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Study on Riboflavin Recovery from Wastewater by a Batch Foam Separation Process

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Abstract: A batch recovery of riboflavin via foam separation from industrial simulative wastewater was studied using a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB). The experimental parameters examined were the surfactant concentration, air flow rate, pH, and foam height. Under optimal operating conditions obtained through an orthogonal experiment, the maximum enrichment ratio of 48.7 was achieved for riboflavin along with 99.3% removal efficiency. The optimal operating conditions had the concentration of CTAB at 0.3 g/L, air flow rate at 400 ml/min, foam height at 90 cm, and pH at 12. Therefore foam separation proved to be an effective method to recover the riboflavin in terms of the good enrichment and removal efficiency.

Keywords: CTAB, enrichment ratio, foam separation, riboflavin, wastewater treatment

INTRODUCTION

Riboflavin (or Vitamin B2) is essential for growth and the production of red cells, antibodies, and cells. It has been widely used in medicine, food, and feed industries (1–3). There are many reports on fermentation and separation of the riboflavin (4–7). The fermentation wastewater has a high-level relative content of the riboflavin which is

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characterized by its deep color. This is then discharged into water bodies, causing serious environmental pollution (8). There are few studies however, on technologies of the riboflavin fermentation wastewater treatment.

Foam separation is a simple and low-cost method, belonging to the adsorptive bubble separation techniques (9). It has been extensively studied for the purpose of removing pollutants such as heavy metal ions and proteins from water by adding surfactant (10–13). This paper investigates foam separation of riboflavin from industrial simulation wastewater solution. Our aim is to assess the feasibility of foam separation as a technique for the recovery and concentration of riboflavin from this waste solution. The concentration of riboflavin could then be further processed as a food ingredient or health supplement, and the resulting clarified wastewater becomes lower in chemical oxygen demand, giving environment benefits.

Foam separation however, cannot be used directly to recover riboflavin because riboflavin solution alone cannot produce foam when aerated. In foam separation processes, the main role is played by a foam producing agent, i.e., surfactant and a collecting agent. The former enables stable formation of foam by bubbling aqueous solutions; while the latter collects the target solutes absorbed on the surface of the foam. During a rise of foam through a drainage section of the column, the interstitial water between foam is drained out by gravity, and solutes are concentrated in the foamate phase along with surfactant. There are a number of reports concerning the combination of such collecting agents and target solutes under various conditions (14–17). In this paper, a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), was added to a riboflavin solution making it possible to foam. The surfactant has a strong interaction with riboflavin which can be transformed into enolate with negative electric charge in alkaline media. When CTAB coexists with the riboflavin anion, the positive charge head of CTAB ($R_1R_2R_3$-NH^+Br) will attract the riboflavin anion solute close to itself by electrostatic forces and then form a complex. So this reagent would be an excellent collector and also performs as a surfactant (Fig. 1). Using this multifunctional reagent would simplify the separation process.

There have been many studies on foam separation including the effect of operating mode (16,18) and foam properties (14,15). Despite this large number of publications, the use of foam separation for the recovery of riboflavin has not been reported. In this study, we designed and built a single batch foam fractionator and the effects of operating factors (surfactant concentration, air flow rate, solution pH, and foam height) were investigated in the batch operation.

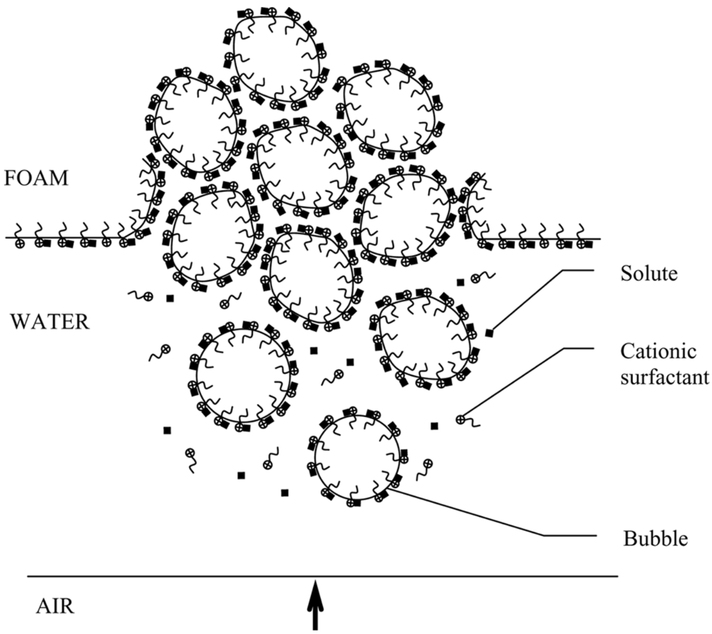

Figure 1. Schematic diagram for the function of the cationic surfactant as a solute collector.

MATERIALS AND METHODS

Materials

The materials used included riboflavin with a purity of 99% (obtained from Tianjin Taihe pharmacy Ltd.), a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB) of analytical grade with a purity of 90% (obtained from Tianjin Chemical Reagents Co. Ltd.), and the chemicals hydrochloric acid and sodium hydroxide (obtained from Tianjin Yingdaxigui Ltd.). All of the above materials were used without further purification. Distilled water was used in all experiments.

Equipment

Figure 2 is a schematic diagram of a batch mode foam separation device. The main column was 100 cm high with an inner diameter of 5 cm and manufactured from transparent polymethyl methacrylate, with a lacunaris stone gas sparger with a height of 10 mm, and a diameter of 15 mm, mounted at the

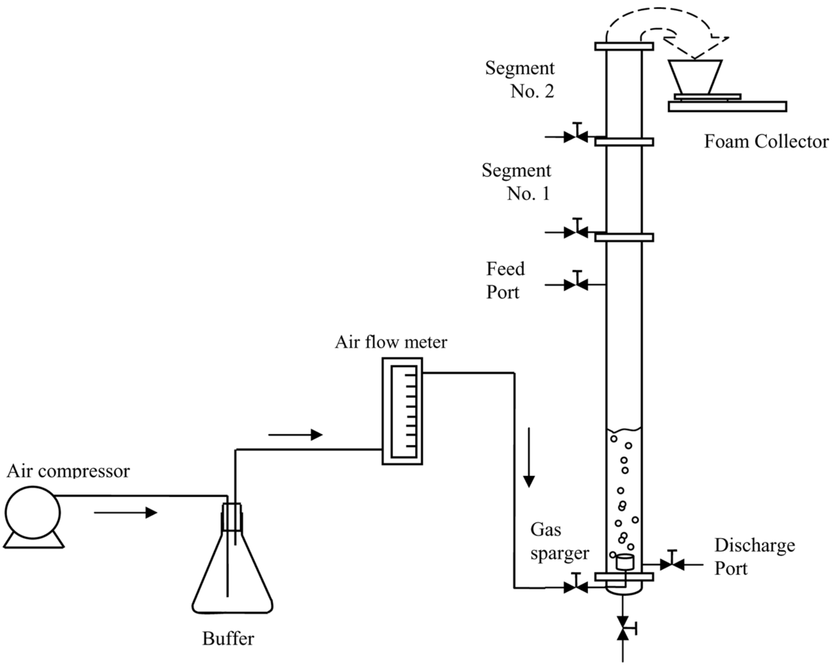

Figure 2. Schematic diagram of a batch mode foam separation apparatus.

bottom of the column. There are also two column sections with a height of 20 cm each to adjust the total height of the column in some experiments.

A electrical magnetic air compressor (AC0-318, Guangdong Hailea GROUP Co. Ltd. China) and rotameter (LZB-3WB, 60–600 mL/min, Wuhuan instrument factory, Tianjin, China) were used to control the flow of compressed air, which was passed through the sparger at the bottom of the column, causing bubbles to form in the liquid. The resultant foam then travelled up the column. A collection spout, fitted over the top of the column, enabled the flow of foam to be directed to a collection vessel. pH measurements were made using a pH meter (pHS-25, Shanghai Jingke industrial Co., Ltd., China).

METHODS

The foaming process column was operated in a batch mode at room temperature. Liquid wastewater was loaded into the column at the beginning of each experiment to a typical height of 50 cm from the bottom of the column and foam was then generated by adjusting the flow rate of air.

The experiments were run until foam ceased to exit the outlet. At the end of the experiments, the riboflavin concentration in the collapsed foam solution and the residual liquid in the column were measured with UV/vis 721 spectrophotometry from Shanghai Jingke industrial Co., Ltd. at 444 nm (19). A good linear relationship in the range from 2 mg/L to 20 mg/L L of riboflavin was found. A standard curve equation was $y = 0.0247 + 0.0232x$, $R = 0.9999$. The critical micelle concentration, CMC, of the surfactant was calculated from the concentration where the specific surface tension versus the surfactant concentration showed an abrupt change in the slope. The pH was adjusted by the addition of NaOH or HCl.

In this study, according to the wastewater simples collected from Tianjin Hebei Pharmaceutical Factory, the typical riboflavin content of the simulation industrial wastewater was approximately 10 mg/L.

The foaming results obtained relate to:

1. effect of initial surfactant concentration range between 0.1 g/L and 0.3 g/L,
2. effect of air flow rate between 300 mL/min and 600 mL/min,
3. effect of pH between 5 and 11,
4. effect of foam height between 50 cm and 90 cm, and
5. performance in orthogonal test approach.

Calculations

Performance indicators used for the foaming process are the enrichment ratio (E) and the removal efficiency (R).

$$E = \frac{C_f}{C_i} \tag{1}$$

$$R(\%) = \frac{C_i V_i - C_r V_r}{C_i V_i} \times 100 \tag{2}$$

Where C_i and C_r are the riboflavin concentrations (g/L) in the initial and residual solution simples, respectively, and C_f is the riboflavin concentration in the collapsed foam solution (g/L). V_i and V_r are the volume (L) of the initial and residual solutions, respectively.

RESULTS AND DISCUSSION

Effect of Initial Surfactant (CTAB) Concentration

The effect of the initial surfactant (CTAB) concentration was investigated by running trials with simulation wastewater solutions. It was found that

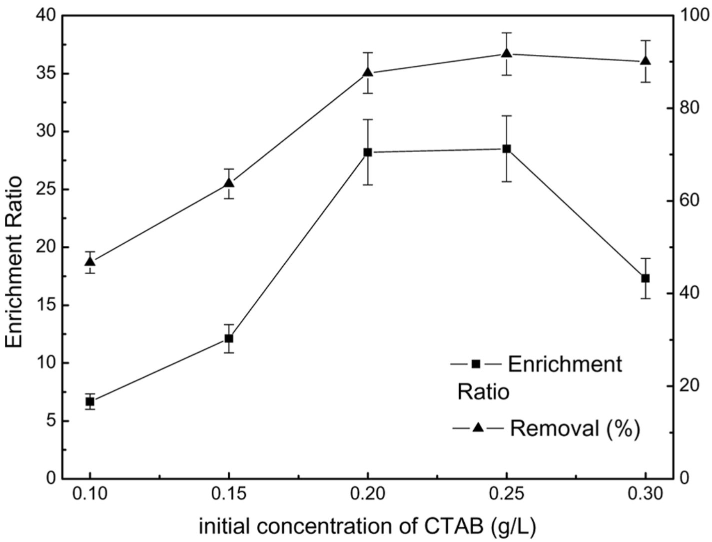

Figure 3. Effect of initial CTAB concentration on the enrichment ratio and removal efficiency. Initial concentration of riboflavin was 10 mg/L; air flow rate, 400 mL/min; foam height, 50 cm; pH, 11.

the surfactant content dissolved into the solution had a significant influence on the performance of foam separation. As shown in Fig. 3, as the surfactant concentration increased, the removal efficiency has increased with it, while the enrichment ratio had first increased to a maximum (slightly lower than 30) before decreased. The CTAB concentration was adjusted stepwise from 0.1 g/L to 0.3 g/L (less than the CMC—0.32 g/L), riboflavin removal efficiency increased from 46.7% to 91.7%, and the enrichment ratio went up from 6.67 (at 0.1 g/L) to 29.5 (at 0.25 g/L), before decreasing to 17.3 at 0.3 g/L (Fig. 3). This can be explained by the following: with the increase of the concentration of the surfactant, more riboflavin molecules can be connected to the surfactant polar "heads" with a positive charge through ionic bonding. However, the concentration of the surfactant cannot be infinitely enhanced. Once all the solute molecules in the bulk liquid are connected to the surfactant, further increase in the surfactant concentration will significantly slow down the rate of drainage of the foam. At the same time, a high level of cationic surfactant content lead to the longer period of total experimental time and the far greater relative losses of the riboflavin, especially in aqueous solution (20). Therefore, the enrichment ratio reduced at the surfactant concentration of 0.3 g/L which is very close to the CMC value. On the other hand, the addition of the surfactant increased the amount of the foam generated and enhanced the volume of the foamate, the collapsed foam product. This is why the removal efficiency just had a slight decline at this concentration.

As shown from the experimental consequence, to realize high enrichment ratio and removal efficiency values, foam separation should be used at the surfactant concentration of 0.25 g/L. These observations didn't agree with the previous studies (21,22), as they show directly the enrichment of surface-active substances, such as SDS and proteins.

Effect of Solution pH

Wastewater solutions at different pH were prepared from the same initial sample using hydrochloric acid and sodium hydroxide. For this experiment a range of pH between 5 and 12 was tested. The test involved loading a liquid solution to a height in the column of 50 cm, then setting an air flow rate of 400 mL/min. The foam height was 50 cm. The results presented in Fig. 4 indicated that as the pH increased, both the enrichment ratio and the removal increased initially until it reached their maximum values before decreasing slightly. The enrichment ratio increased from 4.26 to 28.3, and the removal efficiency increased from 23.2% to 94.0%. It is clear that

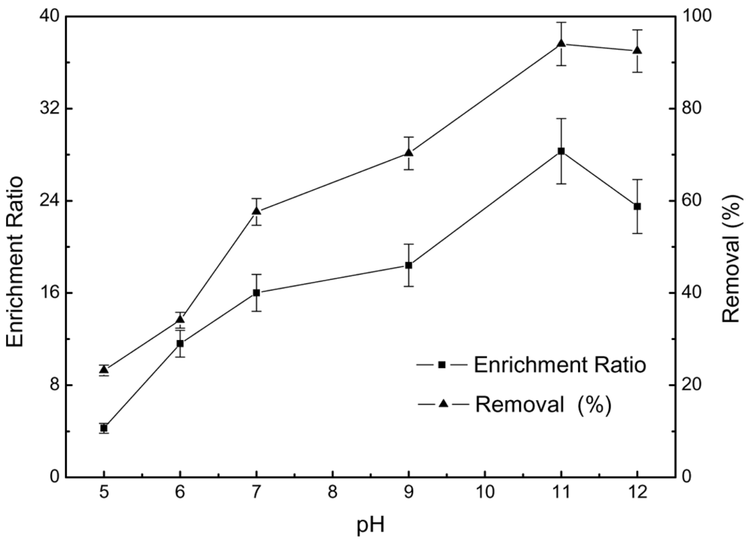

Figure 4. Effect of solution pH on the enrichment ratio and removal efficiency. Initial concentration of riboflavin and CTAB were 10 mg/L and 0.25 g/L, respectively. Air flow rate, 400 mL/min; foam height, 50 cm.

the solution pH had more influence on the removal efficiency than on the enrichment ratio. This is possibly due to the solution pH having a large effect on the riboflavin solubility. Particularly after pH 11, a slight change in the pH value could result in a significant fluctuation of the riboflavin solubility (23). The pK_{a1} and pK_{a2} of the riboflavin are 1.7 and 9.69, respectively. In acidic conditions, riboflavin is neutral. As a result, in alkaline solution, the riboflavin negatively charged moleculars combined better with the cationic surfactant. As pH increased, the solubility of riboflavin increased and it was also easier to form anion solute molecule, which combined with the cationic surfactant, resulting in a better separation performance. But at pH 12 the enrichment ratio and the removal reduced to 25.5 and 92.5%, respectively. There are three possible reasons for the observed decrease. First, the concentration of OH^- in the solution increases as pH increases, thereby OH^- competes with the riboflavin for $R_1R_2R_3\text{-}NH^+Br$. Second, riboflavin is vulnerable to decomposition in a strong alkaline environment (24). Finally, the amount of foam generated from the surfactant has been associated with changes in the surfaces tension when pH has been varied (25).

Effect of Air Flow Rate

Previous research has shown that an increased flow rate of gas increases the rate of foam formation as well as foam bubble size and foam residence time (26). A series of trials using the same solutions were run at different air flow rate between 300 mL/min and 600 mL/min, with the solution pH fixed at 11, in order to verify the effect of the air flow rate on the foaming performance.

The results are presented in Fig. 5. It was found that the foamate volume increased exponentially with increasing air flow rate, while the riboflavin removal increased slightly and the riboflavin enrichment ratio decreased.

These observations agree with those of Brown et al. (27). It is thought that with the rise of air flow rates that more bulk liquid could be transported into the foam and adsorbed onto the bubble surfaces, and so the bubble production would increase. The lower residual time of bubbles in the foam phase and the lower drainage velocity of the interstitial water caused by gravity, had resulted in a higher content of water in foamate. Also at high air flow rate, bubbles moved up rapidly to the top of the column due to the higher liquid entrainment rate. Thus the foamate volume increased rapidly from 52 mL to 156 mL. Similarly, a high air flow rate flux increased the interfacial area for the target substance adsorption and hence the amount of the target entering the foam, so the removal

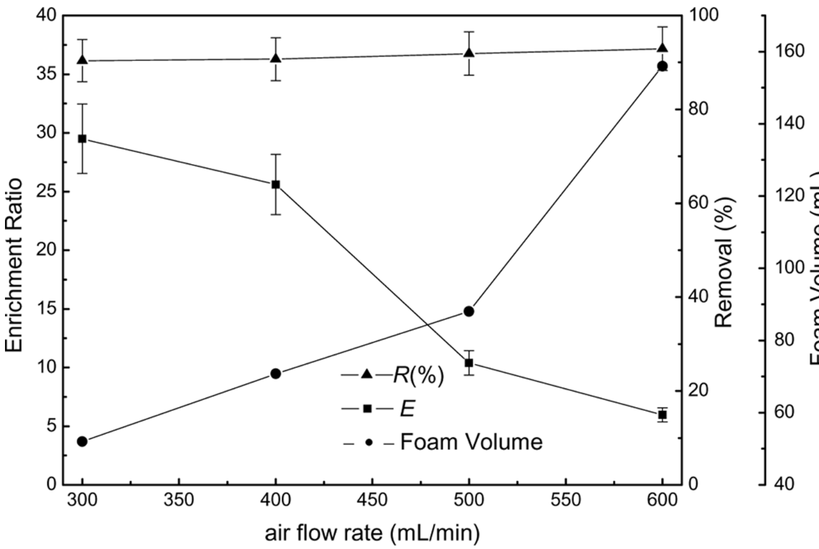

Figure 5. Effect of air flow rate on separation efficiency. Initial concentration of riboflavin and CTAB were 10 mg/L and 0.25 g/L, respectively. Foam height, 50 cm; pH, 11.

fraction increased slightly with the air flow rate. It should be noted, that there could be a trade-off relationship between the removal of riboflavin and the enrichment ratio at a higher flow rate. By considering the comprehensive variables of the enrichment ratio, the removal efficiency and the experiment time, the more appropriate flow rate of 400 mL/min was used.

Effect of Foam Height

In this study the effect of the foam height on the removal efficiency and the enrichment ratio of riboflavin were not investigated as an individual factor. Due to the equipment restrictions, only three height levels of the foam (50 cm, 70 cm, and 90 cm) were used and so the comprehensive study of its influence would be observed in orthogonal experiments in the next section. There are a large number of publications which indicate that as the foam height increased, a longer foam residence time which allowed for more drainage of the liquid in the films resulted in a dryer foam and higher enrichment ratio. With the increase of foam height, the removal fraction decreased because of the increased rate of foam collapse which resulted from the drainage (26,28). Moreover the maximum height that the foam layer could reach depended to some extant upon the amount of the surfactant and the air flow rate.

Orthogonal Experiments

An orthogonal test is a mathematical method to carry out multifactor experiments. It is based on the principium of statistics and orthogonal theory (29). In this paper an orthogonal $L_9(3)^4$ test design in the batch mode was used for optimization of the removal conditions. Nine experiments were performed at surfactant concentration of 0.2 g/L, 0.25 g/L, and 0.3 g/L, solution pH of 10, 11, and 12, air flow rate of 300 mL/min, 400 mL/min, and 500 mL/min, and a foam height of 50 cm, 70 cm, and 90 cm on the basis of single-factor experiments. Table 1 shows the experimental conditions for the riboflavin enrichment and removal. Since various parameters potentially affect the foam separation performance, the optimization of the experimental conditions is a critical step in the development of a treatment method. In fact, the surfactant concentration, solution pH, air flow rate, and foam height are considered to be the most important factors.

The total evaluation index was used for analysis by the statistical method. The results of orthogonal experiments and extreme difference analysis are presented in Table 2. The analysis of variance was performed by statistical software SPSS 12.0 and the result was listed in Table 2. The result indicated that the maximum removal efficiency of riboflavin was 96.6%. However, we cannot select the best removal conditions only based on these outcomes in Table 2, and a further orthogonal analysis was warranted. Thus, the *K* and R values were calculated and listed in Table 2. As seen from Table 2, we can find that the influence to the removal efficiency decreases in the order: $C > A > B > D$ according to the R_R values. The pH of the solution was found to be the most important determinant of the removal efficiency. Compared to the removal efficiency, the most

Table 1. Factors and levels for orthogonal test

Variable	Level 1	Level 2	Level 3
A, surfactant concentration (g/L)	0.2	0.25	0.3
B, air flow rate (mL/min)	300	400	500
C, pH of the solution	10	11	12
D, foam height (cm)	50	70	90

Table 2. Analysis of $L_9(3)^4$ tests results

No.	*A*, surfactant concentration (g/L)	*B*, air flow rate (mL/min)	*C*, pH of the solution	*D*, foam height (cm)	*R* (%)	*E*
1	0.2	300	10	50	82.4	32.7
2	0.2	400	11	70	93.7	31.3
3	0.2	500	12	90	96.6	18.9
4	0.25	300	11	90	89.3	91.9
5	0.25	400	12	50	94.7	22.3
6	0.25	500	10	70	70.2	7.09
7	0.3	300	12	70	95.5	29.9
8	0.3	400	10	90	92.3	49.5
9	0.3	500	11	50	94.6	10.3
K_{1R}	272.7	267.2	244.8	271.7		
K_{2R}	254.2	280.7	277.6	259.3		
K_{3R}	282.4	261.3	286.8	278.2		
K_{1E}	82.9	154.5	89.29	65.3		
K_{2E}	121.29	103.1	133.5	68.29		
K_{3E}	89.7	36.29	71.1	160.3		
R_R	9.40	6.43	14.0	6.27		
R_E	12.8	39.4	20.8	31.7		

Subscript *R* refers to removal efficiency; Subscript *E* refers to enrichment ratio; R refers to the result of extreme analysis.

important determinant of the enrichment ratio was the air flow rate and the influence decreased in the order: B > D > C > A according to the R_E values. In other words, the maximum value of the enrichment ratio of 48.7 along with the removal efficiency of 99.3% was obtained when the surfactant concentration, solution pH, air flow rate and foam height were 0.3 g/L, 12,400 mL/min, and 90 cm, respectively.

CONCLUSIONS

Foam separation is effective in the recovery and removal of riboflavin from simulative industrial wastewater solutions; optimal foaming operation will be dependent on the process variables such as initial surfactant concentration, solution pH, air flow rate, and foam height. It was found that with optimal conditions, it was possible to achieve small volumes of highly enriched foam with approximately 50 times the initial riboflavin concentration and the removal efficiency of 99.3%. An increase in initial surfactant concentration resulted in removal efficiency increase, while the enrichment ratio first increased to a maximum (slightly lower than 30) and then decreased. Changes in pH had a strong effect on the enrichment ratio and the removal efficiency of riboflavin. The enrichment ratio and the removal efficiency increased as pH increased when pH was less than 11. A greater air flow rate could produce a lower enrichment ratio and a slight increase in the removal efficiency. Therefore, raising the surfactant concentration, pH, and air flow rate had a positive impact on foam separation performance. The results presented here for the batch foam separation, are preliminary, and so future work will focus on the wastewater treatment using a continuous process.

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