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Research on Optimization of Liquid Carbon Source Conditions for the Preparation of Yellow Water in Baijiu Brewing

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Abstract

Baijiu wastewater is characterized by large output, high COD content and good biodegradability. It can be used as an additional carbon source in the biological denitrification process of wastewater. However, the phosphorus content in it is relatively high. It is necessary to remove phosphorus from the brewing yellow water first, and then add it to municipal sewage and other sewage with a low carbon-nitrogen ratio.This thesis takes yellow water from Baijiu brewing as the research object. Based on the existing chemical phosphorus removal methods, it is explored and concluded that: compared with the magnesium ammonium phosphate method, the iron salt method and the aluminum salt method, the hydroxyapatite method has a better phosphorus removal effect and the potential for nitrogen removal at the same time, and the COD retention rate is the best. When calcium oxide is added at pH=10, the phosphorus removal effect is the best, and it also has a certain nitrogen removal performance. Moreover, the COD retention rate is relatively high, which meets the research requirements for using the treated yellow water from brewing as an additional carbon source for biological wastewater treatment.

Keywords

Yellow Water; Additional Carbon Source; Sewage Treatment; Phosphorus Removal.

1. Introduction

With the continuous improvement of urban living standards, in the conventional urban domestic sewage treatment, the concentration of organic matter is often getting lower and lower, while the ammonia nitrogen nutrient is getting higher and higher, resulting in a continuous decrease in the carbon-nitrogen ratio (C/N) of sewage, which increases the difficulty of sewage treatment [1]. Traditional additional carbon sources include methanol, acetic acid, sodium acetate, etc. However, the extensive use of traditional carbon sources will increase the operating costs of sewage treatment plants. Baijiu, as a traditional solid-state fermented distilled liquor unique to China. It is reported that for every ton of 65-degree liquor produced, approximately 60 tons of water are consumed and 48 tons of brewing wastewater are generated, resulting in a huge amount of sewage discharge [2]. Brewing wastewater is a kind of high-concentration organic wastewater, containing yellow water with high organic matter, water from the bottom pot and water from soaking grains, etc., and also contains other wastewater such as leachate from discarded grains [3]. The characteristics of large output, high COD content and good biodegradability of liquor wastewater make it possible to use the brewing wastewater as an additional carbon source in the biological denitrification process of sewage. This method can maximize the resource utilization of brewing wastewater and reduce the cost of biological denitrification of wastewater from the source. It is an important development direction in the future. However, according to the standard (T/CSTE 0001-2021), compared with commercial carbon sources, the phosphorus content in brewing wastewater is much higher than the requirement of its mass fraction≤0.006. Therefore, if brewing wastewater is to be used as an additional carbon source for biological nitrogen removal of wastewater, a series of phosphorus removal operations need to be carried out first to avoid being added to the wastewater treatment process. The situation where the total phosphorus content in the effluent exceeds the standard.

2. Materials and Methods

2.1. Test Materials and Reagents

2.1.1. Experimental Materials

The yellow water used for brewing in the experiment was taken from a certain distillery (Yibin, China), and its specific physical and chemical indicators are shown in the following table:

Table 1. Detailed information of the experimental materials

Detection index	Concentration (mg/L)
pH	3.15
COD	121683.35
TN	2453.83
NH^{4+}-N	763.57
NO^{3-}-N	352.25
NO^{2-}-N	2.04
TP	782.43
Protein	7650.57
Polysaccharide	13616.44

2.1.2. Experimental Reagents

The main reagents required in the experiment are shown in the following table:

Table 2. Reagents and drugs required for the experiment

Reagent name	Specification	Manufacturer
Magnesium sulfate heptahydrate	Analytical pure	Chengdu Kelong Chemical Reagent Factory
Calcium oxide	Analytical pure	Chengdu Kelong Chemicals Co., LTD
Ferric chloride hexahydrate	Analytical pure	Shanghai MacLean Biochemical Technology Co., LTD
Aluminium trichloride	Analytical pure	Shanghai MacLean Biochemical Technology Co., LTD
Sodium hydroxide	Analytical pure	Shanghai MacLean Biochemical Technology Co., LTD

2.2. Methods for Determining Experimental Indicators

The content of phosphorus refers to the national standard (GB11893-89), and the ammonium molybdate spectrophotometric method is adopted. The content of total nitrogen was determined by the alkaline potassium persulfate ultraviolet spectrophotometry in accordance with the national standard (GB11894-89). The content of ammonia nitrogen was determined by the Nessler's reagent colorimetric method in accordance with the national standard

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(GB7479-87). The reference standard for the content of nitrate nitrogen (HJT346-2007) adopts the ultraviolet spectrophotometry method. The reference standard for COD content (HJT399-2007) adopts the rapid digestion spectrophotometric method.

2.3. Experimental Design

The commonly used chemicals in chemical phosphorus removal mainly include magnesium salts, calcium salts, iron salts, aluminum salts, etc. For the above four different methods, the best phosphorus removal rate scheme is adopted by referring to relevant literature. Finally, calcium oxide was selected by comprehensively considering the phosphorus removal rate and COD retention rate obtained from the experiment, and then the influence of calcium oxide addition at different pH values was explored.

2.3.1. Magnesium Ammonium Phosphate Method

Referring to relevant literatures [4, 6], magnesium sulfate was selected as the phosphorus removal agent. The same amount of 100ml of brewing yellow water was added to each group. When pH=10.0 and the addition dosage Mg: P= 0.8:1, the effect on phosphorus removal in liquor wastewater was investigated. Place the beaker on the magnetic stirrer, stir for 10 minutes, and let it settle for 20 minutes. After the reaction is complete, take the supernatant for sample testing to determine the indicators such as TP,TN,NH^{4+}-N, and COD.

2.3.2. Hydroxyapatite Method

Referring to relevant literature [5], calcium oxide was selected as the phosphorus removal agent. The same amount of 100ml of brewing yellow water was added to each group. When pH=8.0 and the addition dosage Ca: P= 2:1, the effect on phosphorus removal in Baijiu wastewater was investigated. Place the beaker on the magnetic stirrer, stir for 10 minutes, and let it settle for 20 minutes. After the reaction is complete, take the supernatant for sample testing to determine indicators such as TP,NH^{4+}-N, and COD.

2.3.3. Iron Salt Method

According to relevant references [7], ferric chloride was selected as the phosphorus removal agent. The same amount of 100ml of brewing yellow water was added to each group. At pH=6.0, the addition dosage Fe: P= 2:1 was used to explore the effect on phosphorus removal in liquor wastewater. Place the beaker on the magnetic stirrer, stir for 10 minutes, and let it settle for 20 minutes. After the reaction is complete, take the supernatant for sample testing to determine indicators such as TP,NH^{4+}-N, and COD.

2.3.4. Aluminum Salt Method

According to relevant references [8, 9], aluminium chloride was selected as the phosphorus removal agent. The same amount of 100ml of brewing yellow water was added to each group. At pH=6.0, the dosage of Al: P was 1.7:1 to explore the effect on phosphorus removal from liquor wastewater. Place the beaker on the magnetic stirrer, stir for 10 minutes, and let it settle for 20 minutes. After the reaction is complete, take the supernatant for sample testing to determine indicators such as TP, NH^{4+}-N, and COD.

2.3.5. Addition of Calcium Oxide at Different pH Values

Calcium oxide was selected as the phosphorus removal agent. The same amount of 100ml of brewing yellow water was added to each group. Calcium oxide was added respectively until the pH gradient of the solution was 8, 9, 10, 11, and 12. The influence of adding calcium oxide at different reaction pH values on the phosphorus removal of liquor wastewater was explored. Place the beaker on the magnetic stirrer, stir for 10 minutes, and let it settle for 20 minutes. After the reaction is complete, take the supernatant for sample testing to determine indicators such as TP, NH^{4+}-N, and COD.

2.4. Data Analysis

Use Excel for data processing and analysis; Data processing and plotting were carried out using Origin 2019; Significant difference analysis was conducted using IBM SPSS (Statistics 24).

3. Results and Analysis

3.1. Effects of Different Phosphorus Removal Agents Dosage

3.1.1. Total Phosphorus Removal Effect

The content and removal rate of total phosphorus in different experimental materials are shown in Figure 1. It can be seen from Figure 1 that the magnesium ammonium phosphate method with magnesium sulfate added has the best phosphorus removal rate (73.77%, but there is still a certain gap compared with the removal rate of over 90% in references [10, 11]. The possible reason is that due to the limited experimental conditions in this experiment, the rotational speed setting during the reaction process of the magnesium ammonium phosphate method cannot be controlled. However, during the reaction process, excessive rotational speed leads to an excessively high stirring intensity, which is not conducive to the progress of the flocculation and sedimentation reaction .The phosphorus removal rate of the hydroxyapatite method with added calcium oxide was second only to that of the magnesium ammonium phosphate method (73.02%), and was lower than that of Duan et al. [12]using powdered slag as seed, which had removal efficiencies of 95.36% and 96.54% for pig farm wastewater and concentrated sludge respectively, but was higher than the total phosphorus removal rate of 65% without seed addition. The phosphorus removal rates of the iron salt method with the addition of ferric chloride and the aluminum salt method with the addition of aluminium chloride were both relatively low, at 2.12% and 1.89% respectively, which were significantly different from the removal rates in Ren Mianmian's [13] study (the best rates were 91.8% and 89.7% respectively). The possible reasons are: Organic substances such as glucose, starch and humic acid in the water sample can all have a certain inhibitory effect on the phosphorus removal effect of iron salts and aluminum salts, and the inhibitory effect is proportional to the concentration of organic substances [14], while the COD concentration of the experimental water is relatively high (121,683.35 mg/L). This is also consistent with the result in the following text that the iron salt method and aluminum salt method have a relatively low COD retention rate.

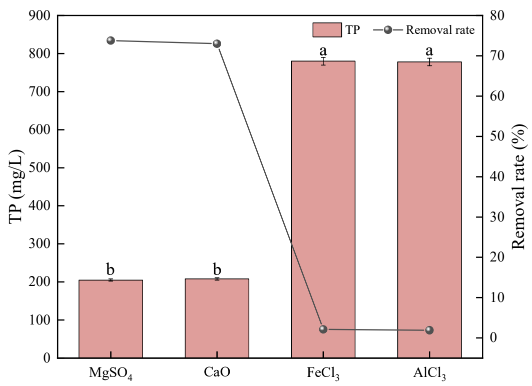

Figure 1. Total phosphorus content and removal rate of different agents

3.1.2. Ammonia Nitrogen Removal Effect

The content and removal rate of ammonia nitrogen in different experimental materials are shown in Figure 2. It can be seen from Figure 2 that the magnesium ammonium phosphate method with magnesium sulfate added has the highest removal rate of ammonia nitrogen, which is 44.45%, which is significantly different from the ammonia nitrogen removal rate of 88.62% in Lin Ming's [11]experiment. The possible reason is that under the reaction condition of Mg:P=0.8 designed in this experiment, its Mg:N is only 0.35. When Mg:N<1.0, the dosage of magnesium salt is insufficient at this time, and there is not enough Mg^{2+} in the solution to react with NH^{4+} and phosphate, thereby resulting in a low removal rate of ammonia nitrogen. The ammonia nitrogen removal rate of the hydroxyapatite method with calcium oxide added is 40.95%. However, NH^{4+} is not involved in the formation process of hydroxyapatite. The possible removal of ammonia nitrogen is [15] : Ca^{2+} ions in hydroxyapatite can undergo ion exchange with NH^{4+}, thereby removing NH^{4+} and reducing the ammonia nitrogen content in the solution. Meanwhile, the iron salt method with ferric chloride addition and the aluminum salt method with aluminium trichloride addition had no obvious removal effect on ammonia nitrogen during the reaction process, and their removal rates were 18.10% and 17.84% respectively.

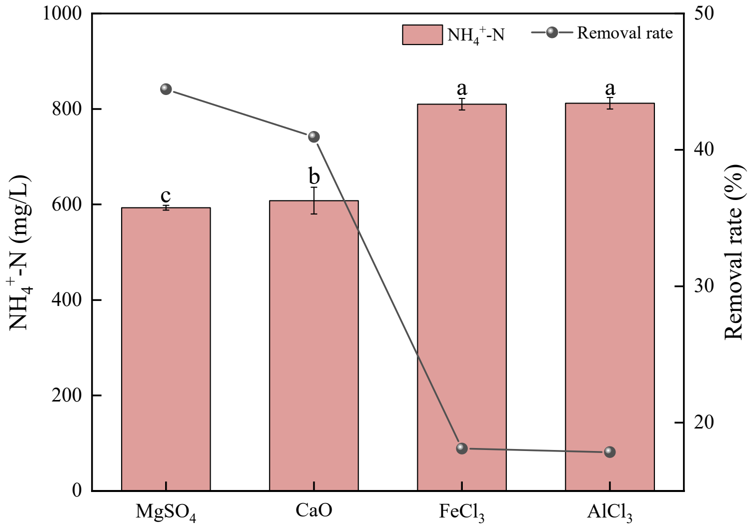

Figure 2. Ammonia nitrogen content and removal rate of different agents

3.1.3. COD Retention Effect

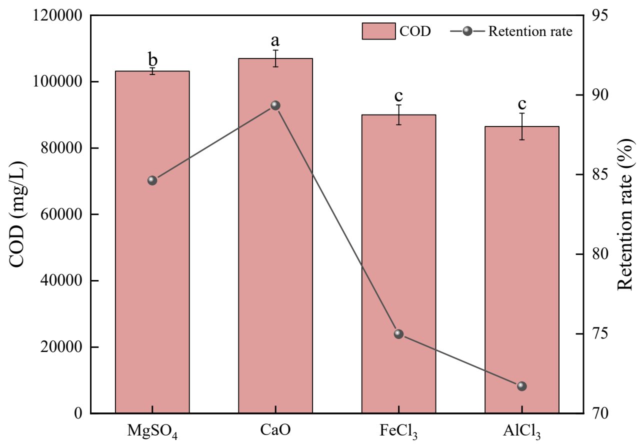

Figure 3. The COD content and retention of different agents

The content and retention rate of COD in different experimental materials are shown in Figure 3. As can be seen from the figure, the retention rates of COD by the magnesium ammonium phosphate method with magnesium sulfate and the hydroxyapatite method with calcium oxide are both relatively high, which are 84.62% and 89.34% respectively. Referring to relevant literature [16, 17]: Macromolecular organic substances are prone to combine with Mg^{2+} to form complexes, while Ca^{2+} has no significant effect on the COD removal efficiency. Therefore, the COD retention rate of the hydroxyapatite method is superior to that of the magnesium ammonium phosphate method, which is conducive to the use of yellow water for phosphorus

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removal in the preparation of external carbon sources. The retention rates of COD by the iron salt method with ferric chloride addition and the aluminum salt method with aluminum chloride addition were both relatively low, at 74.98% and 71.70% respectively. The reason was that some active functional groups in the organic matter underwent chelation reactions with iron and aluminum, resulting in a reduction of the remaining organic matter in the supernatant after phosphorus removal.

3.2. Addition of Calcium Oxide at Different pH Values

3.2.1. Total Phosphorus Removal Effect

The total phosphorus content and removal rate of the hydroxyapatite method under different reaction pH values are shown in Figure 4. As can be seen from the figure, when the pH is between 8 and 10, the phosphorus removal rate of the hydroxyapatite method increases continuously with the increase of pH value. The effect is the best when the pH value is equal to 10, reaching 78.75%. When the pH is between 10 and 12, its phosphorus removal effect gradually weakens. When the reaction pH drops to 12, the phosphorus removal rate decreases to 71.47%, and its phosphorus removal efficiency decreases. It might be due to the co-crystallization of calcium carbonate [12].

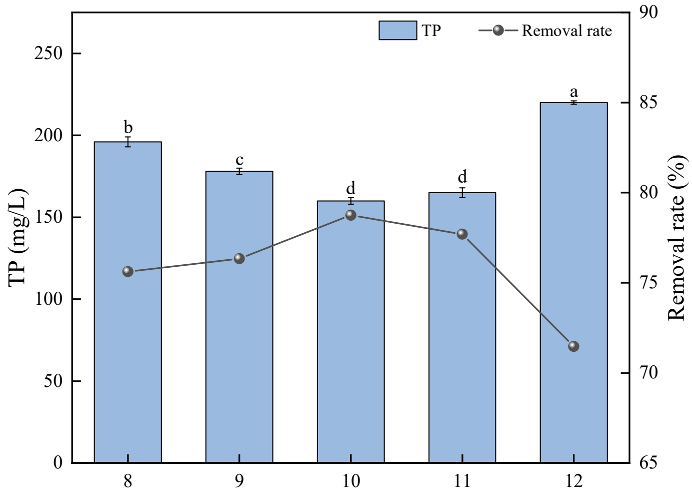

Figure 4. Total phosphorus content and removal rate at different pH values

3.2.2. Ammonia Nitrogen Removal Effect

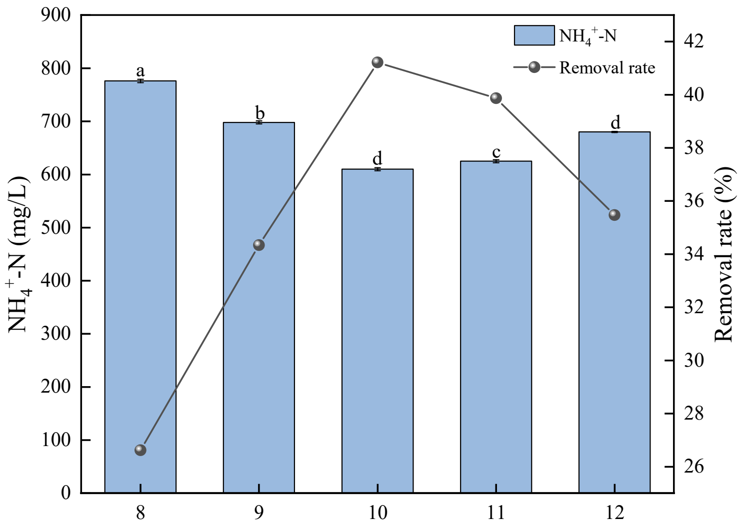

Figure 5. Ammonia nitrogen content and removal rate at different pH values

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The content and removal rate of ammonia nitrogen by the hydroxyapatite method under different reaction pH values are shown in Figure 5. As can be seen from the figure, the trend of ammonia nitrogen removal rate is similar to that of total phosphorus removal rate. When the pH is between 8 and 10, the ammonia nitrogen removal efficiency of the hydroxyapatite method increases rapidly. The effect is the best when the pH value is equal to 10, reaching 41.22%. As the pH value continues to increase, the removal rate of ammonia nitrogen decreases. The possible reason is that the removal rate of ammonia nitrogen is related to the formation of hydroxyapatite. The Ca2+ ions in hydroxyapatite can undergo ion exchange with NH4+, thereby removing ammonia nitrogen [15]. The higher the total phosphorus removal rate, the greater the amount of hydroxyapatite produced. Therefore, the trend of ammonia nitrogen removal is similar to that of total phosphorus removal.

3.2.3. COD Retention Effect

The content and retention rate of COD by the hydroxyapatite method under different reaction pH values are shown in Figure 6. When the pH was 8, the COD retention rate of the hydroxyapatite method was the highest at 82.78%, and the COD retention rate decreased with the increase of pH. When the pH value was further increased to 10-12, the COD retention rate remained relatively stable at about 76%. This might be due to; When the pH is 8, the optimal conditions for the formation of hydroxyapatite have not been reached yet, and thus only a small portion of COD is removed. With the increase of pH value, the amount of calcium oxide added increases, and the ratio of calcium ions to phosphorus reaches the optimal level. Further increase cannot increase the generation amount of hydroxyapatite, while hydroxyapatite removes COD by relying on the many adsorption sites on its surface [18].

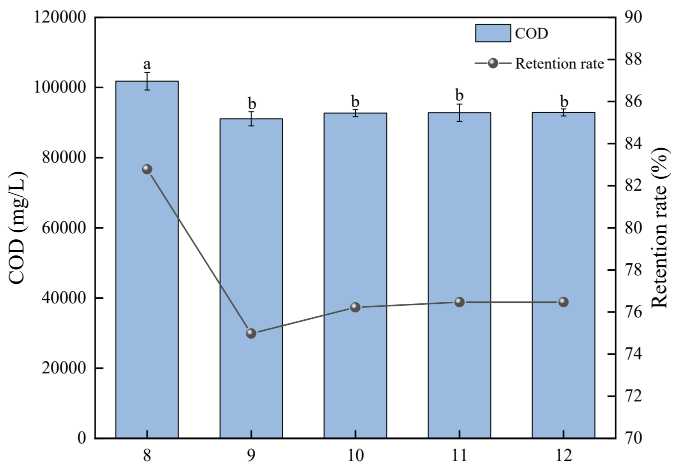

Figure 6. The COD content and retention at different pH values

4. Conclusion

(1)Compared with the magnesium ammonium phosphate method, the iron salt method and the aluminum salt method, the hydroxyapatite method not only has a better phosphorus removal effect but also has the potential for nitrogen removal, and the COD retention rate is the best. It meets the research requirements for using the treated yellow water from brewing as an additional carbon source for biological wastewater treatment. Calcium oxide is recommended as the best phosphorus removal agent.

(2) When calcium oxide is added at different pH values, the phosphorus removal effect is the best at pH=10, and it also has a certain nitrogen removal performance, with a relatively high COD retention rate.

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