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Scientific Paper

BATCH FOAM FRACTIONATION OF SURFACTANTS FROM AQUEOUS SOLUTIONS

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Abstract

Surfactants represent a striking problem in water resources. Foam fractionation enables both defoaming and concentration of surfactants. Foam fractionation process is controled by many process and material parameters that are: airflow rate, foam column geometry, feed concentration and added salt. Optimal conditions were tested on a real sample from industry. A mathematical model that describes the changes in concentration of surfactants along the column was developed.

Key words: foam fractionation, surfactants and wastewaters

Introduction

In the last few decades the human society has been facing with an expanding pollution of surface and ground waters. Sources of pollution are numerous, industry being one of most important. Many industries use surfactants as washing agents that may be harmful or even toxic for aquatic organisms. One of the promising methods for removal of surfactants from wastewaters is foam fractionation[1]. In foam fractionation surfactants adsorb on the gas liquid interface generated by bubbling air into dilute surfactant solution and then are carried along the column to its top. Because of the liquid drainage in the film of foam, there is a concentration effect of surfactants towards the column top. When the outlet foam phase collapses, a concentrated solution (foamate) remains. This method is not limited only to surfactants, but it can be used also for concentration of proteins and other surface-active compounds. Furthermore surfactants can act as a collector and bind metal cations into chelates that can be easily removed by foam fractionation. Aziz and Beheir[2] investigated the removal of Cs-134 and Co-60 from radioactive process wastewater using cetyl pyridinium chloride as a collector.

Chiu and Huang[3] showed the effectiveness of foam fractionation for nonionic organic pollutants removal from an aqueous solution.

Numerous studies have been published on transport phenomena in foam fractionation. Most of them are related to proteins[4,5] and only a few models were proposed for systems containing surfactants.[6] The reason is that surfactants are cheaper and display a more complex behavior when they adsorb on the gas liquid interface. These models[4,5] were made only for proteins due to their specific properties that simplified the proposed material balances. Material balances for the investigated systems were solved by numerical calculations and the result did not include the concentration changes in bulk solution.

Lemlich[7] proposed a simple model for foam fractionation of surfactants. He made several assumptions that are valid only for a dilute surfactant solution. The liquid streams (up flow of entrained liquid in foam and the descending drainage liquid) had constant volumetric flow rates in the column. Complex mechanisms of liquid drainage and coalescence were not included. Roustan and Roques[8] proposed an interesting model for the continuous foam fractionation. Their theory of foam fractionation is based on dimensional analysis. The model takes into account the internal reflux due to drainage of liquid. A correlation was presented between specific production of the column and the parameters characterizing the column geometry and operating conditions. Unfortunately the model is valid only for the concentrations near the critical micelle concentration of the surfactant.

Recently a mathematical model[6] for batch foam fractionation has been developed and tested on an aqueous protein solution. The model described the time-varying total protein concentration profiles along the column in both foam and bulk phases.

The aim of the present work was to study and determine the optimal parameters that control the process of batch foam fractionation of surfactants and then apply it to real samples of industrial wastewaters.

Experimental

Experimental setup is shown in Figure 1. It consists of a Plexiglas cylindrical column of 10 cm outer diameter, 3 mm wall thickness and 125 cm effective height. The model surfactant feed solution in distilled water was charged into the column to the height of 28.5 cm above the bottom. The air (pressure from a compressor was maintained by a regulator) was pre-saturated with water and introduced into the column through a sintered glass diffuser No. 2, located at the bottom of the column. The air bubbles produced were of 100-160 µm in diameter. Foam from the column top was collected with a vacuum pump into a receiver in 30 minutes time intervals, frozen immediately in liquid nitrogen to prevent loss of water and thawed to obtain the collapsed foamate samples. The experiments were conducted in temperature range from 20-25 °C.

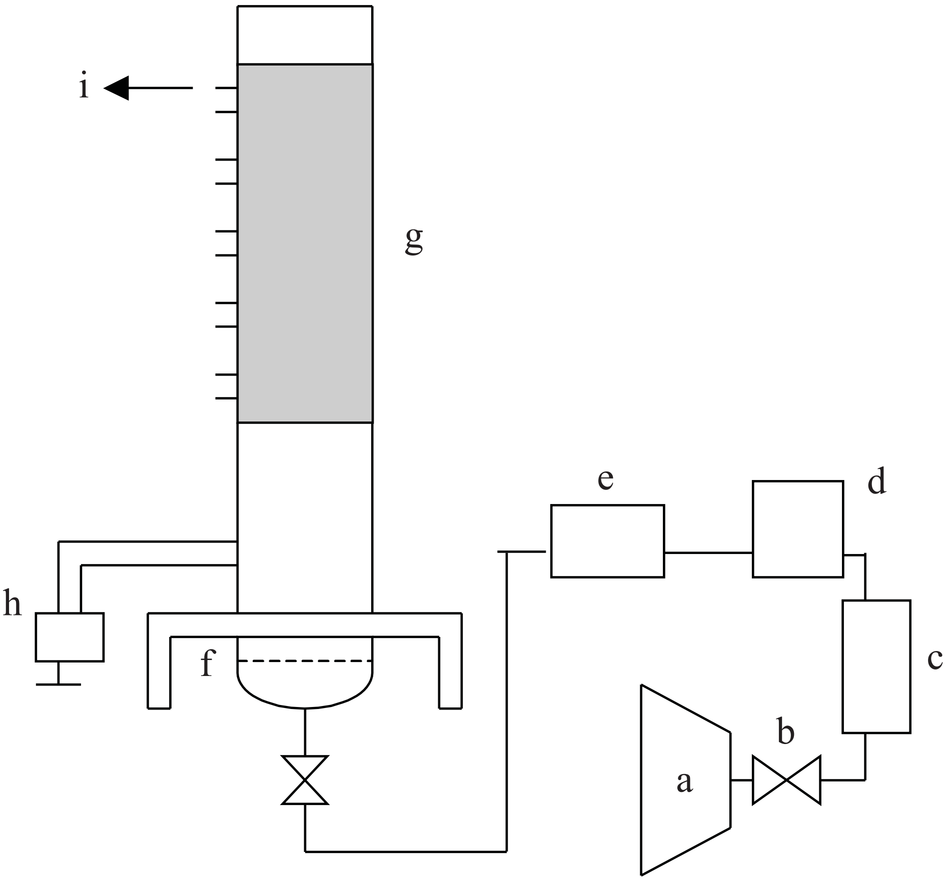

Figure 1. Experimental setup for foam fractionation: a- air compressor; b- needle valve; c- flow meter; d- air suppressor; e- humidifier; f- air sparger; g- column; h- bulk liquid; i- foam withdrawal.

For the determination of process parameters and the process modeling the following technical grade surfactants were used: dodecylbenzene sulfonic acid sodium salt (DBSA, an anionic surfactant, supplied by TEOL), Hyamine 1622 (a cationic surfactant, supplied by SIGMA) and TRITON X-100 (a nonionic surfactant, by FLUKA). Surface tension of the various feed solutions, determined by the ring method, is presented in Table 1.

Table 1. Surface tension of different surfactant solutions at 20 °C.

Surfactant	M (g/mol)	C_0 (M)	γ (mN/m)
DBSA	348.5	8.0×10^{-4}	37.1
Hyamine 1622	448.1	8.0×10^{-4}	49.5
TRITON X-100	624	8.0×10^{-4}	30.8

Industrial samples of wastewaters, containing surfactants, were obtained from various sources: two from cloth dry cleaning companies and one from a car wash station. Their physical properties are given in Table 2.

Table 2. Wastewater parameters for different samples from industry.

PARAMETERS	Usluga*	Labod*	AC**
COD (mg/L)	422	307	156
TOC (mg/L)	99.7	84.5	8.95
Spec. conductivity (mS/cm)	1.306	0.887	0.735
Dry matter (g/L)	1.2	0.768	0.55
Surface tension (mN/m)	35.77	31.9	62.43
C(an. surf.) (mg/l)	11.69	23.37	< 3
C(nonion. surf.) (mg/ml)	32.16	40.5	1

* textile laundry, **car wash service.

Anionic surfactant concentrations in the foamate were analytically determined by two-phase titration method.[9] Nonionic surfactants were determined by photometric analysis described in literature.[10] When the mixture of both surfactant types was present in the solution, they had to be separated by a batch ion exchange method[11] and analyzed with the appropriate method cited above. For the separation of anionic surfactants from the mixture an ion exchange resin DOWEX K-21 was used. Foam samples were collected 60 cm above the gas distributor. Feed concentrations of DBSA, hyamine 1622 and TRITON X-100 were $c_0=8.0\times10^{-4}$ M. Samples of feed solution (bulk liquid) were collected every 30 minutes 5 cm above the gas distributor. Superficial air velocity varied from 0.193 to 0.386 mm/s.

Results and Discussion

The most practical indicator for the performance of the foam column is the enrichment ratio (e), which is defined as the ratio of foamate concentration vs. bulk liquid concentration of the surfactant (1).

$$e=c_f/c_b \tag{1}$$

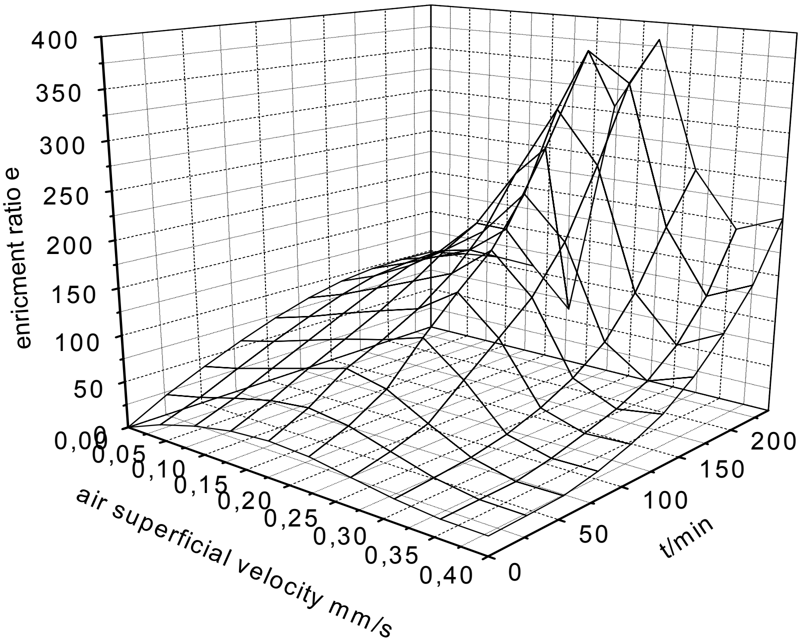

Figure 2. Typical time dependence of enrichment ratio **e** of 0.8 mM DBSA at different air flow rates at 25 °C.

As it is shown in Figure 2, there is an optimal air superficial velocity for each system, for DBSA being 0.241 mm/s (airflow rate 100 ml/min). At higher flow rates there is a decrease of enrichment ratio presumably due to lower residual time of bubbles in foam phase, which causes lower drainage of liquid from foam and consequently there is a higher content of water in foamate.

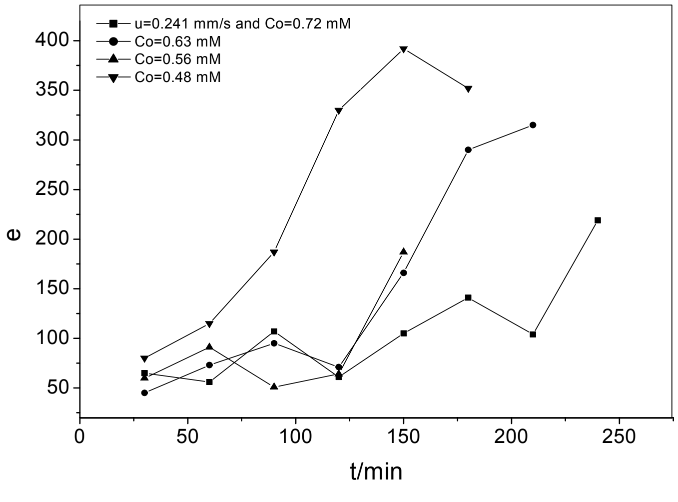

Figure 3. Time dependence of enrichment ratio **e** at different feed solution concentrations of DBSA.

As it is shown in Figure 3 the enrichment ratio increases as feed liquid surfactant concentration decreases, presumably due to higher foam stability at higher surfactant concentration in the foam. The contribution of adsorbed surfactant to enrichment ratio increases since the amount of surfactant in the bulk liquid is smaller.

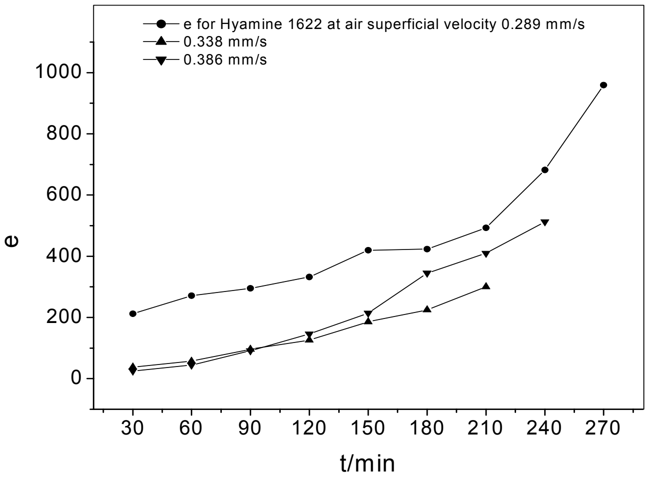

Figure 4. Time dependence of enrichment ratio **e** at different airflow rates for Hyamine 1622.

As it is shown in Figure 4 the results of foaming efficiency are similar for both surfactants (anionic and cationic) only there is a slight difference in the optimal airflow rate. Optimal airflow rate for Hyamine 1622 is higher than for DBSA for about 25%. This is probably because of the lower surface tension for DBSA at the same conditions. Lower surface tension reduces the bubble size in the system and this enhances the process of foam fractionation.

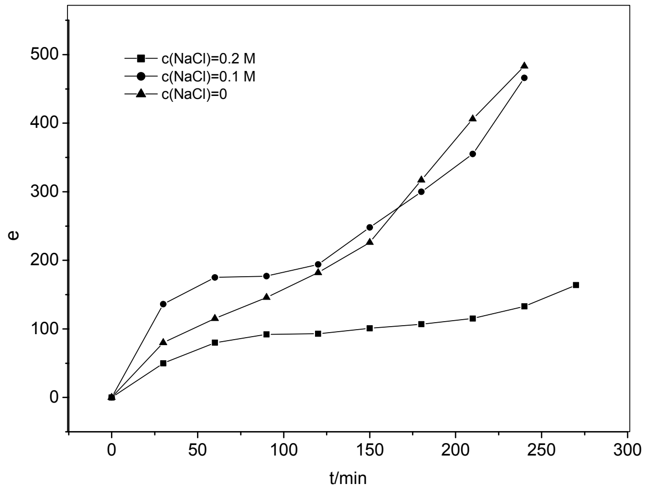

Figure 5. Time dependence of enrichment ratio **e** at airflow rate 0.241 mm/s and different concentrations of added salt for DBSA.

In Figure 5 a decrease of enrichment ratio with added salt can be seen. The presence of salt presumably causes higher stability of liquid in foam and lower drainage, so the liquid phase content in foam is higher. The electrostatic repulsion of adsorbed surfactants in thin films between foam bubbles induced by salt stabilizes liquid drainage from foam.[12]

Foam fractionation of nonionic surfactant solutions gave similar results. The optimal airflow rate for TRITON X-100 was 0.338 mm/s; the highest of all three types used. After obtaining optimal process parameters a mathematical model was developed for batch foam fractionation based on analogies to distillation. This model describes the total surfactant concentrations of both the foam and the bulk solution. Material balances and equilibrium relationships are used to develop the model. Further details are given elsewhere.[6,13]

Equilibrium in the bulk or foam phase at a theoretical stage n is defined by:

$$c_n = K_n C_n \quad n = 1,2, \ldots N \tag{2}$$

where c_n is the surfactant concentration in the upward foamate leaving the equilibrium stage, C_n is the concentration in draining liquid and K_n is the distribution coefficient. In general, K_n varies with the height of the column and time. The liquid drainage flow rates F and foamate flow rates f are described by a mass balance:

$$dV_n/dt = f_{n-1} - f_n + F_{n+1} - F_n - f_{out,n} \tag{3}$$

where V_n is the volume hold-up of the collapsed foam on stage n. The effluent flow rate of collapsed foam leaving each stage $f_{out,n}$ is determined from experimental data and equals the amount of withdrawn sample from each stage divided by the elapsed time (in our case 30 min). The effluent values are then multiplied by a flow factor to give upward foam flow rate, f_n, leaving a given stage n. The flow factor was determined from the parallel experiment with the same conditions, where we established the total volume of generated foam on each stage n. The boundary condition at the top stage is that the flow rate of the foam leaving the stage is set to zero. The column is capped and there is no flow at the top of the column. If we approximate that the left side of equation (3) is negligible or equal to zero, then the F's can be solved from the above equation (3) that turns into a set of linear algebraic equations and can be easily solved with the method of Gauss elimination.

The stagewise mass balance for the bulk solution is:

$$dV_b/dt = F_3 - f_2 - f_{out,b} \tag{4}$$

The term dV_b/dt cannot be neglected since mass is being removed from the column through the sampling ports. Measured bulk liquid volume changes with time are presented in table 3.
Boundary conditions for equation (3) is:

$$dV_n/dt = 0 \quad \text{for} \quad 0 < t < t_f \tag{5}$$

$$f_6 = F_7 = 0 \quad \text{for} \quad n = 6 \quad \text{for} \quad N = 6 \tag{6}$$

where t_f is the sampling time interval, V_b is the volume hold-up of the collapsed foam at the bottom. The total surfactant balance can be written for stage n as:

$$d(c_nV_n)/dt = f_{n-1}c_{n-1} - f_nc_n + F_{n+1}C_{n+1} - F_nC_n - f_{out,n}c_n \tag{7}$$

$$d(c_bV_b)/dt = F_3C_3 - f_2c_b - f_{out,b}c_b \tag{8}$$

Boundary conditions for equation (7) is:

$$d(c_nV_n)/dt = 0 \quad \text{for} \quad 0 < t < t_f \tag{9}$$

The equilibrium relationship from equation (2) was substituted into equations (7,8) and the values K_n's were obtained. Other variables were obtained either from experimental data or calculated from equations (3,4). We assumed steady state in each of the sampling period so that the left side of equation (7) is close to zero and the method of solving these linear equations is the same as in equation (3). After the K_n's were obtained, they were time averaged and using these averaged K's, the surfactant concentrations in the foam and bulk liquid was simulated from equations (7,8). Effluent flow rates for liquid and foam phase and distribution coefficients K_n's are listed in tables 4 and 5. The value of equilibrium constant K_b was determined from the equation (2) in the beginning of the experiment when the foam phase was a few cm above the interface liquid/foam. We assumed that K_b was not changing with time.

Table 3. Measured bulk liquid volume changes with time.

Time (min)	V_b (mL)
0	2406
30	2391
60	2376
90	2361

Table 4. Effluent flow rates of collapsed foam and liquid drainage.

Stage, n	f_n (mL/min)	F_n (mL/min)	$f_{out,n}$ (mL/min)	Flow factor
2(foam phase bottom)	5.670	-	0.366	
3	3.867	5.517	0.097	40
4	1.206	3.810	0.032	38
5	0.208	1.193	0.017	12
6	0	0.205	0.012	14.6
7	-	0	-	-

Table 5. Distribution coefficients K_n's in the model.

Time(min)	K_b	K_3	K_4	K_5	K_6
30	1.240	1.256	2.243	2.497	2.217
60	1.240	1.536	4.444	2.971	1.820
90	1.240	1.608	9.547	2.767	1.560
$K_{aver.}$	1.240	1.199	3.820	2.284	1.606

As we can see on Figure 6 there is a difference between experimental data and simulation results on stage 3 (height of the withdrawal of foamate H=48.7 cm). The explanation for the descending slope at the second stage is probably higher airflow rate than in the original model[6] that presumably causes an extension of surfactant fractionation in the bulk solution. Because of the withdrawal of surfactant from the bulk solution, the concentration decreases and only at a certain height of the column this effect is reversed (stage 3) to an increasing surfactant concentration in foamate due to fractionation in the foam phase. From stage 3 on the obtained simulation data reasonably good fit the experimental data.

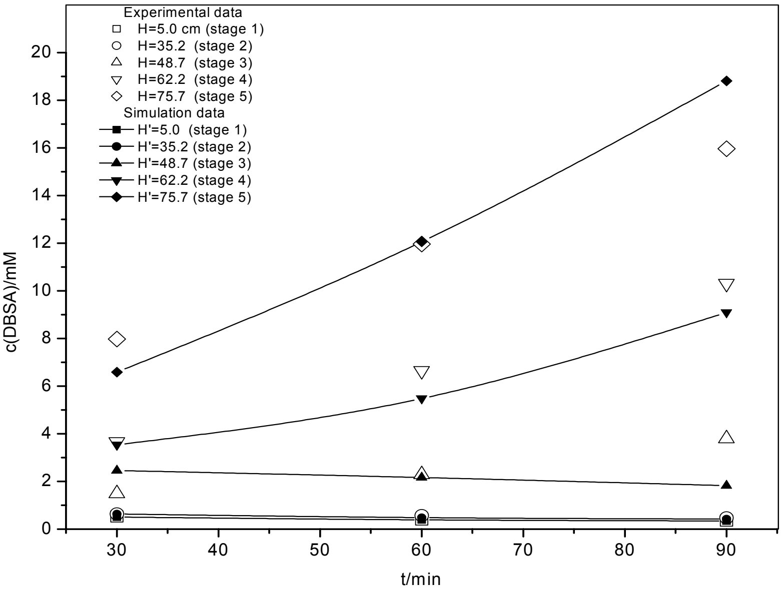

Figure 6. Simulation results of the surfactant concentration profiles in foam and bulk liquid at airflow rate 0.338 mm/s. The points represent the experimental data and the curves represent the simulation results. Stages 1 and 2 represent the height of bulk solution withdrawal and stages 3 to 5 represent the height of foamate withdrawal.

Results of foaming of some industrial wastewaters are presented in Figure 7.

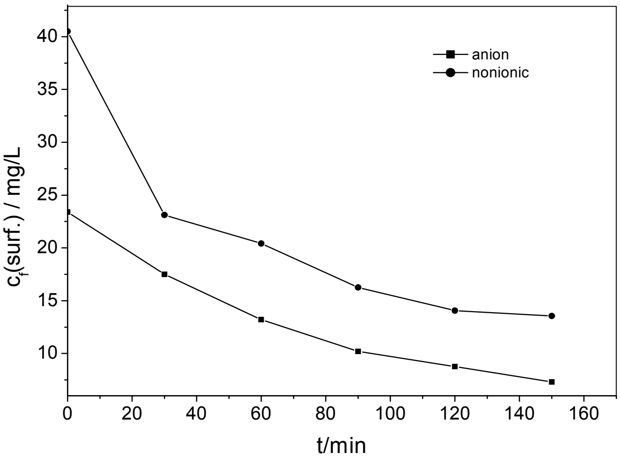

Figure 7. Decrease of surfactant concentration in bulk solution with time for sample from Labod at superficial air velocity 0.338 mm/s.

As can be seen from figure 7, 66% of surfactants have been removed from the bulk solution and recovered in the foamate during 250 minutes under given circumstances. After that time it was no more possible to provide samples of foam and also the concentration in the bulk solution did not change significantly with time.

During the three hours process of foaming the COD values in the laundry wastewater USLUGA reduced from 266 to 186 mg/L and TOC values from 84.5 to 62.6 mg/L.

Both values did not drop significantly because foam fractionation is a specific method only for the separation of surface-active agents. Other organic impurities (softeners, grease, waxes) remained in the wastewater after the process and could not have been removed by foaming. The process is primarily applicable for the recovery of surfactants from wastewaters in order to be recycled.

Conclusions

The experimental results shown enable most important parameters that affect the foam fractionation process to be determined. The optimal parameters for model surfactant solutions were applied in modeling purification of real wastewater samples containing surfactants from various industrial cleaning activities. Since foam fractionation has some similarities with the fractional distillation, a mathematical model was applied that describes the changes of concentration profiles of surfactants in the batch-operated foaming column. The simulation results show good consistency with the experimental results.

Nomenclature

c_f = surfactant concentration in foam, mmol/L
c_b = surfactant concentration in bulk liquid, mmol/L
c_n = surfactant concentration in rising foamate leaving stage n, mmol/L
C_n = surfactant concentration in draining liquid, mmol/L
e = enrichment ratio
f_n = foamate flow rate, ml/min
F_n = liquid drainage flow rate, mL/min
$f_{out,n}$ = effluent flow rate of collapsed foam leaving stage n, mL/min
$f_{out,b}$ = sample withdrawal flow rate of bulk liquid, mL/min
K_n = distribution coefficient
t_f = sampling time interval, min
V_n = volume hold-up of the collapsed foam on stage n, mL
V_b = bulk liquid volume, mL

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Povzetek

Detergenti predstavljajo pereč problem v raznih industrijskih in komunalnih odpadnih vodah. Izpenjevanje z zrakom nam omogoča hkratno zmanjšanje organske obremenitve odpadnih vod in koncentriranje detergentov zaradi možne reciklaže. Glavne procesne in snovne spremenljivke, ki kontrolirajo proces izpenjevanja so: koncentracija in tip detergenta v napajalni raztopini, prisotnost soli, pretok plina in geometrija kolone. Optimalne pogoje izpenjevanja smo testirali na realnih vzorcih odpadnih vod iz industrije. Podan je tudi matematični model, ki opisuje potek koncentracije detergenta vzdolž kolone. Model zadovoljivo opisuje proces frakcioniranega izpenjevanja detergentov iz modelnih raztopin, manj uspešno pa iz realnih vzorcev odpadnih vod.