Study on treatment technology of wastewater from hydrolysis of acid oil

Yuejin Li\textsuperscript{1,2,*}, Zhiyong Lin\textsuperscript{1} and Yali Han\textsuperscript{1}

\textsuperscript{1}College of Chemistry and Chemical Engineering, Binzhou University, Binzhou 256603, PR China
\textsuperscript{2}Shandong Provincial Engineering Research Center for Industrial Wastewater Reclamation, Binzhou 256603, PR China

Liyuejin83@163.com

Abstract. In this paper, the degumming of ferric chloride, calcium hydroxide after the removal of acid acidification hydrolysis of waste oil as raw material, through the treatment process to purify the wastewater. Choose different chemical additives, investigation of different temperature, pH value and other factors, find the best extraction condition. Through the orthogonal test of sodium carbonate, sodium oxalate, barium carbonate, compared with three kinds of chemical additives. The best chemical assistant is sodium carbonate, the best treatment temperature is 80 degrees Celsius, pH value is 8.0. After the reaction, the content of calcium and iron ions were determined by suitable methods. The removal rate of calcium ion is 98%, the removal rate of iron ion is 99%, and the effect of calcium and iron ion precipitation on the subsequent evaporation operation is reduced. Finally, the comparison is made to clarify the Dilute Glycerol water solution.

1. Introduction

The glycerol is an important chemical raw material. It is usually used as antifreeze, emulsifier, synthetic resin, paint, plastic material and so on, which can also be used for spice, pharmacy, cosmetics and national defense industries. According to a survey of China’s glycerol market, the demand for glycerol is far greater than the actual production, and glycerol at extremely high purity is mainly from foreign markets [1].

Glycerol is currently produced by three main methods, naturally, using chemical synthesis, and through biosynthesis. The glycerol is produced by naturally in the actual industrial production [2-3]. Although the glycerol content of this wastewater is relatively small, there are large amounts of organic acids and inorganic salts, such as Ca\textsuperscript{2+} and Fe\textsuperscript{3+}, which can form precipitate, clog the equipment pipeline, and reduce heat transfer efficiency [4]. The environmental may be deeply damaged if the wastewater direct drainage. The glycerol will also be discharged together, it can be waste of raw materials and increased production costs. There are currently several methods available to treat acidified oil wastewater; namely the chemical method, the ion exchange method [5], the electro-purification method [6] and so on. Therefore, the above methods for treating acidified wastewater cannot effectively treat manufacturing wastewater, and lead to glycerol waste.

In this paper, the degumming of ferric chloride, calcium hydroxide after the removal of acid acidification hydrolysis of waste oil as raw material, through the treatment process to purify the wastewater. Added the suitable chemical additives in the raw liquid, which can make the excess Ca\textsuperscript{2+} and Fe\textsuperscript{3+} form precipitate. The precipitate can be separated through filtration[7]. This technology can
recovery high added value glycerol. Solve the pollution of wastewater and improve the economic efficiency of enterprises.

2. Experimental

2.1 Materials
Glycerol, ammonium acetate, glacial acetic acid and acetyl acetone were purchased from Tianjin Evergreen Chemical Reagent Manufacturing Co., LTD (Tianjin, China). Ca(OH)₂ and BaCO₃ were obtained from Tianjin HengXing Chemical Reagent Co., LTD (Tianjin, China). Sodium carbonate anhydrous was obtained from Tianjin North Medical Chemical Reagent Factory (Tianjin, China).

2.2 Analysis method
The EDTA titration[8~9] and the flame atomic absorption spectrometry [10~11] can be used to test Ca²⁺ in water; The ultraviolet spectrophotometric method[12~13], the atomic absorption spectrophotometry[14~15] and the phenanthroline spectrophotometry[16] in water; The acetyl acetone spectrophotometric method can be used to test the content of glycerol [17].

2.3 Single factor experiment
The single factor experiment including chemical additives, pH value and operating temperature on the postprocessing of glycerol, effects of Ca²⁺ and Fe³⁺ content.

2.4 Orthogonal test
Based on the results of single factor experiments, orthogonal tests were conducted on various levels using different factors and a 3³ orthogonal table.

| Level | pH A | Temperature B (℃) | Chemical additives C |
|-------|------|-------------------|----------------------|
| 1     | 7.5  | 70                | Na₂CO₃               |
| 2     | 8.0  | 80                | Na₂C₂O₄              |
| 3     | 8.5  | 90                | BaCO₃                |

3. Results and discussion

3.1 Standard curves of glycerol, Ca²⁺ and Fe³⁺
The fitting equation of the glycerin standard curve was found to be y = 60.4x + 0.035 and R² = 0.99916; The fitting equation of calcium ions was y=0.0312x-0.0051 and R²=0.99862; The fitting equation of the ferri ion was y=0.2695x+0.008 and R²=0.9991.
3.2 Single factor result

Effect of chemical additives on the content of glycerol, $\text{Ca}^{2+}$ and $\text{Fe}^{3+}$. The effects of chemical additives on glycerol concentration, calcium and iron ion concentration were measured in three groups. The results are seen from Figure 1 to figure 3, when sodium carbonate is used as chemical additives, samples of glycerol was the most and the maximum absorban, while $\text{Fe}^{3+}$ was the lowest. However, as can be seen from Figure 2, for $\text{Ca}^{2+}$, when the chemical additives are barium carbonate, its content is the lowest, but because of poor water solubility of barium carbonate, comprehensive consideration, you can use sodium carbonate as chemical additives.

![Fig. 1 Effects of chemical additives on the content of glycerol](image1)

![Fig. 2 Effect of chemical additives on the content of calcium ion](image2)

![Fig. 3 Effect of chemical additives on iron ion conten](image3)
3.3 Effect of temperature on the content of glycerol, Ca$^{2+}$ and Fe$^{3+}$

As shown in Figure 4 can be seen with the temperature rise, the glycerol content reached a peak at 80 ℃, when the temperature is higher than 80 ℃, glycerol content but a significant decline, so for glycerin, the best operating temperature of 80 ℃.

From Figure 5 and figure 6 can be seen as the increase of temperature, the Ca$^{2+}$ and Fe$^{3+}$ content decreased obviously at the temperature of about 80 ℃, and decreased to the minimum value at the temperature of 80 Fe$^{3+}$, and the content of Ca$^{2+}$ and the content increased obviously after. Therefore, the optimal operating temperature is 80 ℃ for calcium and iron ions.

To sum up, as the glycerol content is relatively high, Ca$^{2+}$, Fe$^{3+}$ content reached the minimum, will not affect the evaporation of the subsequent operation, select the operating temperature of 80 ℃.

![Fig. 4 Effect of operating temperature on the content of glycerol](image1)

![Fig. 5 Effect of operating temperature on the content of calcium ion](image2)

![Fig. 6 Effect of operating temperature on iron ion content](image3)
3.4 Effect of pH value on the content of glycerol, Ca2+ and Fe3+

Figure 7 to Figure 9 shows the effect of pH on the content of glycerol, Ca\(^{2+}\) and Fe\(^{3+}\) during the post-processing operation. From Figure 7, the glycerol content slightly fluctuated before pH = 8.0, reached the peak, the maximum glycerol content, when pH > 8.0, the glycerol content decreased significantly. Therefore, the pH value should be controlled at about 8.0 to obtain the maximum glycerol content and increase the recovery rate of glycerol. As can be seen from Figure 8 and Figure, the content of Ca\(^{2+}\) and Fe\(^{3+}\) decreases when the pH value is less than 8, and when the pH value is 8.0, the content of Ca\(^{2+}\) and Fe\(^{3+}\) is reduced to the minimum value, and the pH value is more than 8.0, and the content of Ca\(^{2+}\) and Fe\(^{3+}\) is obvious. In order to obtain the highest glycerol content and the lowest Ca\(^{2+}\), Fe\(^{3+}\) content, the need to control the pH value of 8.0 or so.

![Fig. 7 Effect of pH value on the content of glycerol](image1)

![Fig. 8 Effect of pH value on the content of calcium ion](image2)

![Fig. 9 Effect of pH value on iron ion content](image3)
4. Orthogonal test

4.1 Orthogonal test of glycerol content

Table 2 Orthogonal test of glycerol content

| Serial number | pH A | Temperature B (°C) | Chemical additives C | Glycerol (g/L) |
|---------------|------|--------------------|----------------------|----------------|
| 1             | 1    | 1                  | 1                    | 0.0126         |
| 2             | 1    | 2                  | 2                    | 0.0084         |
| 3             | 1    | 3                  | 3                    | 0.0094         |
| 4             | 2    | 1                  | 3                    | 0.0094         |
| 5             | 2    | 2                  | 1                    | 0.0127         |
| 6             | 2    | 3                  | 2                    | 0.0122         |
| 7             | 3    | 1                  | 2                    | 0.0089         |
| 8             | 3    | 2                  | 3                    | 0.0126         |
| 9             | 3    | 3                  | 1                    | 0.0118         |

It can be concluded from Table 2 that the primary and secondary factors affecting the glycerol content in the post-treatment operation are: pH > temperature > chemical additives. Treatment conditions: chemical assistant is Na₂CO₃, the operating temperature is 80°C, the suitable pH value is about 8, and the content of glycerin in the sample is about 0.0127 g/L. The difference between the three factors was found to be very close to the three values, so the effect of the three factors on the glycerol content was not very obvious. Compare the magnitude of the three factors was found to be very close to the three values, so the effect of the three factors on the glycerol content was not very obvious. In analyzing the influence of three factors on the experimental results, the main factors affecting the Ca²⁺ and Fe³⁺ contents can be analyzed, and finally consider the impact of the material content of the primary and secondary factors.

4.2 Orthogonal test of calcium ion content

Table 3 Orthogonal test of calcium ion content

| Serial number | pH | Temperature (°C) | Chemical additives | Ca²⁺(mg/L) |
|---------------|----|------------------|--------------------|------------|
| 1             | 1  | 1                | 1                  | 7.0544     |
| 2             | 1  | 2                | 2                  | 10.9006    |
| 3             | 1  | 3                | 3                  | 0.9967     |
| 4             | 2  | 1                | 3                  | 0.9647     |
| 5             | 2  | 2                | 1                  | 5.0673     |
| 6             | 2  | 3                | 2                  | 10.9647    |
| 7             | 3  | 1                | 2                  | 11.2532    |
| 8             | 3  | 2                | 3                  | 1.0288     |
| 9             | 3  | 3                | 1                  | 8.5288     |

K₁ = 18.9198, K₂ = 17.0288, K₃ = 20.8108, t₁ = 6.3066
As can be seen from table 3 that the primary and secondary factors affecting the Ca\(^{2+}\) content in the post-treatment operation are chemical additives> pH> operating temperature. Optimum processing conditions for: use BaCO\(_3\) do chemical additives, the best operating temperature is 70 °C, the best pH value of 8.0, Ca\(^{2+}\) content in the sample is 0.9647 mg/L. Compare the three factors of the range, the range C factors is bigger, but A and B by close very range, so the pH and temperature on the influence of Ca\(^{2+}\) content is not very obvious. Analysis respectively.

4.3 Orthogonal test of iron ion content

| Serial number | pH  | Temperature (°C) | chemical additives | Fe\(^{3+}\) (μg/mL) |
|---------------|-----|------------------|--------------------|---------------------|
| 1             | 1   | 1                | 1                  | 0.0445              |
| 2             | 1   | 2                | 2                  | 1.8738              |
| 3             | 1   | 3                | 3                  | 0.0556              |
| 4             | 2   | 1                | 3                  | 0.1410              |
| 5             | 2   | 2                | 1                  | 0.0259              |
| 6             | 2   | 3                | 2                  | 1.8664              |
| 7             | 3   | 1                | 2                  | 1.1131              |
| 8             | 3   | 2                | 3                  | 0.0371              |
| 9             | 3   | 3                | 1                  | 0.0371              |
| K\(_1\)       | 1.9740 | 1.1948         | 0.1076             |
| K\(_2\)       | 1.2912 | 2.0408         | 4.8534             |
| K\(_3\)       | 1.9294 | 1.9591         | 0.2337             |
| t\(_1\)       | 0.6580 | 0.3982         | 0.0358             |
| t\(_2\)       | 0.4304 | 0.6802         | 1.6178             |
| t\(_3\)       | 0.6431 | 0.6530         | 0.0779             |
| R             | 0.68274 | 0.84601      | 4.7458              |

It can be seen from Table 4 that the primary and secondary factors affecting the Fe\(^{3+}\) content in the post-treatment operation are chemical additives> pH> operating temperature. The optimum treatment conditions were as follows: the chemical additive was Na\(_2\)CO\(_3\), the operating temperature was 80 °C, the pH value was 8.0, and the iron content in the sample was 0.0259 μg / L. Similarly, the comparison of the three factors of the range, A factor and B factors are relatively close to the value, so when the same chemical additives, temperature and pH value of Fe\(^{3+}\) content is not obvious.

Because Ca\(^{2+}\) and Fe\(^{3+}\), glycerol, present in the sample at the same time, In the process of treatment need to obtain a higher glycerol content and the lowest Ca\(^{2+}\),Fe\(^{3+}\) content, in order to carry out the subsequent evaporation operation, so the choice of treatment conditions need to consider the impact of the three substances in the primary and secondary factors. The content of Ca\(^{2+}\) and Fe\(^{3+}\) was relatively low under the condition of relatively high glycerol content. For glycerol and Ca\(^{2+}\), the two factors influencing the common content of temperature and pH value and pH > temperature; for Ca\(^{2+}\) and Fe\(^{3+}\), the two factors affecting the content of chemical additives; and the temperature in the effect of three kinds of material content, are not the dominant factor. To sum up, the main factors affecting the three substances in the whole experiment were chemical additives> pH> operating temperature, so the treatment conditions were as follows: the chemical assistant is Na\(_2\)CO\(_3\), the operating temperature is 80 °C, the pH value is about 8.0.

4.4 Verification experiment
An orthogonal experiment to investigate aftertreatment of wastewater from dilute glycerol production showed that the optimal temperature was 80°C, the best pH was 8.0 and the best chemical additives was Na₂CO₃. In addition, the order of affecting factors was chemical additives > pH > temperature.

An orthogonal experiment to investigate aftertreatment of wastewater from dilute glycerol production. Acid hydrolysis of waste oil by postprocessing process, not completely in the waste water CaSO₄ and FeCl₃ completely eliminated, but significantly decreased the Ca²⁺ in wastewater, the content of Fe³⁺, at the same time, reduce the precipitation effect on subsequent evaporation operation, is conducive to the recycling of glycerol. And glycerol with the length of the heating time will be to varying degrees, the occurrence of different degrees of polymerization and decomposition, so in practice must be used vacuum evaporation operation to ensure that the glycerol products of high quality and high yield.

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### Table 5 Verification test of optimal processing conditions

| number | pH   | Temperature (°C) | chemical additives | Glycerol (g/L) | Ca²⁺ (mg/L) | Fe³⁺ (μg/mL) |
|--------|------|------------------|--------------------|---------------|-------------|-------------|
| 1      | 8.0  | 80               | Na₂CO₃             | 0.0102        | 5.1314      | 0.0705      |
| 2      | 8.0  | 80               | Na₂CO₃             | 0.0117        | 7.3108      | 0.0408      |
| 3      | 8.0  | 80               | Na₂CO₃             | 0.0092        | 5.9006      | 0.0333      |
| mean   |      |                  |                    | 0.0103        | 6.1142      | 0.0482      |

According to the above table, the content of glycerol was 0.0103 g/L, the content of Fe³⁺ was 0.0482 g/mL, and the content of Ca²⁺ was 6.1142 mg/L. After calculation, the removal rate of Fe³⁺ reached 99%, and the removal rate of Ca²⁺ reached to 98%. Compared with BaCO₃, Na₂CO₃ is highly soluble in water, so Na₂CO₃ is selected as a chemical additive for the post-treatment process.
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