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Recovery of Fumaric Acid from Industrial Wastewater by Chemical Extraction and Stripping

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Abstract: The study on chemical extraction and stripping for the recovery of fumaric acid from low concentration organic acid wastewater has been carried out. The parameters influencing the extraction efficiency were investigated, including extractant concentration, the initial pH, the volume ratio of water to oil (W/O), the extraction temperature, and the concentration of n-octanol. The heat effect of the extraction process, the formation of acid-amine complexes, and the corresponding equilibrium constant were determined. In the optimum condition that kerosene/N_{7301}/n-octanol was 2:2:1, pH was 0.5, W/O was 1:1, and the temperature was 303K, through chemical extraction and stripping, the COD_{cr} value of fumaric acid wastewater decreased from 71040 mg/l to 8411 mg/l, and the overall COD_{cr} removal rate reached 88.16%, and the extraction efficiency of fumaric acid was 70.67%. The extractant was regenerated by a stripping process with 2% NaOH, and the stripping rate almost arrived at 100%. The regenerated extractant was cycled seven times without decreasing extraction efficiency and the stripping rate. And fumaric acid was obtained by adjusting the pH of the salt from stripping. After extraction, the fumaric acid wastewater can be further treated by oxidation or biodegradation to environmentally acceptable levels.

Keywords: Chemical extraction, fumaric acid, organic wastewater, COD removal rate, N_{7301}

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INTRODUCTION

As a very important raw material of organic chemistry, fumaric acid (trans-butene diacid), has been applied in many fields including food, medicine, and light industry. Anon (1) reported that current US consumption of fumaric acid was about 40 million pounds per year. There are three main methods of the synthesis of fumaric acid:

1) obtained from benzene as a raw material by a set of processes such as oxidation, hydrolyze, isomerization, and crystallization;
2) produced via the acid-catalyzed isomerization of maleic acid by adding a certain amount of thiourea into the offgas of the phthalic anhydride production process, and mainly employed for sizing resins for the paper industry (2–4);
3) produced by fermentation from mold Rhizopus arrhizus (5).

And wastewater produced in the production process of fumaric acid exhibits low pH, high COD_{cr} value, high thiourea concentration, and low biodegradability.

Recently, some researchers have given different methods to treat fumaric acid wastewater, including microelectrolysis of iron and carbon, catalytic microwave oxidation, peroxide oxidation, bio-contact oxidation, and anaerobic hydrolysis (6–8). Although the COD_{cr} value of the wastewater can be decreased greatly by these methods, fumaric acid is degraded and cannot be reused in the processes.

Solvent (liquid-liquid) extraction is often effective for recovery of low-volatility carboxylic acids from aqueous solution due to some unique characteristics such as high selectivity, high efficiency, low temperature needed, low energy consumption, and low cost (9, 10). In the past two decades, solvent extraction, especially chemical extraction, has been widely used to remove efficiently organic acids from industrial effluents to environmentally acceptable levels or to recycle the organic acids back to the original process (11–16). King (17) also reported that chemical extraction was an efficient method for separating polar organic substances with low concentration. Then chemical extraction is considered as an alternative process for the treatment of fumaric acid wastewater.

In this work, chemical extraction-stripping of fumaric acid wastewater was carried out. In addition, the influencing factors of extraction efficiency as well as the heat effect of the extraction process were investigated and the optimum operating conditions were obtained.

MATERIALS AND CHEMICALS

All chemicals used in these experiments were of analytical grade. The extractant and diluent selected were trialkylamine (N_{7301}, Feixiang Chemicals Co.,

Table 1. Physical and chemical characteristics of the fumaric acid wastewater

Appearance	Yellow, opacity
pH	1.73
Color (multiple)	1200
COD_{cr} (mg/l)	71040
Fumaric acid (g/l)	6.47
Main components	Fumaric acid, thiourea

Ltd., Jiangsu, China) and kerosene (Fd-wzsh Co., Ltd., Zhejiang, China), respectively. The physical and chemical characteristics of fumaric acid wastewater obtained from Ningbo Yuantai Fine Chemistry Co., Ltd. (Zhejiang, China) are listed in Table 1.

EXPERIMENTAL UNIT AND PROCEDURES

A schematic diagram of the laboratory scale of the extraction-stripping test unit is shown in Fig 1. The fumaric acid wastewater was extracted by trialkylamine N_{7301} in kerosene and n-octanol. After extraction, the loaded organic phase was stripped by the NaOH solution and the extractant was regenerated.

The experiments were carried out in beakers as follows:

1. Taking a certain amount of N_{7301}, kerosene, and n-octanol into a beaker over a thermostat magnetic stirrer and turning on it;

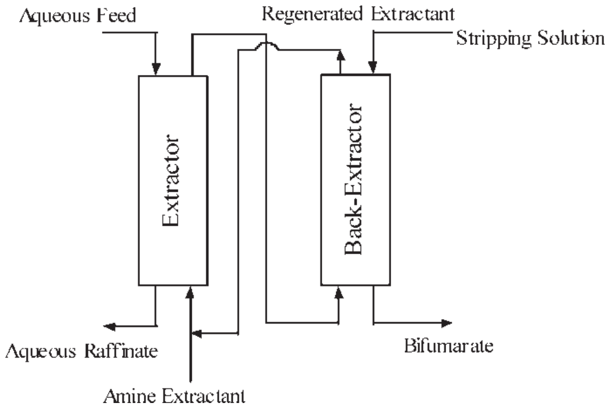


Figure 1. Apparatus for extraction and stripping experiments.

2. Adding the fumaric acid wastewater with pre-adjusted pH value into the uniformly mixed phase of (1);
3. Turning off the stirrer after 1 h, dripping the mixer into a tap funnel, and separating the laminate phases after 20 min;
4. Analyzing the water quality of the bottom level of (3)-relatively acid-free aqueous raffinate (water phase);
5. Stripping the top level of (3)-acid-loaded extract (organic phase) with NaOH solution and separating after 10 min, then the top level is the regenerated extractant and the bottom level is the sodium salt which can be reused in the production process.

ANALYTICAL METHODS

The concentration of fumaric acid was measured by UV spectrophotometer S53/54 at 240 nm. pH values were measured by a Digital Acidimeter (pH/ISE 868, ORION). The color of wastewater and the COD_{cr} values were measured by the method proposed by the Standard Methods for the Examination of Water and Wasterwater 1998 (18).

RESULTS AND DISCUSSION

The extraction efficiency is described as the COD_{cr} removal rate (%), which is defined as follows:

$$\textit{The}\ \mathrm{COD_{cr}}\ \textit{removal rate}\ (\%) = \frac{[\mathrm{COD_{cr}}]_f - [\mathrm{COD_{cr}}]_r}{[\mathrm{COD_{cr}}]_f} \times 100 \qquad (1)$$

The Formation of the Amine-Acid Complex

The extraction reaction can be shown as following:

$$mR_3N(o) + H_2A \xrightarrow{H_2SO_4} H_2A \cdot (R_3N)_m(o) \qquad (2)$$

Where, H_2A and (o) represent the fumaric acid and organic phase, respectively.

When pH > 7, the amine-acid complex is soluble in alkali and stripped by NaOH solution:

$$H_2A \cdot (R_3N)_m + NaOH \rightarrow NaHA + mR_3N(o) + H_2O \qquad (3)$$

And the distribution ratio D is defined as the ratio of the concentration of fumaric acid in the acid-loaded extract (organic phase) to that in the acid-free aqueous raffinate. The equilibrium constant K and distribution ratio D of extraction process are given by:

$$K = \frac{[H_2A \cdot (R_3N)_m]}{[R_3N]^m[H_2A]}; \quad D = \frac{[H_2A \cdot (R_3N)_m]}{[H_2A]} \tag{4}$$

Thus the relationship between K and D can be written as:

$$K = \frac{D}{[R_3N]^m} \tag{5}$$

And Eq. (5) can be rewritten as follows:

$$\lg D = \lg K + m \lg [R_3N] \tag{6}$$

Thus, according to Eq. (6), by measuring the distribution ratio at a different concentration of the extractant, the relationship between the distribution ratio and the concentration of the extractant at the given temperature is shown in Fig. 2. By fitting the data, the slope and intercept of the fitted linear regression line obtained is 1.6 and 0.55 respectively. Therefore, it can be considered that the fumaric acid is extracted mainly as a ratio of 1.6:1 to extractant. The corresponding equilibrium constant K is equal to 3.548.

Furthermore, infrared spectroscopic experiments were undertaken to investigate the extraction behavior of fumaric acid with the amine extractant. Figure 3 shows the spectra in the 500–4000 cm^{-1} region resulting from the complexation of 0.05 $\mathrm{mol \cdot L^{-1}}$ fumaric acid with 0.05 $\mathrm{mol \cdot L^{-1}}$ N_{7301} in kerosene and n-octanol, and Fig. 4 from the mixture of 0.05 $\mathrm{mol \cdot L^{-1}}$ N_{7301} in kerosene and n-octanol. Compared with the spectra in Fig. 4, there are two significant peaks that appeared in Fig. 3. One band is present at 1698.90 cm^{-1}, assigned to the $\nu - (C = O)$ of a carboxyl, which also

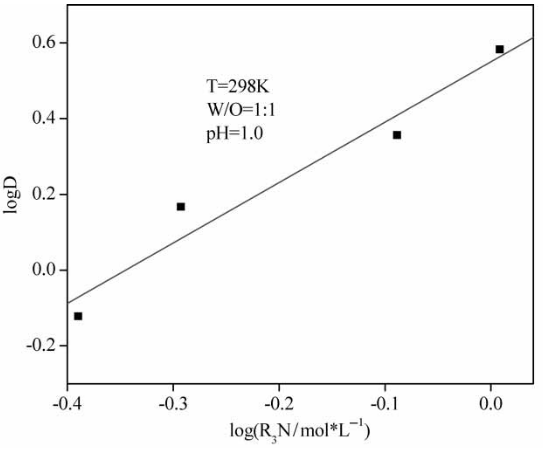


Figure 2. The distribution ratio D as a function of the concentration of extractant.

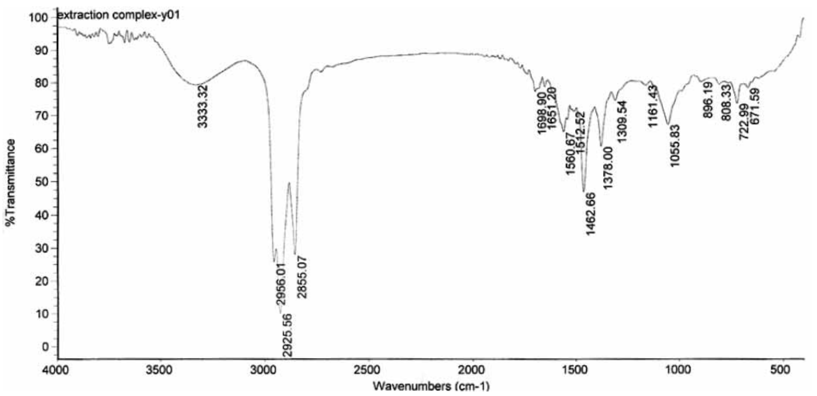
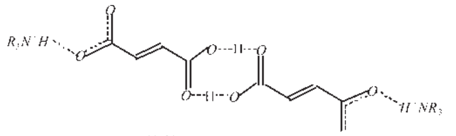
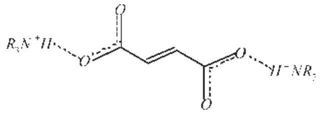


Figure 3. IR spectra of complexation 0.05 mol · L^{-1} fumaric acid with 0.05 mol · L^{-1} N$_{7301}$ in kerosene and n-octanol.

demonstrates the H bond in the complexation. Another band appears at 1560.67 cm^{-1}, assigned to the $\nu - (COO^{-})$ of a carboxylate, which illustrates the chemical complexation of fumaric acid with the amine extractant N$_{7301}$. The possible formations of fumaric acid-amine complexes in kerosene and n-octanol are (1, 2), (1, 1) complex formation. And the possible structures of fumaric acid-amine complexes are described below:


(1,1)


(1,2)

Effect of Extractant Concentration (Kerosene/N$_{7301}$)

For systems with more than one amine per complex, there is a significant effect of the total amine concentration on the loading of the extractant which is defined as the total concentration of acid in the organic phase divided by the total concentration of amine in the organic phase-at low acid concentrations. It is clearly shown in Fig. 3 that the COD$_{cr}$ removal rate was strongly dependent upon kerosene/N$_{7301}$. The COD$_{cr}$ removal rate increases with increasing concentration of extractant when kerosene/N$_{7301}$$<$1 and decreases afterwards. And the strong extraction is obtained around kerosene/N$_{7301}$ of 1:1. The "inert" diluent kerosene added was to adjust the parameters of the extraction process such as viscosity, density, interfacial tension and so on, so that the extraction behavior was simplified and became feasible. Also the water co-extraction decreased. However, the distribution ratio of the extraction process also decreased with the kerosene added.

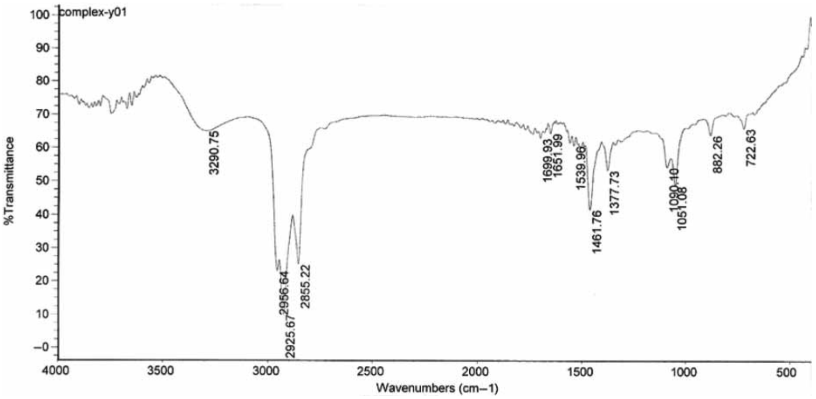


Figure 4. IR spectra of mixture of 0.05 mol $\cdot$ L^{-1} N_{7301} in kerosene and n-octanol.

Effect of pH

According to G. F. Guan (19), when di-carboxylic acids were extracted by trialkylamine, pH has great effect on the distribution ratio of the extraction process, and the relationship can be expressed as follows:

$$D = \left(K_1 + K_2 \frac{K_{a1}K_{a2}}{[H^+]^2}\right) \bigg/ \left(1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2}\right) \tag{7}$$

Therefore, the pH of the initial solution also can affect the extraction reaction and the efficiency since the distribution ratio greatly depends on pH. The change of COD_{cr} removal rate shows a bell shape with the pH from $0.3 \sim 2.0$ demonstrated in Fig. 4. The COD_{cr} removal rate indicates a maximum at $pH = 0.5$. It can be explained that there are more protons available for the carrier to be protonated with increasing $[H^+]$ in the feed phase, resulting in the extraction rate increases. While at high proton concentration, fumaric acid would be in the form of molecules other than ions, which makes the complex efficiency decrease and leads to the decreasing extraction rate. On the other hand, at high acid concentration, the acid-amine complex is easier to aggregate to form the second organic phase, which also will result in the decrease of the extraction efficiency.

Effect of W/O

Figure 5 illustrates that the COD_{cr} removal rate changes little at first and decreases rapidly later when the W/O increases. The optimum W/O obtained is about 1:1. At low W/O, which means the high loading of the extractant, and the extraction efficiency is high. As increasing W/O, the

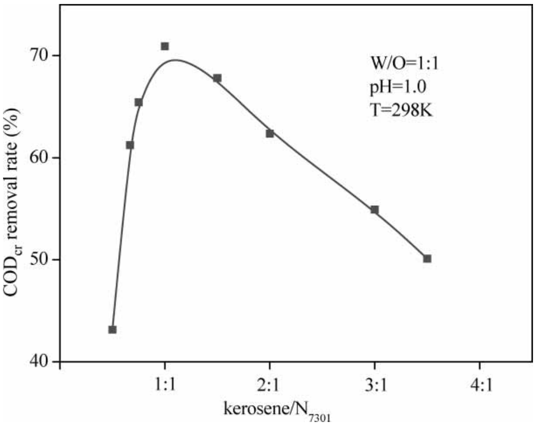


Figure 5. The COD$_{cr}$ removal rate as a function of kerosene/N$_{7301}$.

extractant is saturated gradually by wastewater, making the extraction efficiency decrease and causing the low COD$_{cr}$ removal rate.

Heat Effect of Extraction Process

The temperature is a very important influencing factor of the extraction process. Supposing that the enthalpy of the process keeps constant, and the thermodynamics process of extraction is a macroscopic one and then the following relationship is obtained:

$$K = K_0 \exp(-\Delta H/RT) \tag{8}$$

And Eq. (8) can be given in another way:

$$\ln K = \ln K_0 - \Delta H/RT \tag{9}$$

Substitution Eq. (9) into Eq. (6) the following equation is obtained:

$$\ln D = \ln K_0 + m \ln[R_3 N] - \Delta H/RT \tag{10}$$

And Eq. (10) can be rewritten as follows:

$$\ln D = \ln D_0 - \Delta H/RT \tag{11}$$

In which

$$\ln D_0 = \ln K_0 + m \ln[R_3 N] \tag{12}$$

Then the change of distribution ratio with temperature is depicted in Fig. 6.

The slope of the line in Fig. 6 is 0.71591, i.e., $\Delta H = -5.952\, J/mol$. Thus the extraction process is an exothermic one and it is unfavorable for

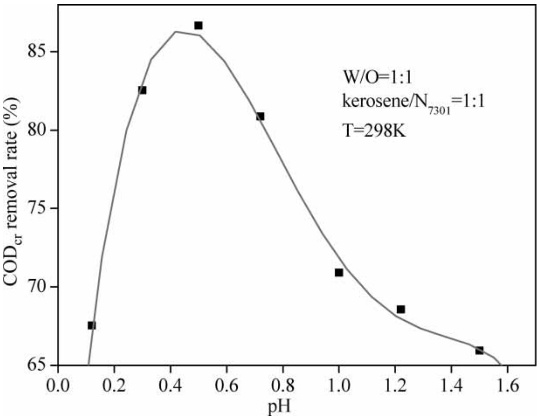


Figure 6. The COD_{cr} removal rate versus the initial pH value of the wastewater.

the extraction to increase the temperature above 303 K, which is the same as the theoretical background (the complexation reactions involve proton transfer or hydrogen-bond formation and are expected to be exothermic).

Effect of Extraction Temperature

Eq. 11 illustrates that the extraction efficiency also depends on the extraction temperature. From Fig. 7 it can be observed that the COD_{cr} removal rate increases with increasing extraction temperature to 303 K, and then it again decreases when the temperature is above 303 K. The best operation temperature obtained is about 303 K. The increasing temperature can make the viscosity of the organic phase lower while below 303 K, and then the

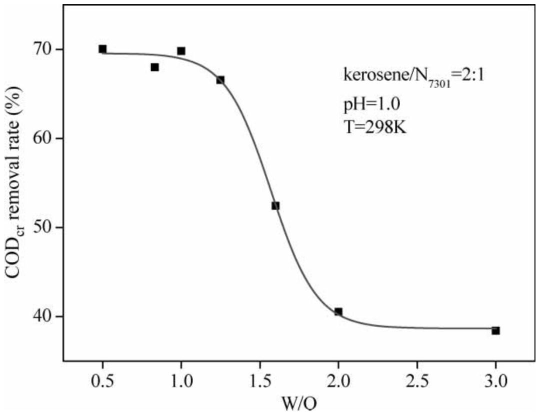


Figure 7. The COD_{cr} removal rate versus the volume ratio of wastewater to extractant.

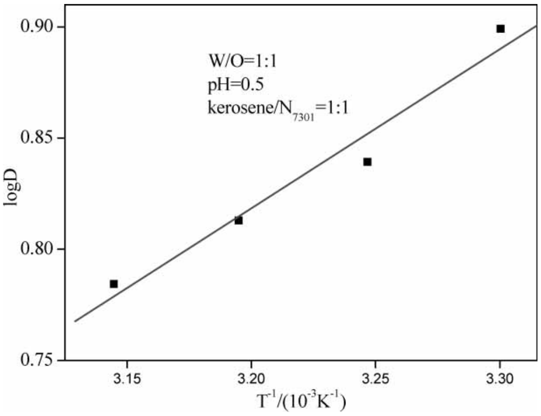


Figure 8. The dependence of distribution ratio on the temperature.

efficiency is enhanced. While above 303 K, the increasing temperature also can make the equilibrium constant smaller for the extraction process is an exothermic one and the solubility of the extractant in water is enhanced, which reduces the extraction efficiency and thus leads to low COD_{cr} removal rate.

Effect of n-Octanol

In this study, the extraction of fumaric acid with the organic phase of N_{7301} with only kerosene revealed the appearance of a second organic phase, which made the extraction process complicated and difficult to operate. Then the "active" diluent n-octanol was added to the organic phase. Experimental results show that adding n-octanol not only can make the extraction process simple and easier to do but also can affect the extraction efficiency. Figure 8 demonstrates the effect of n-octanol concentration on the COD_{cr} removal rate. From Fig. 8 we can observe that adding a certain amount of n-octanol in extractant enhances extraction efficiency, while too much n-octanol added reduces efficiency. A reasonable explanation is that n-octonal prevents the amine-acid complexes from interacting strongly with one another so that the activity coefficients of the organic-phase species do not change much with respect to composition, and a separate phase is avoided. However, adding too much n-octanol also makes the solubility of the extractant in water enhance, resulting in the COD_{cr} removal rate decrease.

Stripping with NaOH Solution

The extractant was regenerated by back-extraction following a change in the pH of the acid-loaded extract phase after extraction, also called the pH-swing

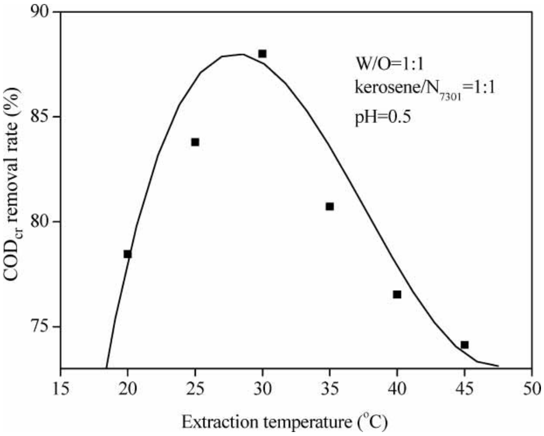


Figure 9. The COD_{cr} removal rate as a function of operation temperature.

process. In this study, we found that the best concentration of stripping NaOH solution was 2%, and the optimum volume ratio of acid-loaded extract to stripping solution was 2:1. The stripping rate almost reached 100%.

Circulating Times of Regenerated Extractant Used

From Fig. 9 we can see that the extractant regenerated by one stripping step can be reused in the next extraction step, and the COD_{cr} removal rate and

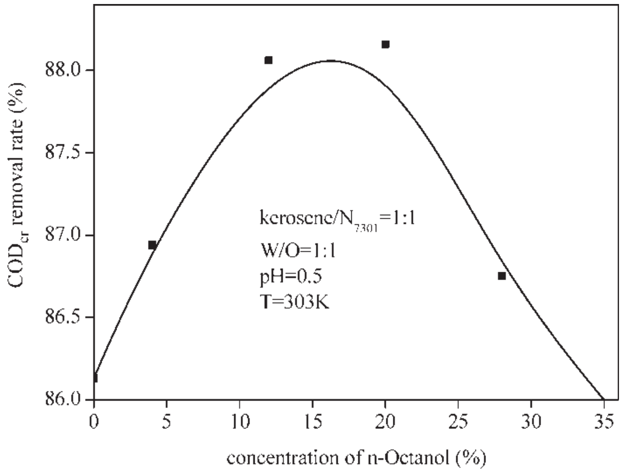


Figure 10. The effect of n-Octanol on the COD_{cr} removal rate.

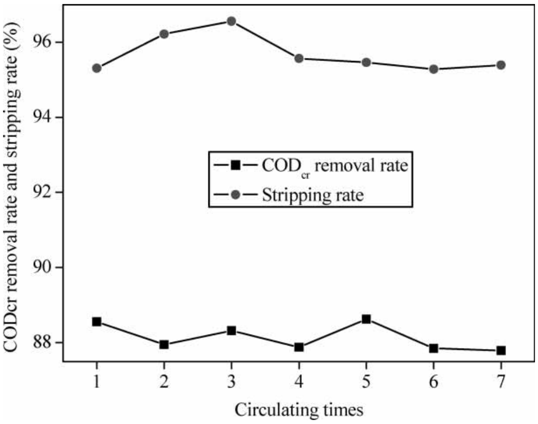


Figure 11. The effect of circulating times on the COD$_{cr}$ removal rate.

stripping rate almost keep constant even the regenerated extractant is used 7 times, which greatly reduces the operation cost and makes the industrial application feasible (Figures 10 and 11).

CONCLUSIONS

Chemical extraction and stripping for the treatment of fumaric acid wastewater was investigated. And the following results were obtained:

1) The extraction efficiency depends on the extractant concentration, the initial pH, the volume ratio of water to oil (W/O), and the extraction temperature. The optimum condition was that kerosene/N_{7301}/n-octanol of 2:2:1, pH of 0.5, W/O of 1:1, and temperature of 303 K.
2) The overall COD$_{cr}$ removal rate could reach 88.16% and extraction efficiency of fumaric acid was 70.67%.
3) The stripping solution used was 2% NaOH and the stripping rate could reach 100%. The regenerated extractant could be cycled about seven times without decreasing significant extraction efficiency and stripping rate.
4) Adding n-octanol in the organic phase prevents the appearance of the second organic phase, which not only makes the extraction behavior simple but also makes the process easier to do.
5) And fumaric acid was obtained by adjusting the pH of the bifumarate solution. After extraction, the fumaric acid wastewater can be further treated by oxidation or biodegradation to environmentally acceptable levels.

NOMENCLATURE

K	equilibrium constant
D	extraction distribution ratio of fumaric acid
H_2A	fumaric acid
b	proportionality coefficient
K_1, K_2	constants
K_{a1}, K_{a2}	dissociation constants of fumaric acid
COD_{cr}	chemical oxygen demanded
N_{7301}	amine extractant

Subscripts

f	feed phase
r	raffinate phase

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