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**Research Article**

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# Acid-Catalyzed Pretreatment of Wastewater from Glycerin Production

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**ABSTRACT**

*During acid-catalyzed glycerol production, wastewater was deacidified and degummed to determine the best treatment conditions. When $Ca(OH)_2$ was used as the deacidification agent, the optimum treatment temperature, pH and reaction time were 60℃, 10 and 15 minutes, respectively. After the reaction, the $SO_4^{2-}$ concentration was 2.3736 mg/L and its removal ratio was 99.97%. Following deacidification, degumming was necessary. For this process, the best degumming flocculant was $FeCl_3$, the optimum temperature was 60°C and the best pH was 6. The final concentration of $SO_4^{2-}$ was 2.1836 mg/L and the removal ratio could reach up to 99.973%.*

**Keywords**: Glycerin; Wastewater; Deacidification; Unglued; Sulfate; Degumming; Flocculant

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## INTRODUCTION

Glycerol has a very wide range of applications in daily life as well as in industry. The demand for glycerol has increased sharply since the First World War because it is used as a raw material for making gunpowder. 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 [2]. During natural production, glycerol is extracted from oils, primarily using saponification [3], but also by oil hydrolysis [4]. In chemical synthesis [5], glycerol is mainly synthesized from raw petrochemical products. Worldwide, natural methods are preferred over synthetic methods [6-7].

Natural methods lead to the production of high volumes of acidified wastewater. Although the glycerol content of this wastewater is relatively small, there are large amounts of organic acids and inorganic salts, such as $Ca^{2+}$, which can form precipitate, clog the equipment pipeline, and reduce heat transfer efficiency [8]. Moreover, direct discharge of wastewater into the environment will have a significant impact on the ecosystem, as well as on the credibility and reputation of the enterprise. Additionally, any glycerol remaining in the wastewater will be lost, resulting in wasted raw materials and increased cost. There are currently several methods available to treat acidified oil wastewater; namely, the chemical method, in which chemicals are added to increase the solution ash content, the ion exchange method [9], which is suitable for waste streams with few organic impurities, and the electro-purification method, in which anodes tend to be adhered to by aluminum soap and other contaminants , resulting in the need for regular cleaning. In addition to this shortcoming, electro-purification methods have not yet been industrialized.

Aerobic organisms are generally used in biological treatment methods. When fatty acid containing waste water is treated with the improved anaerobic activated sludge process, reactors are greatly influenced by suspended solids, as well as the concentrations of oil and fat. Biofilm methods [11] result in good hydraulic conditions, strong anti-impact loads and high biological concentrations. Under the same operating conditions, a biofilm system will produce better results than an activated sludge system, but biofilm methods have limited ability to remove oil, SS and chroma, and they also require pretreatment. Moreover, the correct enzyme is needed for wastewater treatment;

therefore, the methods are not being industrialized. Based on comparison of the above methods, biofilm systems are effective at treating sewage, and the activated sludge system is inferior to the former since it needs pretreatment. Therefore, the above methods for treating acidified wastewater cannot effectively treat manufacturing wastewater, and lead to glycerol waste. In this study, orthogonal experiments and a series of other operations were used to optimize deacidification and degumming [12], as well as to prepare for the next step of multi-effect evaporation [13] and rectification [14].

## EXPERIMENTAL SECTION

### Materials

$FeCl_3$, methanol, $AlCl_3$, acetic acid and $Ca(OH)_2$ were obtained from Tianjin North Medical Chemical Reagent Factory (Tianjin, China). $BaCO_3$ and acetyl acetone were purchased from Tianjin Evergreen Chemical Reagent Manufacturing Co., LTD (Tianjin, China).

### Analysis method

The acetyl acetone spectrophotometric method can be used to test the content of glycerol [15]. For this method, glycerol yield = the lower fluid volume * w(the lower glycerin volume)/the theoretical glycerol production * 100% [16].

### Experimental procedure

**Deacidification:**

Orthogonal experiments were conducted using the $3^3$ orthogonal table to investigate various levels and factors. These consisted of single factor experiments conducted as previously described [12].

**Table 1: Deacidification factors and levels of orthogonal experiments**

| Level | Factor | | |
|---|---|---|---|
| | pH A | Temperature B (℃) | Time C (min) |
| 1 | 6 | 40 | 5 |
| 2 | 8 | 50 | 10 |
| 3 | 10 | 60 | 15 |

**Degumming**

Based on the results of single factor experiments, orthogonal tests were conducted on various levels using different factors and a $3^3$ orthogonal table.

**Table 2: Degumming factors and levels of orthogonal experiments**

| Level | Factor | | |
|---|---|---|---|
| | Flocculant A | *PH* B | Temperature C (℃) |
| 1 | $FeCl_3$ | 2 | 40 |
| 2 | $KAl(SO_4)_2{\cdot}12H_2O$ | 4 | 50 |
| 3 | $AlCl_3$ | 6 | 60 |

## RESULTS AND DISCUSSION

### Standard curves of glycerol and $Ba^{2+}$

The fitting equation of the glycerin standard curve was found to be $y = 60.4x + 0.035$ and its linear correlation coefficient was $R^2 = 0.99916$. The fitting equation of barium ions was $y = 0.0068x + 0.0003$ and its linear correlation coefficient was $R^2 = 0.9974$. Therefore, the trace sulfates can be tested according to the barium ion standard curve.

### Analysis of deacidification process

The optimum conditions, which can be determined from Table 3, were A3B1C3, which indicates pH = 10, 40°C, and a reaction time of 15 min. The orthogonal test results showed that the order of influencing factors was pH>reaction time>reaction temperature. After deacidification treatment, a variety of acids and other impurities in glycerol wastewater were greatly reduced, and 99.97% of the acid was removed.

**Table 3: Deacidification orthogonal test**

| Number | pH A | Temperature B (℃) | Time C (min) | $SO_4^{2-}$ (mg/L) |
|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 3.7523 |
| 2 | 1 | 2 | 2 | 3.8825 |
| 3 | 1 | 3 | 3 | 3.4251 |
| 4 | 2 | 1 | 2 | 2.7421 |
| 5 | 2 | 2 | 3 | 3.1324 |
| 6 | 2 | 3 | 1 | 3.5234 |
| 7 | 3 | 1 | 3 | 2.3736 |
| 8 | 3 | 2 | 1 | 3.0104 |
| 9 | 3 | 3 | 2 | 2.4137 |
| $K_1$ | 3.687 | 2.956 | 3.4287 | |
| $K_2$ | 3.133 | 3.3418 | 3.0128 | |
| $K_3$ | 2.599 | 3.1207 | 2.977 | |
| $k_1$ | 1.229 | 0.9853 | 1.1429 | |
| $k_2$ | 1.044 | 1.1139 | 1.0043 | |
| $k_3$ | 0.866 | 1.0402 | 0.9923 | |
| R | 0.363 | 0.1286 | 0.1506 | |

**Analysis of degumming process**

**Single factor result:**

**Effect of flocculant on degumming:** The effects of flocculant on the sulfate concentrations were determined for each experiment. A shown in Figure 1, sulfate content was lowest when ferric chloride was used as the flocculant. Therefore, ferric chloride could be used as a flocculant.

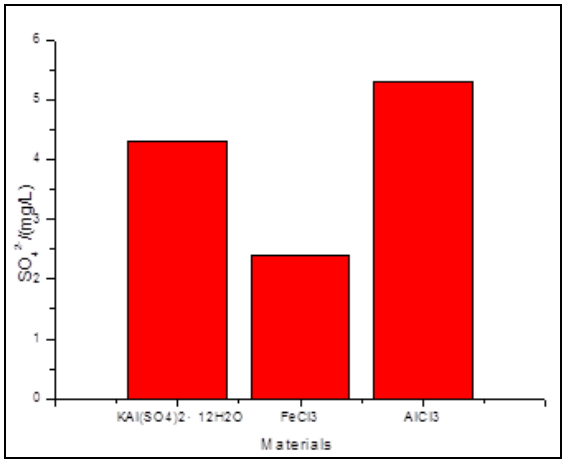


**Figure 1: Single-factor experimental design to test the flocculant.**

**Effect of temperature on degumming:** According to the single factor of the flocculant, with ferric chloride as the flocculant, the effects of temperature on degumming could be studied under a certain acidity. As shown in Figure 2, as temperature increased, the sulfate content was significantly reduced until 60°C, above which there was no further significant reduction. Additionally, the lowest sulfate content was observed at about 62.5°C. Therefore, during the degumming process the temperature should not be too low, otherwise the reduction of sulfate will not be significant. However, the temperature should not be too high because of energy costs and the potential to increase sulfuric acid content.

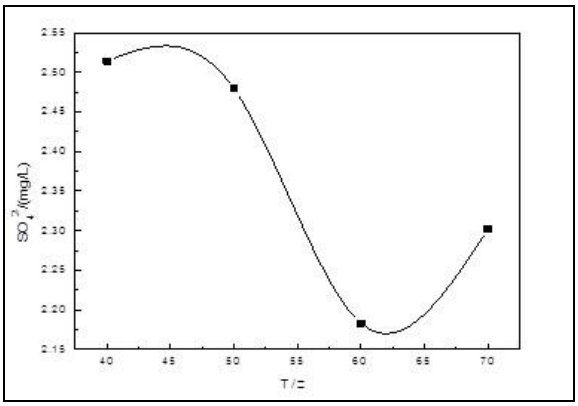


**Figure 2: Single-factor experimental design to test temperature effects**

**Effect of acidity on degumming:** As shown in Figure 3, the reduction rate of sulfate was significant below pH = 6, above which the reduction of sulfate slowed. These findings suggest that at pH> 6, the sulfate was decreasing but at a slower rate. Moreover, high pH was not conducive to the precipitation of protein and other impurities [12]. Therefore, pH = 6 was used in this study.

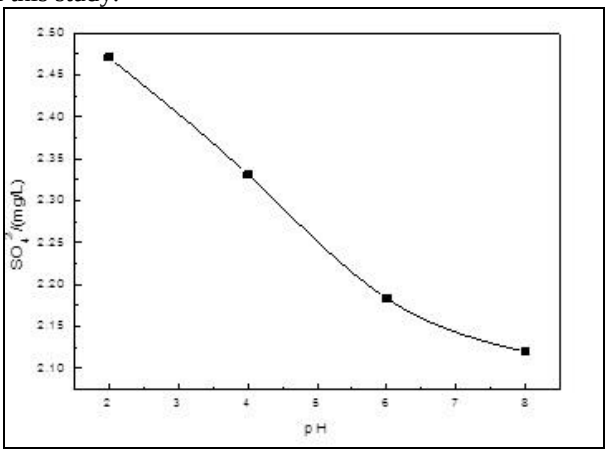


**Figure 3: Single-factor experimental design to test acidity**

**Unglued orthogonal test:** The orthogonal tests of flocculant, pH and temperature (3 factors and 3 levels) based on the results from previous single-factor experiments are listed in Table 4.

**Table 4: Unglued orthogonal test**

| | Flocculant A | pH B | Temperature C (℃) | $SO_4^{2-}$(mg/L) |
|---|---|---|---|---|
| 1 | $FeCl_3$ | 2 | 40 | 2.514 |
| 2 | $FeCl_3$ | 4 | 50 | 2.479 |
| 3 | $FeCl_3$ | 6 | 60 | 2.1836 |
| 4 | $KAl(SO_4)_2{\cdot}12H_2O$ | 2 | 50 | 7.867 |
| 5 | $KAl(SO_4)_2{\cdot}12H_2O$ | 4 | 60 | 5.928 |
| 6 | $KAl(SO_4)_2{\cdot}12H_2O$ | 6 | 40 | 3.8606 |
| 7 | $AlCl_3$ | 2 | 60 | 7.5121 |
| 8 | $AlCl_3$ | 4 | 40 | 6.112 |
| 9 | $AlCl_3$ | 6 | 50 | 4.1032 |
| $K_1$ | 7.1766 | 17.893 | 12.4866 | |
| $K_2$ | 17.6556 | 14.519 | 14.4492 | |
| $K_3$ | 17.7273 | 10.148 | 15.6291 | |
| $k_1$ | 2.3922 | 5.9644 | 4.1622 | |
| $k_2$ | 5.8852 | 4.8397 | 4.8164 | |
| $k_3$ | 5.9091 | 3.3825 | 5.2097 | |
| R | 3.5169 | 2.5819 | 1.0475 | |

As shown in Table 4, the order of influencing factors was flocculant > pH > temperature. Additionally, the optimum treatment conditions were as follows: ferric chloride as the flocculant, 60°C, pH 6 and a sulfate content of 2.1836 mg/L.

## CONCLUSIONS

1. An orthogonal experiment to investigate pretreatment of wastewater from acid-catalyzed glycerol production showed that the optimal temperature for deacidification was 40°C, the best pH was 10 and the best reaction time was 15 min. In addition, the order of affecting factors was pH > reaction time > reaction temperature.
2. The experimental results also showed that the best flocculant was $FeCl_3$, the best temperature was 60°C and the optimum pH was 6. The order of influencing factors on degumming was flocculant > pH > temperature.
3. After deacidification and degumming treatment, glycerol wastewater still contained a small amount of $CaSO_4$ and $FeCl_3$. Accordingly, additional treatment processes should be conducted to remove these above-mentioned impurities. Generally, the slightly soluble calcium sulfate will be converted into insoluble sulfate and calcium salts, followed by filtration to separate the precipitate. If it is still difficult to remove these impurities, they can also be transformed into water-soluble salts, which will be removed during the subsequent distillation operation.

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