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Research on Mechanism of Air Stripping Enabled Ammonia Removal from Industrial Wastewater and Its Application

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In this paper, the stripping method was used to deal with the wastewater with high concentration of ammonia generated in the industrial production process, and the effects of blowing time, waste water pH, stripping temperature and gas-liquid volume ratio on the maximum removal rate of ammonia were investigated by experiments. The experimental results show that the gas - liquid ratio is linear to the stripping efficiency at 50 °C and strongly alkaline. And it can be deduced that the effect of different air flow rates on the blowout efficiency at gas-liquid ratio below 1000 is not significant. In this paper, the maximum air flow rate is 2L/min, and the maximum reaction time (stripping time) is 120min, so the maximum gas-liquid ratio is only 800. At the same time, this paper also explored the reaction mechanism of ammonia removal via the stripping method and its application in ammonia removal from industrial wastewater produced by monosodium glutamate.

1. Introduction

With the development of industry and agriculture and the improvement of people's living standards, the emission of nitrogenous compound wastewater has increased dramatically, which has attracted much attention as the main source of the environment pollution. Ammonia is an important pollutant to the water eutrophication and environmental pollution. Upon entering water, the ammonia can lead to water hypoxia, breeding harmful aquatic organisms that poison fish, and humans who eat such fish tend to be slightly poisonous or even dead (Hu et al., 2003). In addition, ammonia also affects the oxygen transport by fish gills, and the high concentration of ammonia will even kill fish. A large amount of ammonia wastewater discharged into the rivers and lakes has brought difficulties in the industrial wastewater treatment. When the chlorine disinfection is adopted, ammonia and chlorine will produce chloramine, which clearly have increases chlorine consumption rate and further drives great demands for chlorine. Ammonia is converted to nitric acid, and nitrates are further converted to ammonium nitrite with a serious three-pronged effect that directly affects human health, for which the treatment of ammonia nitrogen wastewater has become a hot issue in today's water treatment (Huang et al., 2014). At present, ammonia nitrogen wastewater treatment methods are as follows: air stripping, ion exchange, chemical precipitation, membrane separation, chemical oxidation, biological method, etc. As for the treatment of ammonia wastewater, domestic researches mainly focus on the materialization method, while biological methods are rarely used. It is of great practical significance to seek practical treatment technology with small investment, reliable operations and high efficiency for the processing of industrial ammonia wastewater (Wilfried and Chakkrit, 2015).

1.1 Classification of industrial ammonia wastewater

According to the different concentrations, industrial ammonia wastewater can be divided into three categories, namely (1) low concentration of ammonia nitrogen wastewater: NH_3 <50mg/L; (2) moderate concentration of ammonia nitrogen wastewater: NH_3 is 50-500mg/L; (3) low concentration of ammonia nitrogen wastewater: NH_3> 500mg/L. High ammonia concentration wastewater is generally derived from the production process of coke, ferroalloy, coal gasification, hydrometallurgy, oil refining, animal husbandry, chemical fertilizers, man-made fibers and incandescent lamps that are all extremely complex and have different types of industrial wastewater ammonia concentration in the ever-changing state (Xiang H, et al., 2011). Moderate concentration

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of ammonia wastewater is generally derived from fertilizer, oil refining, rubber, synthetic rubber, dairy production, pharmaceutical, farming, paper, leather and other industries; Low concentration of ammonia wastewater generally comes from canned food, vegetables, starch, grain food processing industry and anti-corrosion, paint ink, and other industries.

1.2 Introduction to the blowout method

The air stripping method is currently used for the treatment of ammonia waste. The blown off ammonia can be recycled, but most is directly discharged into the air. Therefore, when using the air stripping method, we should not only pay attention to how to improve the efficiency of ammonia bleed, but also take the initiative to prevent secondary pollution. If the emitted ammonia is discharged directly into the atmosphere, it is necessary to consider whether the total amount of free ammonia emitted is in line with the ammonia emission standards (Lee et al., 2013). Ammonia returns to the earth in the atmosphere by gas deposition (60%), aerosol deposition (22%), rainfall (18%), etc. After the set of animals and animals have a stimulating and toxic effect; When there are sulfur dioxide emissions near the point, the atmosphere of ammonia, the atmosphere of sulfur dioxide and water generate ammonium sulfate aerosol. The air stripping process of ammonia refers to that adjusting the PH value of wastewater to transform the ammonia in the ion state into molecular ammonia, and then blowing the air into the wastewater (Zhang et al., 2009). For the ammonia in the wastewater is usually present in equilibrium with the state of ammonium ions (NH_4^+) and free ammonia (NH_3), the equilibrium relationship between NH_4^+ and NH_3 in water is as follows:

$$NH_4^+ + OH^- \; f \; NH_3 + H_2O \qquad (1)$$

The percentage distribution between ammonia and ammonia ions can be calculated by using the following formula:

$$K_a = K_W / K_b = (C_{NH_3} . C_{H^+}) / C_{NH_4^+} \qquad (2)$$

Where: K_a - ionization constant; K_w - water ionization constant; K_b - Ionization of ammonia; C - substance concentration
This equilibrium is related to pH and temperature. At pH 7, only NH_4^+ ions are present in the solution, and when pH is 12, the solution is fully soluble NH_3. Ammonia stripping is to raise the pH and temperature of the wastewater, and then provide sufficient gas and water to blow the ammonia from the solution. The air stripping ammonia removal method is stable and easy to control, with simple operations. But this method is also easy to fill the fouling, affecting the operations of the equipment. When the water temperature is low, the air stripping efficiency is low, blowing off after the completion of the callback value. In addition, the wastewater after stripping treatment still contains a small amount of ammonia and cannot meet the discharge standard. So the air stripping method is often used for the pretreatment of high concentration of ammonia nitrogen wastewater (Ma H R, et al., 2010). How to improve the efficiency of air stripping, how to avoid secondary pollution and how to control the production process and scale production in the process of industrialization call for much attention.

1.3 The ammonia removal process by air stripping

The air stripping method has the advantages of high denitrification rate, flexible operations and small footprints. The stripping method is often domestically used for treating high concentration ammonia nitrogen wastewater, and the ammonia can be recycled. In order to ensure the continuous operations of the production line, the sewage treatment system must be implemented in three stages. (Wu et al., 2010).
When the water level reaches the high level, the industrial wastewater is discharged into the accident pool. When the regulation tank's water level reaches the low level, the accident pool lift pump will lead wastewater in the accident pool to the adjustment pool. Adjust the pool lift pump to transfer the wastewater from the conditioning tank to the primary stripping tower, which is controlled by the regulating valve of the lift pump outlet. The wastewater is added to the primary stripping tower before adding NaOH to adjust the pH of the wastewater to 11. The wastewater enters the tower from the top of the first-stage stripping tower and flows from the top of the tower along the gap in the packing. The air is entrained with steam from the bottom of the tower into the tower, forming convection with the wastewater. Air will waste water in the ammonia nitrogen blown off the wastewater into the bottom of the bottom of the collection tank. Similarly, the wastewater flows through the secondary stripping tower and the tertiary stripping tower. Three-stage stripping tower lift pump will strip the bottom of the wastewater to the mixing reaction tank, with HCl added to adjust the pH between 6 to 9 (Song et al., 2008). Ammonia content in wastewater is detected by the ammonia nitrogen analyzer. If the discharge standard is reached, it will be transported to the park sewage treatment plant for further treatment. If

failing to meet the discharge standard, the wastewater will be transported to the regulating tank and be re-stripped (Wang et al., 2013).

2. Object of study, purpose and experimental program

2.1 Research objects

The research object of this paper is to simulate the industrial high concentration ammonia wastewater (concentration> 500m/L) produced by the fertilizer industry. This kind of waste water generally has the characteristics of high temperature, high ammonia, high flow rate, low organic matter and it is difficult to conduct biochemical treatment.

2.2 Research purposes

High concentration of ammonia wastewater treatment in domestic is always difficult to solve. Different regions, different seasons, different industrial enterprises' emissions of ammonia nitrogen wastewater conditions are different, and the existing governance methods are difficult to achieve a high degree of unity of social benefits, environmental benefits and economic benefits of (Min and Yi, 2016). Therefore, the purpose of this paper is to try a new method for the treatment of high concentration of industrial ammonia wastewater, to explore its application feasibility and reaction mechanism, which lays the foundation for further researches.

2.3 Experimental program

Based on the physical and chemical properties of ammonia volatilization and oxidation, and through the comparison, this study adopts the method of gas-phase ammonium oxidation as the follow-up method based on the stripping method. Under the action of the catalyst and a certain temperature range, we will strip the ammonia for oxidation, and the possible oxidation products are NOx, N_2, H_2O, hydrazine and so on. And the oxidation products are mainly N_2 and H_2O by temperature control. The wastewater treated by the experiment was made by artificial dispensing, and the NH_3 concentration was 1024 m/L. The effects of pH value, water temperature, stripping time and addition amount of No. 1 denitrification on the denitrification rate were obtained by the static test, and the reasonable design parameters were provided for the engineering design.
The experimental protocol is as follows:
(1) In the atmospheric pressure, strong alkaline conditions, by heating and drumming into the excess air, the NH_3 in the waste water is transformed to the gas phase;
(2) with air as the carrier gas, through its carrying NH_3 into the catalyst with quartz catalyst tube, heating with electric heating, digital temperature control equipment to control the reaction temperature, in a certain temperature range, the oxygen and ammonia in the air produce oxidation reaction in a series of catalytic; (3) The concentration of NH_3 and NO_2 in the reaction tube was measured by the atmospheric sampler, and the NH_3 concentration in the water samples before and after the reaction was measured.
(3) Study on Treatment of High Concentration Ammonia Wastewater by Stripping Method under Normal Pressure and Gas - phase Ammonia Catalytic Oxidation.
According to the change of NH_3 concentration in the gas phase, the conversion rate of NH_3 was calculated, and the removal rate of ammonia in ammonia-containing wastewater was calculated according to the change of NH_3 concentration in the liquid phase and the amount of NH_3 in the gas phase. The formation rate of N_2 was calculated according to the concentration of NO_2 in the gas phase. The experimental flow diagram is shown in Figure 2.

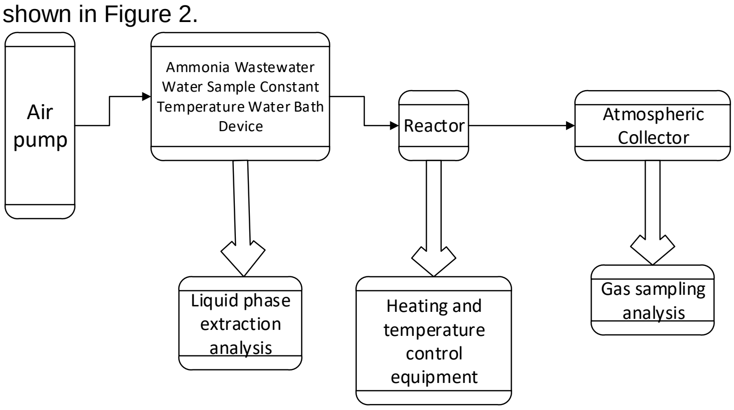

Figure 2: Analysis of Ammonia Catalytic Oxidation Process for Treatment of Ammonia Wastewater at Normal Pressure

3 Test results and discussion

3.1 Effect of temperature and pH on stripping effect

Take the amount of ammonia wastewater, and control the amount of NaOH dosage for different pH. The gas-liquid ratio is 3000:1; stripping time is 9h; and select the different temperature and solution pH to carry out the experiment. The experimental results are shown in Figure 3 and Figure 4.

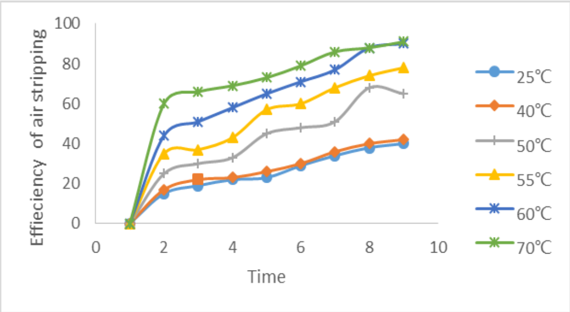

Figure 3: Effect of Temperature on the Stripping Effect

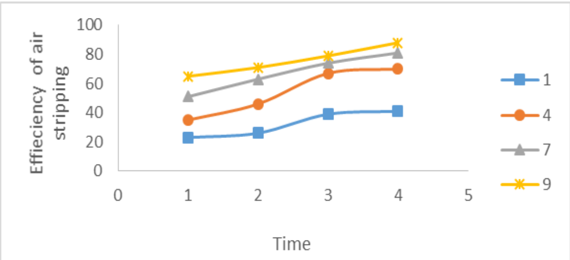

Figure 4: Effect of pH on the Stripping Effect

It can be seen from Fig.3 that the stripping efficiency increases with the stripping time, and the temperature change has obvious effect on the stripping efficiency. Stripping at 25 °C and 40 °C can only reach about 44 %, and when the water temperature rose to above 50 °C, after stripping 6h, the efficiency can reach 54%. From the effect of pH change on the stripping efficiency in Fig. 4, it can be seen that the pH is above 9.5 and stripping after 6h can guarantee more than 50% of the blowing efficiency.

3.2 Effect of gas - liquid ratio on stripping experiment of ammonia - nitrogen wastewater

According to the results of the stripping method for the treatment of high concentrations of ammonia wastewater, pH and temperature are two key factors in the removal of NH_3 from water. The higher the water temperature and the pH value, the more favorable the NH_3 escape. When the temperature and pH value are constant, the gas-liquid ratio also has a certain impact. Therefore, we conduct experiment to study the relationship between gas-liquid ratio and blow-off effect. Experimental conditions: simulated ammonia waste water 300ml, pH = 14, water temperature 50 °C, temperature 25 °C, stripping time 120min. The measured water sample is diluted by 100 times, so the calculated NH_3 concentration multiplied by 100 is the actual water sample concentration, and the experimental results are shown in Table 1.

Table 1: Gas-liquid Ratio Test Data

Test number	Gas-liquid ratio	Absorbance	Concentration of NH_3 in wastewater	Stripping efficiency
1	2000	0.576	366	66.8
2	2200	0.481	322	71.2
3	2500	0.434	289	76.7
4	2800	0.339	190	81.4
5	3000	0.256	123	88.3

The graph shows that the gas-liquid ratio is linear with the stripping efficiency at 50 °C and strongly alkaline, and it can be deduced that the effect of different air flow rates below 1000 on the stripping-out efficiency is not significant. In this experiment, the waste water volume is 300ml; the maximum air flow rate is 2L/min during stripping and catalytic oxidation; the maximum reaction time (stripping time) is 120min, so the maximum gas-liquid ratio is only 800. It can be argued that, for the purposes of this experiment, the total amount and volume change of NH_3 are negligible under different conditions of flow (<2 L/min) of air at the same time, and ammonia is actually "boiled out." Different air flows only bring about different concentration of gas phase NH_3.

4 Study on the Reaction Mechanism of Ammonia by Stripping

It is generally believed that the reaction of NH3 and 02 can be expressed as a stoichiometric equation:

$$\begin{aligned} &A: 4NH_3 + 5O_2 = 4NO + 6H_2O \\ &B: 4NH_3 + 4O_2 = 4N_2O + 6H_2O \\ &C: 4NH_3 + 3O_2 = 2N_2 + 6H_2O \end{aligned} \tag{3}$$

The reaction of NH_3 with NO can be expressed as:

$$4NH_3 + 6NO = 5N_2 + 6H_2O \tag{4}$$

The reaction of A, B, and C can occur at 900 °C. The equilibrium constant is $K_1 = 10^{53}$; $K_2 = 10^{61}$; $K_3 = 10^{63}$. The equilibrium constant of the three reactions is large, so the reaction to the left can be regarded as irreversible. From $K_3 > K_2 > K_1$, it is known that the reaction of NH_3 oxidation to N_2 is the most complete, and the final product of NH_3 oxidation can be all N_2 (Hao et al., 2008). When there is a catalyst, the reaction of NH_3 with O_2 has the mechanism of "selective catalytic oxidation(SCO)". Denote NH_3 (a) and O (a) to represent the ammonia and oxygen in the adsorbed state, and the two reaction mechanisms are described below:

$$\begin{aligned} &NH_3 + s \leftrightarrow NH_3(a) \\ &O_2 + 2^* \leftrightarrow 2O(a) \\ &NH_3(a) \rightarrow NH_2(a) + OH(a) \\ &NH_2(\mathrm{a}) + O(\mathrm{a}) \rightarrow NH(\mathrm{a}) + OH(\mathrm{a}) \\ &NH_3(\mathrm{a}) + OH(\mathrm{a}) \rightarrow NH_2(\mathrm{a}) + H_2O(\mathrm{a}) \\ &NH_2(\mathrm{a}) + OH(\mathrm{a}) \rightarrow NH(\mathrm{a}) + H_2O(\mathrm{a}) \\ &NH\ (\mathrm{a}) + OH(\mathrm{a}) \rightarrow N(\mathrm{a}) + H_2O(\mathrm{a}) \\ &NH(\mathrm{a}) + O(\mathrm{a}) \rightarrow N(\mathrm{a}) + OH(\mathrm{a}) \\ &NH_X(\mathrm{a}) + NH_Y(\mathrm{a}) \rightarrow N_2H_{X+Y}(\mathrm{a}) \\ &N_2H_{X+Y}(\mathrm{a}) + (X+Y)OH(a) \rightarrow N_2(g) + (X+Y)H_2O \end{aligned} \tag{5}$$

Foreign scholars tend to believe that, under the condition of excessive oxygen oxidation, the SCO mechanism is suitable for describing the way of ammonia catalytic oxidation. This experiment detects the presence of NO and confirms this view (Shaji, et al., 2012).

5 Application of Stripping Method

MSG production process can be divided into high, medium and low concentrations of organic wastewater. High concentration of wastewater, which is glutamic acid mother liquor, has a strong acid, high COD, ammonia nitrogen, and sulfate and a series of characteristics, so it brought more difficulties for the management work especially that the high concentration of ammonia nitrogen will produce a strong inhibition of biological activity. In this experiment, the ammonia removal experiment of high concentration monosodium glutamate wastewater was carried out by stripping method, which provided the basis for its application in actual production.

5.1 Primary ammonia bleaching purification process

Because of the low cost of running, mature process, high stripping efficiency, stable operation and suitable for the treatment of high concentration ammonia nitrogen, it is widely used at home and abroad. Therefore, this method uses stripping method to remove high concentration ammonia in wastewater (Wu et al., 2001). Due to the high ammonia content in alkaline solution, it will react with heavy metal ions to produce complexes that is difficult to deal with, and will play a buffer in the regulation of the time.

5.2 Secondary ammonia bleaching purification process

Ammonia stripping tower selects polypropylene ladder ring as packing tower. The best pH value is 11, and the best temperature is room temperature. It directs high gas to water than the free ammonia in the waste water to the air, and then uses dilute acid on ammonia gas to purification absorption. Absorbent solution is dilute sulfuric acid solution, and after cleaning the tail gas to the high-altitude discharge, the absorption of sulfuric acid solution can be made semi-finished products, which can also be applied to the monosodium glutamate plant area of green trees. The pH value of the secondary stripping tower is 11, and the stripping efficiency is about 90% at room temperature. After the secondary stripping, the concentration of ammonia can reach the biochemical pool for the treatment.

6. Conclusion

The effect of blowing time, waste water pH, stripping temperature and gas-liquid volume ratio on ammonia removal rate was investigated by using stripping method to treat high concentration ammonia wastewater produced in industrial production. At 50 °C and strongly alkaline condition, the gas-liquid ratio is linear with the stripping efficiency. And it can be deduced that the effect of different air flow rates below 1000 on the blowout efficiency is not significant. The maximum air flow rate of this experiment is 2L/min, and the maximum reaction time (stripping time) is 120min, so the maximum gas-liquid ratio is only 800. At the same time, this paper also explores the reaction mechanism of ammonia removal in stripping method and the application of ammonia in industrial wastewater produced by monosodium glutamate.

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