Ethylbenzene Removal by Froth Flotation Under Conditions of Middle-Phase Microemulsion Formation II: Effects of Air Flow Rate, Oil-to-Water Ratio, and Equilibration Time

Ummarawadee Yanatatsaneejit[a]; Sumaeth Chavadej[a]; Pramoch Rangsunvigit[a]; John F. Scamehorn[b]

[a] The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand [b] Institute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma, USA

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Ummarawadee Yanatatsaneejit, Sumaeth Chavadej, and Pramoch Rangsunvigit

The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

John F. Scamehorn

Institute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma, USA

Abstract: Dihexyl sulfosuccinate (aerosol MA or AMA) was used to prepare microemulsion solutions in a study of the froth flotation process in batch mode to remove emulsified ethylbenzene from water. Oil removal, surfactant removal, and enrichment ratio were used to evaluate the performance of froth flotation. In this study, the effects of air flow rate, oil-to-water ratio, and equilibration time were investigated. A very high air flow rate was found to create more turbulence in the froth flotation column, resulting in low oil removal. As the oil-to-water ratio decreases, the enrichment ratio increases, whereas the oil removal slightly decreases. The froth flotation column with a feed solution in which the oil and water had been allowed to equilibrate was found to yield much higher ethylbenzene removal than that with a nonequilibrium feed solution. When the feed solution was agitated for 40 minutes to induce a state closer to equilibrium than with no mixing, the ethylbenzene removal was nearly as high as that with the equilibrium feed solution.

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INTRODUCTION

Froth flotation can be utilized in a variety of separation processes (1–5). Froth flotation is widely used in the area of mineral processing (6). However, it can also be used for wastewater treatment (7) as is studied here. In previous work (8), it was found experimentally that the highest removal of emulsified ortho-dichlorobenzene corresponded to the formation of a Winsor Type III microemulsion in the oil-water system in which an excess oil phase and excess water phase are in equilibrium with a "middle-phase", which is a microemulsion containing almost all the system surfactant. Chavadej et al. (9) concluded that most of the removed oil (ortho-dichlorobenzene) came from the excess oil phase rather than from the middle phase in the Winsor Type III microemulsion. In a continuation of our work, the relationship of the ultra-low interfacial tension characteristic of Winsor Type III microemulsions and the oil removal efficiency in a flotation column was studied and presented in Part I of this series of papers (10) with ethylbenzene as the oil. It was revealed that the ultra-low interfacial tension was not a sole factor causing the high effectiveness of froth flotation; foam formation and foam stability were also shown to be important parameters. The importance of foam stability was also observed by Carre et al. (12).

In many previous studies of froth flotation to remove emulsified oil from water, an initial oil-to-water ratio of 1:1 was used (9, 13, 14). This is because microemulsion phase studies are traditionally carried out at this initial oil-to-water ratio. However, wastewater with emulsified oil typically has lower oil-to-water ratios (6, 15). Therefore, the effect of initial oil-to-water ratio is investigated in this study. Previous studies from our group have correlated froth flotation efficiency to equilibrium phase behavior of oil/water systems (8–10, 13). However, equilibration of microemulsion systems can be very slow, in extreme cases taking months. Since actual wastewaters will not have time to equilibrate, the effect of equilibration time is investigated here, as well as the effect of agitation during equilibration. Finally, the effect of air flow rate is discussed in this paper.

EXPERIMENTAL SECTION

Materials

Ethylbenzene with 98% purity from Fluka Company was used as emulsified oil in this work. Dihexyl sulfosuccinate (aerosol MA or AMA) with 80% purity from CYTEX Corporation, Los Angeles, CA was used as surfactant here. Analytical grade sodium chloride (NaCl) was obtained from Aldrich Chemical Company, Inc. Deionized water was used in all experiments. All chemicals were used as received.

Methodology

The surfactant concentration and salinity are expressed as percent by weight based on the aqueous solution in this study. Figure 1 depicts the schematic diagram of the experimental froth flotation system used in this study. The system consisted of a glass cylindrical column with 5-cm inside diameter and 120-cm height and operated in a batch mode. Filtered air was introduced into the bottom of the column with various flow rates through a sintered glass disk, having pore size diameters about $16-40\,\mu m$.

Microemulsions formed with 0.3 wt% AMA and 3 wt% NaCl was selected for froth flotation experiments since these systems can exhibit low oil/water interfacial tensions (IFT) and form a Winsor Type III microemulsion (10). Interfacial tension was measured with a spinning drop tensiometer (Krüss, GmbH model). To study effect of equilibration time, different systems having three equilibration times were prepared for flotation experiments. For a nonequilibrium system, 750 mL of sample solution with various oil-to-water ratios was immediately transferred to the froth flotation column after mixing. For an "induced" equilibrium system, another 750 mL of sample solution with an 1:1 of oil-to-water ratio was agitated by using a mechanical stirrer at 2000 rpm for 40 minutes using a stirrer at 800 rpm before being introduced to the flotation column. For the equilibrium system, 750 mL of sample solution with an oil-to-water ratio of 1:1 was kept in an incubator at 30°C for 1
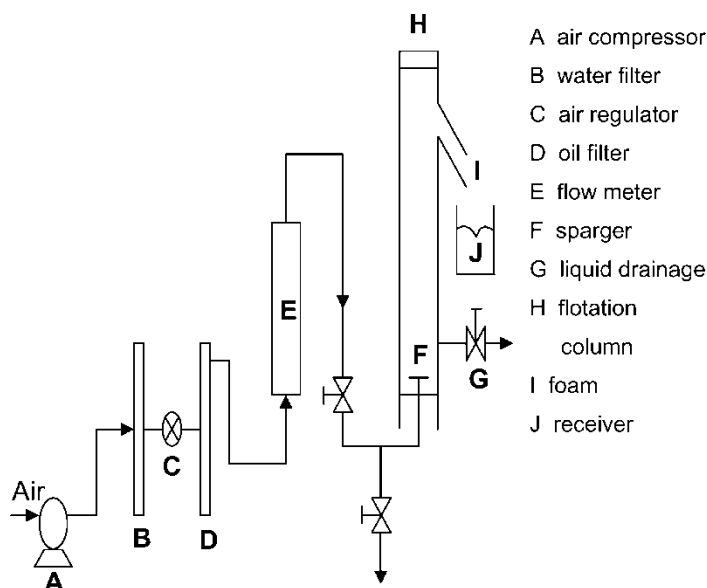

A air compressor
B water filter
C air regulator
D oil filter
E flow meter
F sparger
G liquid drainage
H flotation column
I foam
J receiver

Figure 1. Schematic diagram of the froth flotation system.

month, which was shown to be long enough to reach equilibrium before being used in the flotation experiments. After the solution was transferred into the column, air was introduced to the column at various flow rates. The foam overflown from the column was collected over different time intervals and each froth was broken to analyze concentrations of ethylbenzene in the collapsed froth. Moreover, the solution remaining in the column was collected at the same interval of time for analysis of ethylbenzene and AMA concentrations. The experiments were stopped when no foam was overflowing from the column. To analyze the concentration of ethylbenzene, a GC-Headspace (Perkin Elmer) was used whereas the titration method, ASTM D1681-92, 1997, was employed to analyze the concentration of surfactant.

To measure foamability and foam stability, 250 mL of sample containing desired amounts of ethylbenzene and AMA was transferred to the same column used in the froth flotation experiment. The filtered air was introduced through the solution at flow rates of 100, 130, 150, and 200 mL/min until the foam height in the column was constant. The time required for the foam volume to collapse by half was recorded. For this experiment, the air flow rate could not exceed 200 mL/min because foam overflowed from the column. All froth flotation as well as foamability and foam stability experiments were carried out at room temperature (25–27°C).

RESULTS AND DISCUSSION

In this study, wt% is based upon the aqueous system consisting of water, salt, and surfactant (not including oil). In this paper, IFT is referred to the interfacial tension between excess oil and excess water phases. Foamability is defined as a ratio of maximum foam height to initial solution height, whereas foam stability ($t_{1/2}$) is the time required for the foam volume to collapse to half of the maximum height.

Effect of Oil-to-Water Ratio on IFT

The phase behavior of the ethylbenzene system having different AMA and NaCl concentrations was presented in Part I of this series (10). Therefore, only the effect of oil-to-water ratio upon phase behavior is discussed here. The system having a minimum IFT (at optimum salinity) at an oil-to-water ratio of 1:1 was selected to determine the effect of oil-to-water ratio on IFT. As shown in Fig. 2, IFT is in the same order of magnitude when the oil-to-water ratio increases from 1:19 to 1:1. This finding is beneficial to froth flotation operation, since oil-to-water ratios in industrial wastewaters are often much less than those in microemulsion phase behavior experiments where an oil-to-water ratio is traditionally set at unity.
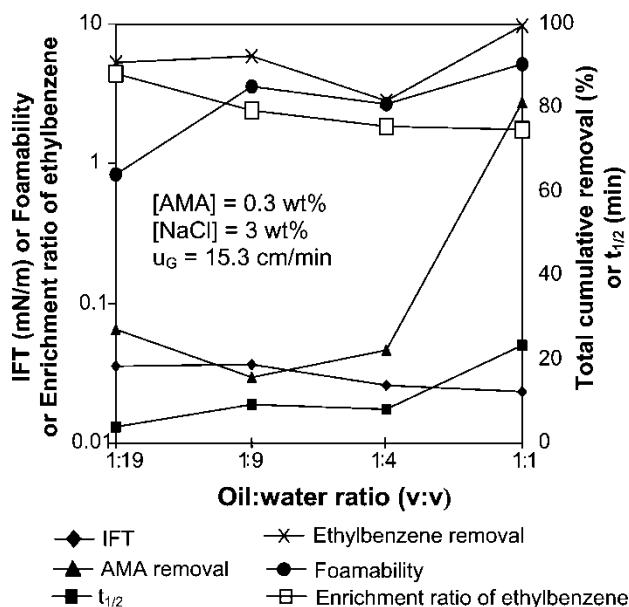
Figure 2. Effect of oil-to-water on process parameters.

Foam Formation and Foam Stability

From Fig. 2, both foamability and foam stability increase slightly with increasing ratio of oil-to-water. At a low oil-to-water ratio, the viscosity of the total solution is also low, resulting in a higher drainage rate of water from foam lamellae. Therefore, foam rupture occurs easily. In case of a high oil-to-water ratio, the high oil content in solution leads to high resistance to oil movement within the restricted volume of the Plateau borders. Since the oil drops in the Plateau borders drain slower than the surrounding aqueous phase, they get trapped in the Plateau borders due to high viscosity. The confined structure of the Plateau borders basically squeezes the oil drops into the close-packed configuration, so the area available for the flow of the water out of the Plateau borders decreases. Foam drainage is slowed down, resulting in a higher foam stability when oil-to-water ratio increases (11). Air flow rate is one of the vital parameters in dispersed-air flotation systems including froth flotation. In this paper, superficial velocity (u_G), which is a volumetric air flow rate divided by the cross-sectional area of the flotation column, is reported instead of a volumetric air flow rate. From Fig. 3, as expected, increasing u_G increases foam formation monotonically because there are more bubbles passing through the solution. Zouboulis, Lazaridis, and Zamboulis (5) also observed that a higher air flow rate resulted in a greater amount of foam generated. Both ethylbenzene and AMA removals will be discussed in detail in the next section.
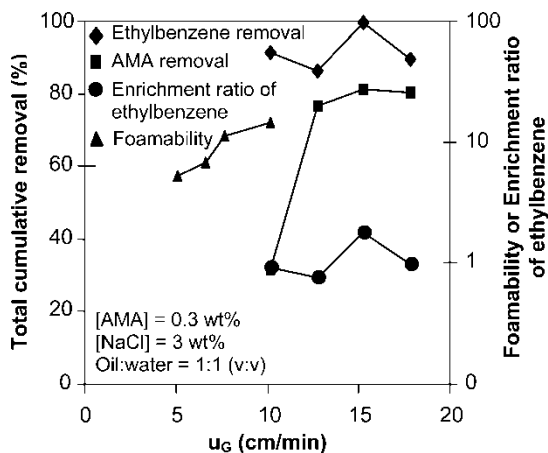
Figure 3. Effect of superficial air velocity on process parameters.

Froth Flotation Performance

Concentrations of 0.3 wt% AMA and 3 wt% NaCl were selected for froth flotation experiments since the system offers an ultra-low interfacial tension (0.052 mN/m) at a low AMA concentration (10).

Removal of Ethylbenzene and Surfactant

The effects of oil-to-water ratio on IFT, total cumulative ethylbenzene removal, total cumulative AMA removal, enrichment ratio of ethylbenzene, foamability, and foam stability are shown in Fig. 2. The total cumulative ethylbenzene removal (as a percentage) exhibits a minimum with increasing oil-to-water ratio. The percent removal of surfactant also exhibits a minimum at a certain oil-to-water ratio (1:9), although a different ratio (1:4) from the minimum ethylbenzene removal was observed. The highest enrichment ratio of ethylbenzene corresponds to the lowest oil-to-water ratio. This is because the solution viscosity increases with increasing oil-to-water ratio, leading to lower water drainage rate from foam lamellae. The foamability and foam stability monotonically increase and IFT monotonically decreases with increasing oil-to-water ratio. There is a substantial increase in ethylbenzene removal, AMA removal, and foamability as oil-to-water ratio increases from 1:4 to 1:1. These results are rather surprising in that much more total oil is removed as oil-to-water ratio increases as the fraction removed even increases. This is associated with substantially increasing AMA removal, which is caused by substantially increasing foamability and modestly decreasing IFT.

Figure 3 shows the effects of u_G on total cumulative ethylbenzene removal, total cumulative AMA removal, enrichment ratio of ethylbenzene, and foamability. The total cumulative ethylbenzene removal is not much affected by u_G. An increase in u_G leads to more bubbles passing through the solution (16), which would tend to increase oil removal. However, a very high u_G affects the flow pattern in the solution, and the circulation velocity induced by the bubble swarm rising through the column is responsible for the turbulence at the froth/collection zone interface (16), resulting in ethylbenzene adsorbed in the froth being partly entrained back into the solution. These two contradictory effects approximately cancel each other, resulting in little effect of u_G on oil removal. Unlike ethylbenzene removal, u_G causes an increase in AMA removal, especially in the range of u_G from 10.2 to 12.7 cm/min. However, AMA removal seems to reach a plateau when u_G is greater than 12.7 cm/min. This is because some froth is dissolved back into the solution because of the turbulent flow pattern in the solution at high u_G. The enrichment ratio of ethylbenzene is lower than 1 when u_G is lower than 15.3 cm/min. When enrichment ratio is equal to or less than unity, no separation is achieved: i.e., the oil is not enriched in the collapsed foam relative to the solution.

Since equilibration in microemulsion systems can be very slow in some cases (months), and much shorter oil/water equilibration times are practical in actual wastewater treatment systems, we have investigated the effect of contact or equilibration time once the oil, water, and surfactant are mixed together. Three cases are considered: the nonequilibrium system where the solution is immediately transferred to the flotation column after mixing, the induced equilibrium system where the solution is intensely agitated after mixing, and equilibrium systems that are equilibrated for a month. Table 1 shows IFT, total cumulative ethylbenzene removal, total cumulative AMA removal, enrichment ratio of ethylbenzene, and foam flow rate for these three systems. An aqueous solution containing 0.3 wt% AMA and 3 wt% NaCl was selected to form microemulsions with ethylbenzene at an oil-to-water ratio of 1:1 in this study because it provides an ultra-low interfacial

Table 1. Effect of equilibration conditions on process parameters

System	IFT (mN/m)	Total cumulative ethylbenzene removal (%)	Total cumulative AMA removal (%)	Enrichment ratio of ethylbenzene	Foam flow rate (mL/min)
Non-equilibrium	2.388	40.59	82.94	1.76	1.34
Induced equilibrium	0.674	87.79	64.39	1.11	2.28
Equilibrium	0.052	99.29	63.18	1.18	3.59

tension with a middle phase microemulsion (10). As shown in Table 1, the highest ethylbenzene removal is achieved with the equilibrium system, associated with the highest foam flow rate and lower IFT. It is interesting to note that the induced equilibrium system gave an ethylbenzene removal much higher than the nonequilibrium system, but lower than the equilibrium system. The results indicate that a short period of time (40 minutes in this study) of vigorous agitation is long enough to move the system substantially towards its equilibrium state. Unlike ethylbenzene removal, AMA removal in the nonequilibrium system is much higher than those of the other two systems. This is because in both the induced equilibrium and equilibrium systems, a large fraction of surfactant is present in a bicontinuous structure in the middle phase compared to the nonequilibrium system. The surfactant molecules in the bicontinuous structure are not well transferred to the foam, so the surfactant removal in overhead froth is much lower for equilibrium than the nonequilibrium system. In addition, a large fraction of surfactant in bicontinuous structures in both induced equilibrium and equilibrium systems helps to retard the water drainage rate from foam lamellae, resulting in lower enrichment ratios of ethylbenzene. It is somewhat surprising that lower AMA removal corresponds to higher oil removal, implying that as long as enough surfactant is being removed to generate sufficient foam, decreasing the IFT can improve oil removal despite lower surfactant removal.

Dynamics of Flotation

Dynamic froth flotation results are shown in Figs. 4–8. The dynamic removal of ethylbenzene and AMA as a function of oil-to-water ratio are shown in Figs. 4 and 5, respectively. As shown in Fig. 4, ethylbenzene removal is not a monotonic function of oil-to-water ratio with the order changing with time. Despite a lack of systematic variation in ethylbenzene removal with oil-to-water ratio, this variable can have a large influence. For example, at 90 minutes, ethylbenzene removal arises from 55.71% to 91.14% as the oil-to-water ratio varies from 1:4 to 1:1. From Fig. 5, the 1:1 oil-to-water ratio yields a substantially higher AMA removal fraction than lower ratios with the 1:4 to 1:19 ratios not showing a systematic trend. The lack of a clear correlation between AMA removal and ethylbenzene removal as previously noted is confirmed in these dynamic studies.

From Figs. 6 and 7, while superficial air velocity can have a substantial effect on both ethylbenzene and AMA removal, there is a lack of systematic trends as u_G increases.

For the observation of the effect of the equilibration condition on dynamic ethylbenzene removal (Fig. 8), the nonequilibrium system has a much lower ethylbenzene removal as compared to the equilibrium and induced-equilibrium systems, which showed similar ethylbenzene removal
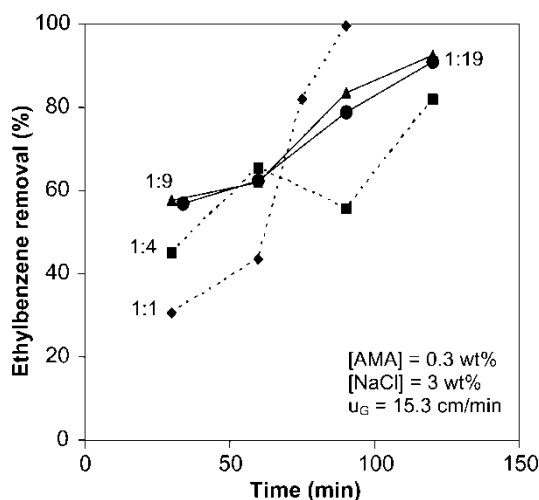
Figure 4. Dynamic removal efficiency of ethylbenzene at different oil-to-water ratios (1:1, 1:4, 1:9, and 1:19 v:v).

characteristics. Practically, vigorous agitation can move the Winsor Type III microemulsion system toward equilibrium and high oil removal efficiency without the very long equilibration times required in quiescent systems. Clearly, this pre-equilibration step is key to an economic process using the microemulsion approach and deserves further study.
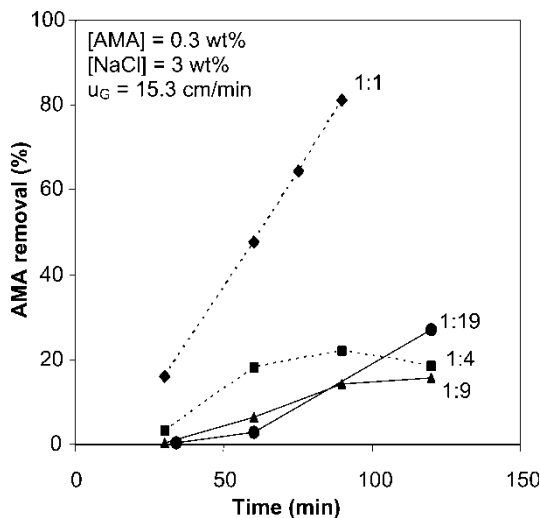

Figure 5. Dynamic removal efficiency of AMA at different oil-to-water ratios (1:1, 1:4, 1:9, and 1:19 v/v).
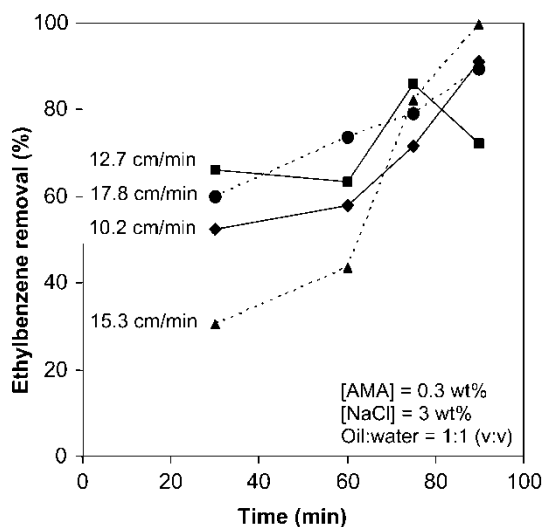
Figure 6. Dynamic removal efficiency of ethylbenzene at different superficial air velocities.

CONCLUSIONS

In this study, the performance of froth flotation is indicated by oil removal, enrichment ratio, and surfactant removal. The effects of operating variables in the flotation column such as superficial velocity, oil-to-water ratio, and
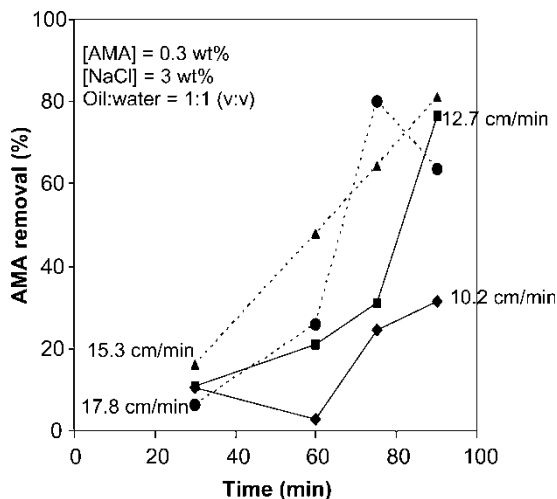

Figure 7. Dynamic removal efficiency of AMA at different superficial air velocities.
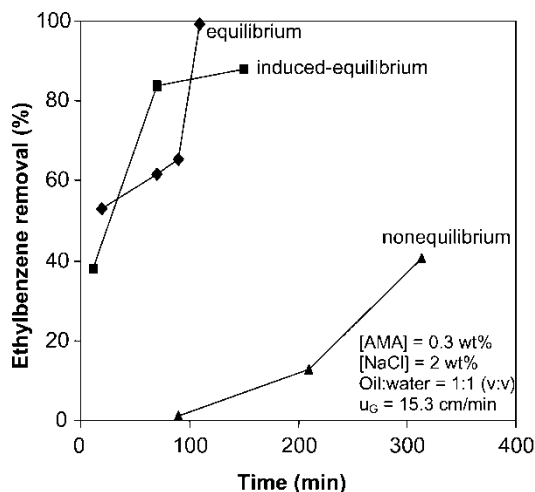
Figure 8. Dynamic removal efficiency of ethylbenzene for different equilibration conditions.

equilibration time were investigated systematically. The superficial velocity used in froth flotation operations should be optimized to obtain the proper balance between the foam production rate and the water back-entrainment rate in order to achieve the maximum performance of froth flotation. As oil-to-water ratio decreases, the enrichment ratio of ethylbenzene increases, but oil removal slightly decreases. In addition, to apply this research to real applications, agitation of the solution for only 40 minutes (induced equilibrium) before being transferred to the froth flotation was found to yield ethylbenzene removal almost as high as an equilibrated system.

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