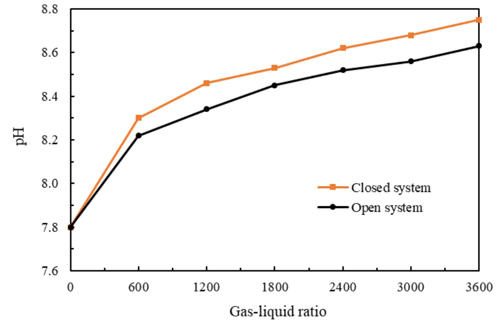

Fig. 6. Effects of system state on pH of Membrane concentrate

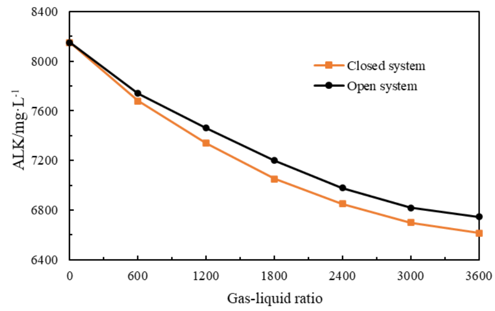

Fig. 7. Effects of system state on alkalinity of Membrane concentrate

3.3 Effect of different dosages of calcium oxide on the effluent of the first stage tower

According to the above experimental results, and considering the experimental effect and economy, the temperature of 40°C is selected as the experimental temperature, and the gas-liquid ratio is 3600 for the experiment. The effluent of the first-stage tower is taken as the test water sample, and different dosages of alkali are added to the effluent. The pH change of the water was investigated, and the test was carried out in the untreated concentrated liquid at the same time as a parallel test. The test results are shown in Figure 8. When the dosage of the alkali agent was 8g, the pH of the effluent increased by 0.44 to 9.01, and the pH of the untreated membrane concentrate increased by 0.46 to 8.26.

When the dosage of CaO is greater than 10g/L, the two pH curves increase significantly. This may be because CaO has removed most of the alkalinity at this time, and the buffering capacity of the treatment solution is weakened, so the pH increase rate becomes faster.Similarly, when the pH of the solution is raised to 9, the membrane concentrate treated by the first-stage tower needs to consume 8g of CaO, and the untreated membrane concentrate needs to consume 12g/L.When the pH is raised to 10.5, the membrane concentrate treated by the first-stage tower needs to consume 15g/L of CaO, and the untreated membrane concentrate needs to consume 20g/L.Therefore, when adding CaO as a means to increase the pH of the solution, the mass of CaO required for the membrane concentrate after the primary tower stripping treatment is about 25% lower than that of the untreated membrane concentrate.

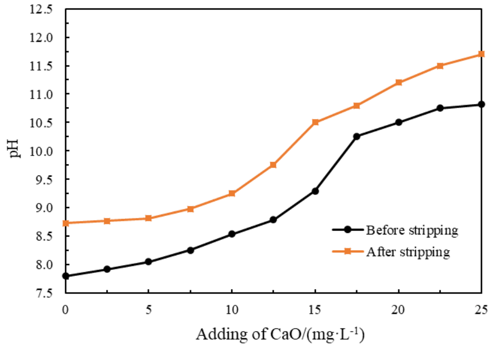

Fig. 8. Effects of the dosage of calcium Oxide added on the pH of the effluent of the first stage tower

3.4 Effect of second-stage stripping on ammonia nitrogen in effluent

Figure 9 shows the removal rate curve of ammonia nitrogen in the effluent from the secondary stripping tower when the CaO addition amount is 15g, 20g, 25g. When the gas-liquid ratio of the secondary tower is 600, and the amount of CaO added to the inlet water is 25g/L, the ammonia nitrogen content in the effluent from the se condary tower is 250.5mg/L, and the removal rate is 6 0%.When the amount of CaO added to the influent water is 20g/L, the ammonia nitrogen content of the effluent is 262.92mg/L and the removal rate is 58%. When the amo unt of CaO added is 15g, the ammonia nitrogen content i s 281.7mg/L and the removal rate is 55%. . When the gas -liquid ratio is 2400, the growth rate of ammonia nitroge n removal slows down. When the CaO dosage is 15g/L, 20g/L, 25g/L, the ammonia nitrogen content is 150 mg/L, 138.7 mg/L, 137.72 mg, respectively /L, the removal rat e is 76%, 77%, 78%. When the gas-liquid ratio is 3600, t he maximum ammonia nitrogen removal rate correspond ing to the dosage of the three calcium agents is 83.1%, 8 5%, and 86% respectively. At this time, the ammonia nit rogen content of the secondary tower effluent is 105 mg/ L, 93.9mg /L, 87.6mg/L.

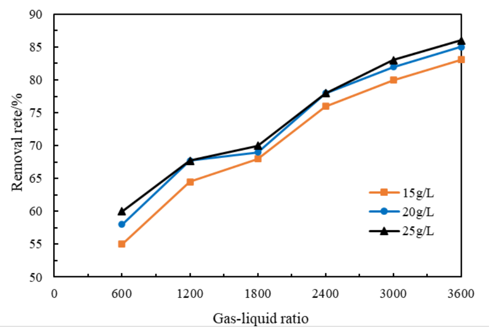

Fig. 9. Effects of second-stage stripping on ammonia nitrogen in effluent

3.5 Effect of second-stage stripping on COD in effluent

As shown in Table 2, when the dosage of CaO added in the effluent of the first-stage tower is 15g/L, 20g/L, and 25g/L, the COD of the solution drops from 5821, 6250, 4317mg/L to 3103, 2465, 2763mg, respectively /L, the average removal rate is 27%, 42%, 36%,This may be because the addition of CaO leads to an increase in the electrolyte concentration in the membrane concentrate, a decrease in the thickness of the colloidal electric double layer, aggregation and precipitation between particles, and the formation of $CaCO_3$ and $Mg(OH)_2$ precipitation, which has a coagulation effect[15-18].Then use a two-stage tower for stripping under the condition of a gas-liquid ratio of 3600.The COD of the membrane concentrate after adding alkaline agent increased to 3612, 2720, 3349mg/L,This may be because NH_4^+ and OH^- in the membrane concentrate continuously combine to form NH3 during the ammonia stripping process. The electrolyte concentration in the solution decreases, the thickness of the colloidal double layer increases, the cohesion between the colloids weakens, and the coagulation effect weakens [17-18].

Table 2. Variation of COD after adding CaO and ammonia stripping

Dosage of calcium oxide (g·L^{-1})	COD of the effluent /(mg ·L^{-1})	COD after adding Calcium Oxide		COD after stripping	
		Content/ (mg· L^{-1})	Removal rate/%	Content/ (mg· L^{-1})	Removal rate/%
15	4250	2635	38	3358	21
20		2677	37	3060	28
25		2720	36	3315	22

4 Conclusion

（1）The higher the stripping temperature of the first-stage tower was, the greater the increase in the pH value of the anaerobic digestion solution was in the same time, the greater the decrease in alkalinity was, and the better the stripping effect. When the gas-liquid ratio is set to 2400 and the experimental temperature is 20°C, 30°C, and 40°C, the pH of the solution rises from the initial 7.8 to 8.32, 8.49, and 8.55, respectively, and the removal rate of ammonia nitrogen is 1.2%. 4.7%, 7.7%. When the gas-liquid ratio is 3600 and the experimental temperature is 20°C, 30°C, and 40°C, the pH of the solution rises from the initial 7.8 to 8.4, 8.54, 8.63, respectively, and the removal rate of ammonia nitrogen is 2.2% and 5.2%, 11.8%.

（2）Through the closed loop cycle, CO_2 in the air can be effectively removed, and the partial pressure difference between the free CO_2 in the liquid phase and the CO_2 in the gas phase can be increased. When the gas-liquid ratio is 3600 and the stripping temperature is 40°C, the pH of the biogas slurry after the closed cycle treatment reaches 8.75, and the alkalinity is also reduced from the initial 8150 to 6615mg/L.

（3）When CaO is added to the effluent of the first-stage tower, the COD of the concentrate will decrease due to coagulation and the mechanism of compressing the electric double layer, and the PH value will also increase.After the second-stage ammonia stripping, COD increases. Under the condition of gas-liquid ratio of 3600, the whole system is running, and when CaO is added at 25g/L, the COD removal rate is 22.4%, and the ammonia nitrogen removal rate is up to 86%.

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