

CHAPTER III
REMOVAL OF TRACE Cd²⁺ USING CONTINUOUS MULTISTAGE ION
FOAM FRACTIONATION: PART I—THE EFFECT OF FEED SDS/Cd
MOLAR RATIO

3.1 Abstract

In this research, a continuous multistage ion foam fractionation column with bubble-cap trays was employed to remove cadmium ions from simulated wastewater having cadmium ions at a low level (10 mg/L). In this study, sodium dodecyl sulphate (SDS) was used to generate the foam. An increase in feed SDS/Cd molar ratio enhanced the removal of Cd. However, the SDS concentration above a certain level resulted in wetter foams, leading to having a high volume of generated foam that lowered both the enrichment ratio and separation factor of the Cd. The SDS recovery tended to increase with increasing feed SDS/Cd molar ratio. The molar ratio of SDS/Cd in foamate was found to be close to the theoretical adsorption molar ratio of 2/1 on the air–water interface of foam when the system was operated at a feed SDS/Cd molar ratio in the range of 2/1 to 7/1. Ion foam fractionation has been demonstrated in this study to be a promising technique for high heavy metal removal (more than 99%) for a feed having a low heavy metal concentration in the ppm (mg/L) level.

Keywords: ion foam fractionation; heavy metal; cadmium removal; sodium dodecyl sulfate

3.2 Introduction

The removal of heavy metal ions is of particular interest in hazardous waste management due to their severe toxicity to living organisms. Their high solubility in aquatic environments makes them accumulate in the food chain [1]. Numerous treatment techniques are now available for removing heavy metal ions from aqueous solutions. These include chemical precipitation, solvent extraction, ion exchange, membrane filtration, and electrolysis. However, these mentioned techniques are not considered to be economically feasible for treating large volumes of wastewaters containing heavy metals at low levels due to the high operational cost, which results from large volumes of chemicals and/or high energy consumption [2,3]. It has been shown that when treating a large volume of dilute wastewater with solvent extraction, the loss of the solvent and the high cost of the energy are significant economic problems [4]. Most electrolytic processes are ineffective at low heavy metal concentrations due to the low mass-transfer rate, leading to high energy consumption [5]. Lime precipitation has been found to be one of the most effective heavy metal removal techniques, if the heavy metal concentration is higher than 1000 mg/L; however, it still requires a large amount of lime and produces a large quantity of residue [3].

Adsorptive bubble separation, including foam fractionation, is based on the selective adsorption or attachment of materials onto the surfaces of gas bubbles rising through a solution [6]. The foam fractionation of ions is similar to ion flotation but uses an excess of surfactant or a proper frother to produce stable foam [7]. This process offers many advantages for the treatment of industrial wastewaters compared to other treatment processes, including: low space and energy requirements; simple plant design, operation, and scale-up; and low capital and operating costs [8]. Not only surfactants are removed by adsorption at the air-liquid interfaces, but other components that form complexes with the surfactants also tend to be concentrated [9].

Foam fractionation processes can be used to concentrate and remove dissolved materials, including surface active solutes from aqueous solutions. In a foam fractionation operation, air is introduced into the system to generate air

bubbles, and surface active solutes adsorb preferentially at the bubble–liquid interface. The bubbles proceed upwards to the top of the column to produce foam. This foam layer (froth) can physically be separated from the bulk liquid and the surface active solutes are simultaneously removed. Only a small volume of entrained liquid is carried with the bubbles into the foam phase (froth) due to the gravitational liquid film drainage. Once the foam collapses, the concentrated liquid (foamate) contains the surface active solute at a much higher concentration than that found in the feed. To maximize the separation efficiency in terms of the enrichment ratio and the removal of the surfactant, the foam fractionation column has to produce just sufficiently stable foam with high liquid film drainage [10].

In removing trace heavy metal ions from a dilute wastewater with large volume, the ion foam fractionation appears to be particularly promising [11]. Ion flotation <foam fractionation> was shown to have the highest copper recovery to the lowest residual copper concentration as compared with ion, precipitate, and sorptive flotation [12]. Ion foam fractionation was found to offer high metal removal ($\approx 100\%$) at a low feed metal concentration (50 mg/L) with both low chemical and energy costs [3]. However, the main problem of ion foam fractionation is that nearly complete removal ($>99\%$) always yields a large volume of foamate with a low heavy metal enrichment ratio while dry foam always comes with low heavy metal removal efficiency [13,14,15].

Ion foam fractionation has many attractive features for removing trace metal ions from aqueous solutions [12-17]. However, most of the studies were in lab scale with a single stage and batch mode of operation [14-15,17-20] while a few of them were carried out in continuous mode [13,21]. Only one study focused on process design to reduce the interstitial liquid or liquid hold-up in the foam [21]. Further development of ion foam fractionation equipment and processes is still needed to improve the separation efficiency by reducing liquid hold-up in the foam without causing foam collapse.

From our previous study, the separation efficiency of multistage foam fractionation for the recovery of cetylpyridinium chloride (CPC), a cationic surfactant, from water was found to be much higher than that in a single-stage system, especially in terms of the enrichment ratio and % recovery of the CPC [22].

In this present study, we extend the application of continuous multistage foam fractionation with bubble-cap trays for the removal of trace heavy metals. The purpose of this work was to demonstrate continuous multistage ion foam fractionation for the removal of trace heavy metals from wastewaters. Cadmium was selected as a model heavy metal and sodium dodecyl sulfate (SDS) was used to generate foam in the present work. The effect of feed SDS/Cd molar ratio was investigated.

3.3 Experimental

3.3.1 Materials

Sodium dodecyl sulfate (SDS) and cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) with a purity of 97 % and > 99 %, respectively, were obtained from CARLO ERBA REAGENTI (Italy) and used as received without further purification. Deionized water was used in all experiments.

3.3.2 Setup of The Multistage Foam Fractionation Unit

The multistage ion foam fractionation apparatus used in this study and the arrangement and the dimensions of the bubble-caps in each tray are shown in Figure 3.1. The multistage ion foam fractionation column was made from an acrylic cylinder with a 17.4 cm inner diameter and was assembled to have different trays of up to 5 stages. Each tray had 22 bubble caps with a weir height of 6 cm and a cap diameter of 2 cm. The tray spacing was 15 cm. Each bubble cap tray, except the lowest tray, had a downcomer with a diameter of 4 cm to allow liquid overflow to a lower tray. The liquid level in each tray was fixed at a weir height of 3 cm. On the top tray, there was a foam column having the same inner diameter (17.4 cm) and different foam outlet heights at 30, 60, and 90 cm.

3.3.3 Operation of The Multistage Foam Fractionation Unit

The ion foam fractionation system with 5 trays was operated in continuous mode in this study. A 10 mg/L Cd feed solution was prepared by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in deionized water. SDS was then added into the feed

solution to have different feed SDS/Cd molar ratios. The feed solution was continuously fed into the top of the column at different feed flow rates in the range of 25–100 mL/min corresponding to the feed flux flow rate of 1–4 L/min m² by using a peristaltic pump (Masterflex[®], L/S[®] Digital Drives). Compressed air from an air compressor was introduced below the bottom tray and the air flow rate was regulated in the range of 30–100 L/min using a rotameter. Due to insignificant influence of temperature on the performance of ion foam fractionation in the range of 15 °C to 34 °C, [13], the experiments were carried out at room temperature, 25–27 °C. The foam at the top of the column was collected by allowing it to flow out at different foam heights of 30, 60, and 90 cm. The collected foam was left to collapse by itself to obtain foamate.

The studied system was first operated to determine the time to establish steady state, which was around 6 h. Steady state was ensured when all measured parameters were invariant with time. After steady state conditions, samples of the feed solution, the collapsed foam solution (foamate), and the effluent were collected and analyzed for SDS and Cd concentrations. All samples were acidified with concentrated nitric acid to a pH below 2 for preservation. Both volumetric flow rates of foamate and effluent were also measured. The data were obtained from at least three runs and the average data were used to assess the process performance of the multistage ion foam fractionation system. By performing mass balances of the cadmium and the SDS, the average error was found to be less than 10 %.

3.3.4 Analytical Methods

The concentration of SDS was measured by a total organic carbon analyzer (Shimadzu, TOC-VCSH). The concentration of cadmium ions was determined by an atomic adsorption spectroscope (AAS, Varian, SpectrAA 300). To eliminate SDS interference on the cadmium analysis, a cadmium standard solution containing SDS at the same concentration as in any diluted sample was used for obtaining the calibration curve [23]. According to the AAS specification, the measurement range of cadmium with high accuracy is 0.02–3 mg/L. Exceeding this concentration range, the calibration plots usually deviate from linearity. Therefore, all sample solutions were diluted to approximately a 1 mg/L Cd concentration before

the analysis. The recommended wavelength of 228.8 nm for cadmium analysis was employed in the analysis. The surface tension was measured by using a drop shape analysis instrument (Kruss, DSA 10). The pendant technique was used to measure the surface tension of surfactant solutions containing different concentrations of SDS, $\text{Cd}(\text{NO}_3)_2$ and NaNO_3 . The sample chamber temperature was kept constant at room temperature (25–27°C) and the humidity in the sample chamber was kept saturated in order to minimize the evaporation effect during measurements.

3.3.5 Calculations

The process performance of the studied multistage ion foam fractionation column was assessed by calculating the enrichment ratios of SDS and Cd, % SDS recovery, % Cd removal, the foamate volumetric ratio (V_f/V_i), the residual factors of SDS and Cd, and the separation factors of SDS and Cd [24]. All assessment parameters are described as follows:

$$\text{Enrichment ratio} = C_f/C_i, \quad (3.1)$$

$$\% \text{ SDS recovery or } \% \text{ Cd removal} = (V_i C_i - V_e C_e)(100)/(V_i C_i), \quad (3.2)$$

$$\text{Residual factor} = C_e/C_i, \quad (3.3)$$

$$\text{Foamate volumetric ratio} = V_f/V_i, \quad (3.4)$$

$$\text{Separation factor} = C_f/C_e, \quad (3.5)$$

where C_f and C_i are the surfactant or Cd concentrations in the foamate (collapsed foam solution) and in the influent (feed), respectively. C_e is the SDS or Cd ion concentration in the effluent stream, and V_i , V_f , and V_e are the volumetric flow rates of feed, foamate, and effluent, respectively.

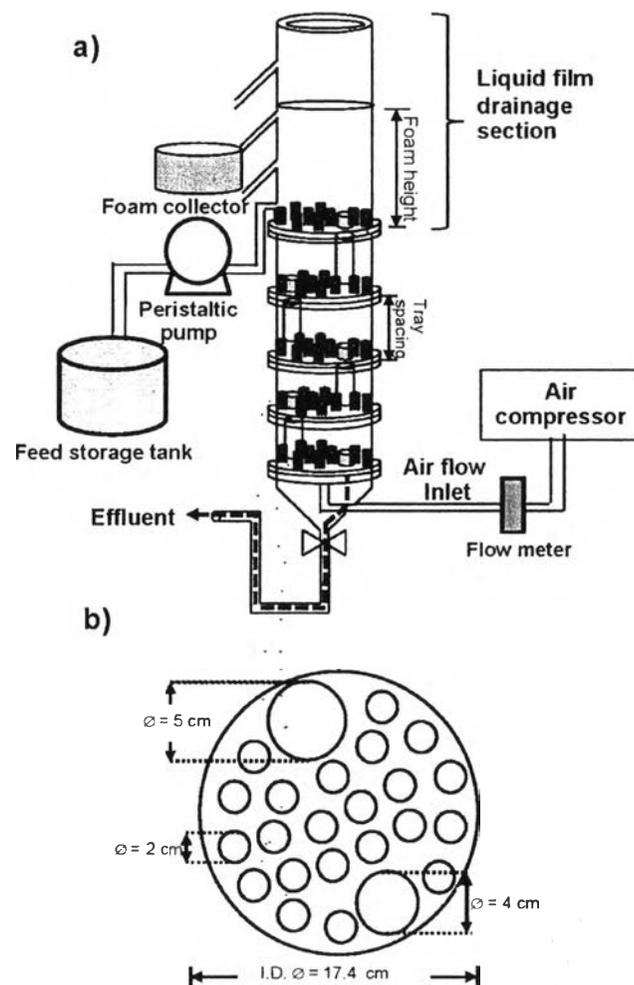


Figure 3.1 (a) Schematic of a multi-stage foam fractionation unit and (b) schematic of a base of a tray (top view).

3.4 Results and Discussion

3.4.1 Operating Limits

A multistage ion foam fractionation unit must be designed properly to allow it to function well. Both air and foam flow only through the bubble caps of the tray. The liquid flows only through the downcomer, not through the bubble caps. The liquid is not completely wept out through the perforations. The liquid is carried over with the generated foam at minimum. Finally, air does not bubble up through the downcomers. All of these requirements lead to various operating limits of the

multistage ion foam fractionator. In order to have a stable operation and functioning of a multistage ion foam fractionation column, both the air and liquid flow rates must be regulated within the proper ranges to meet several requirements. Three important operational conditions— foam formation, flooding, and weeping/dumping—are considered to be the constraints of the operation of ion foam fractionation. A sufficient air flow rate is needed in order to produce stable foam to reach the foam outlet at the top tray. The definition of flooding in ion foam fractionation operation is analogous to that in a distillation column. The flooding is defined as “excessive accumulation of liquid inside the column” [25]. Hence, the flow rate of the effluent is not constant. For any given low or moderate air flow rate, downcomer flooding can occur at very high liquid flow rates. As a result, the liquid level in each tray becomes higher than the overflow weir of the downcomer because of the limitation of the liquid flow through the downcomer. For any given liquid flow rate, entrainment flooding occurs at very high air flow rates, causing some liquid to be carried upward to an upper tray. The last operational problem is dumping. This phenomenon is caused by a low air flow rate. The pressure exerted by the air is insufficient to hold up the liquid on the tray. Therefore, liquid starts to leak through the bubble caps; that is, the liquid on all trays will crash (dump) through to the base of the column.

Figure 3.2 shows the boundaries of the operational zone of the studied multistage ion foam fractionator operated at a feed SDS/Cd molar ratio of 7/1 and a number of stages of 5. When the system is operated at a very low air flow rate, it has a low foam production rate, leading to low removal. However, a longer foam residence time derived from a low air flow rate led to a dry foam with a high enrichment ratio. On the other hand, when it is operated at a very high air flow rate, a large fraction of the liquid in the column is transferred into the foam phase, leading to a low enrichment ratio. A high air flow rate, however, results in a high foam production rate and a high mass transfer surface area available for heavy metal ion adsorption, leading to higher removal. When the system is operated at a very high liquid flow rate, the separation efficiency expectedly decreases. This is attributed to a lower residence time of the liquid in the column. Therefore, the optimum conditions, in which both % removal and enrichment ratio are high, should be located far away from the boundary lines, represented by a dash line called the “optimum zone”, as

depicted in Figure 3.2. With increasing surfactant concentration, the entrainment flooding line tends to shift to lower air flow rates and the downcomer flooding line tends to shift to higher feed flow rates, while the insufficient foaming region tends to be contracted because of higher ability for foam formation. The values of both air flow rate and liquid flow rate located in the operational zone were used to run all experiments in order to avoid all of the operational constraints (dumping, insufficient foam, and flooding).

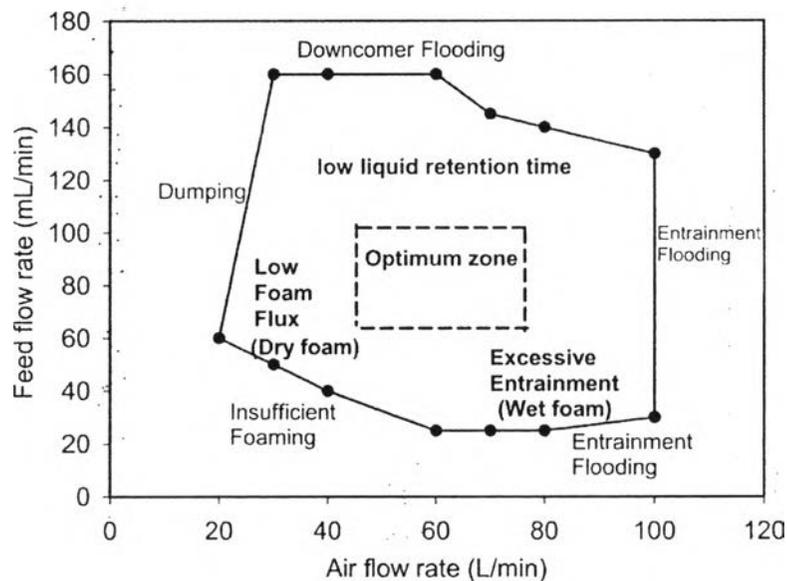


Figure 3.2 Boundaries of the operational zone of the studied foam fractionator at a feed SDS/ Cd molar ratio of 7/1, a foam height of 60 cm, a feed Cd concentration of 10 mg/L, and the number of trays equal to 5.

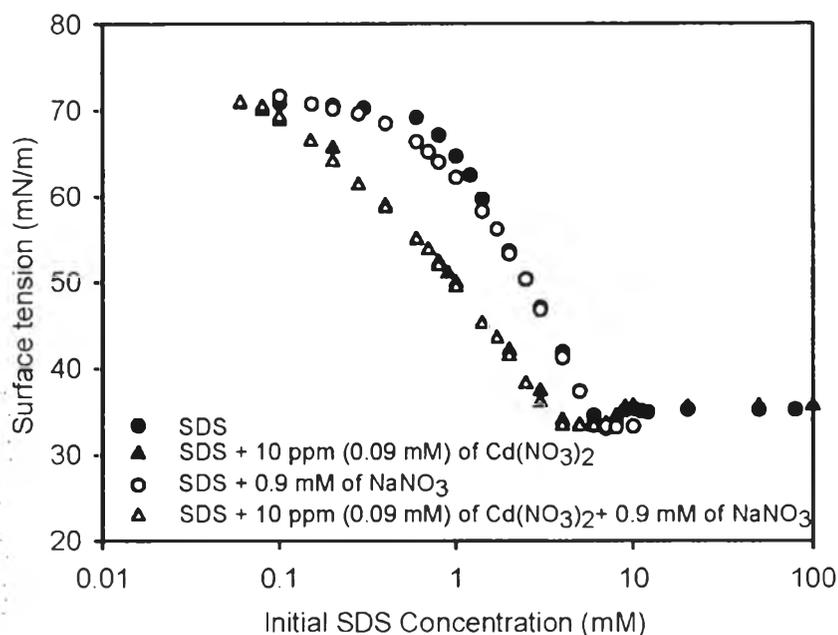


Figure 3.3 Surface tension isotherms of SDS with various concentrations of $\text{Cd}(\text{NO}_3)_2$ and NaNO_3 at 25 °C to 27 °C.

3.4.2 Surface Tension Isotherm Results

The plots of surface tension versus the log of initial SDS concentration at different added cadmium ($\text{Cd}(\text{NO}_3)_2$) and added sodium (NaNO_3) concentrations are shown in Figure 3.3. The molecular area of adsorbing SDS or the surface excess concentration of SDS at the air–water interface can be determined as a function of the bulk SDS concentration by applying the Gibbs adsorption equation:

$$\Gamma = -\frac{1}{nRT} \frac{d\gamma}{d \ln C} \quad (3.6)$$

where Γ is the surface excess concentration or adsorption density of surfactant ion (DS^-), γ is the equilibrium surface tension, C is the bulk SDS concentration, R is the gas constant, T is the absolute temperature and, prefactor (n) is equal to 2 or 1 for SDS in the absence or in the presence of an excess concentration of electrolyte with the common counterion (Na^+), respectively [26]. However, in the presence of an excess concentration of electrolyte with different counterions from the surfactant (i.e.

Cd^{2+}), the adsorption of the surfactant ion (DS^-) is also expressed well by the Gibbs adsorption equation with $n = 1$ [27]. As shown in Figure 3.3, the addition of NaNO_3 does not have a significant effect on the surface tension isotherm of the SDS for both cases of with and without $\text{Cd}(\text{NO}_3)_2$. In contrast, there was a significant shift of the surface tension isotherm of SDS for both cases of with and without NaNO_3 when $\text{Cd}(\text{NO}_3)_2$ was added. The results suggest that the surface excess concentration of SDS increases significantly in the presence of Cd^{2+} because the divalent cadmium ions coadsorb preferentially more than the monovalent sodium ions [28].

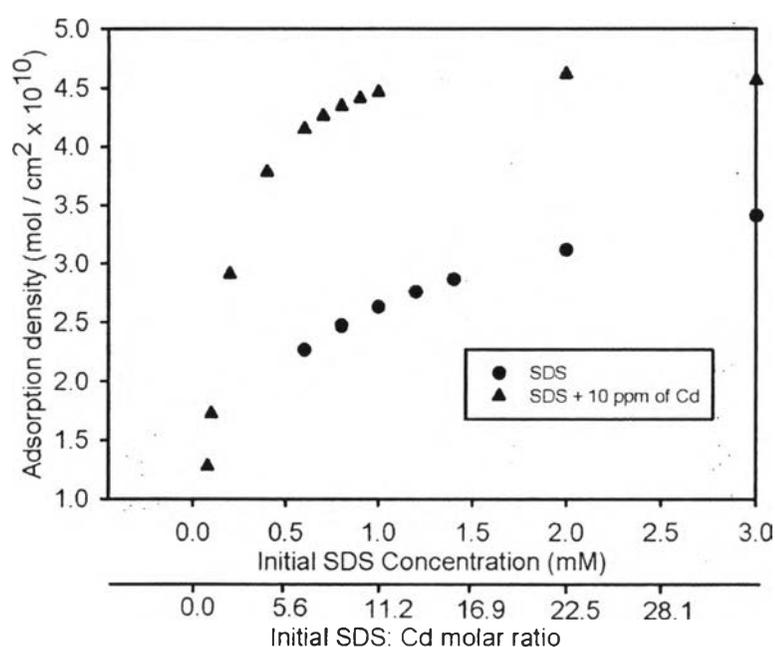


Figure 3.4 Adsorption density as a function of concentration of SDS and SDS with 10 mg/L of Cd^{2+} at 25 °C to 27 °C in the absence of NaNO_3 .

The experimental surface tension data (Figure 3.3) at SDS concentrations below their critical micelle concentrations (CMC) at different Cd concentrations were well fitted by using second-order polynomial regressions. The calculated values of the adsorption density of SDS at different conditions are shown in Figure 3.4.

In the absence or presence of Cd ions, the adsorption density of the dodecyl sulfate ion was found to increase with increasing bulk SDS concentration

and to reach a plateau at high bulk SDS concentrations, indicating that the surface excess concentration has reached a constant saturated (maximum) value. The maximum surface excess concentrations of SDS for both systems, with and without cadmium, were found at about a quarter of their CMCs, as shown in Figure 3.4 and Table 3.1. The CMC, the surface tension at the CMC (γ_{cmc}), the negative logarithm of SDS concentration in the bulk phase required to obtain a surface pressure of 20 mN/m (pC_{20}), and the saturated surface excess concentration (Γ_m) of the SDS with and without counterions of Cd^{2+} and Na^+ are shown in Table 3.1. The values of the CMC and γ_{cmc} were determined from the reflection points in the γ -log C curves. The CMC value can be related to the standard free energy of micellization. The pC_{20} can be related to the Gibbs free energy of adsorption of a component from bulk liquid to the bubble surface and the efficiency of surfactant adsorption [26].

Table 3.1 Calculated values of CMC, γ_{cmc} , pC_{20} , and saturated surface concentrations (Γ_m) of SDS alone and in the presence of cadmium and sodium ion concentrations

Surfactant solution	CMC (mM)	γ_{cmc} (mN/m)	pC_{20}	Γ_m (mol/cm ²)
SDS	7.5	33.6	2.68	3.4×10^{10}
SDS + 0.09 mM Cd^{2+} (10 ppm)	4.5	33.4	3.12	4.6×10^{10}
SDS + 0.9 mM Na^+	6.0	33.4	2.69	3.5×10^{10}
SDS + 0.09 mM Cd^{2+} (10 ppm) + 0.9 mM Na^+	4.5	33.5	3.10	4.6×10^{10}

During the rising of air bubbles through a solution, the convective diffusion resistance is relatively low because of the strong turbulence resulting from air bubble rising [29,30]. The equilibrium adsorption density of the SDS-Cu system was found to be reached in about 1 s [11]. Therefore, the equilibrium surface tension

and adsorption density can be obtained within short residence times of bubbles in the studied ion foam fractionation system. It is interesting to note that, for the studied system with a feed cadmium concentration of 10 mg/L, the adsorption densities of both cadmium and dodecyl sulfate ion were found to reach about 90 % of the maximum values at a bulk SDS concentration of 0.7 mM, corresponding to a SDS/Cd ratio of 8/1 (see Figure 3.4).

At an added Na^+ concentration of 0.9 mM, it was found that the pC_{20} of the SDS with cadmium ions is higher than that without cadmium ions, whereas the CMC is lower, as shown in Table 3.1. These results suggest that both micellization and adsorption at the air–water interface are promoted more with an addition of the cadmium ions, as indicated by the high surface activity of cadmium counterion (Cd^{2+}) as compared to sodium ions. This can be explained in that cadmium ions can easily penetrate the surface layer (Stern layer) and neutralize the charge of the adsorbed surfactant anions (DS^-) more effectively than sodium ions because of the attractive force between the divalent cation Cd^{2+} ions and the SDS ion, facilitating the dehydration of the Cd^{2+} [31,32]. The results presented above suggest that, in the presence of surface active dodecyl sulfate anion (DS^-), the Cd^{2+} exhibits higher apparent surface activity than the Na^+ . Hence, Cd^{2+} can be carried out with foam by adsorbing on the bubble surface, with insignificant competitive adsorption of sodium ions dissociated from the SDS.

3.4.3 Correlation of Cd and SDS in Foamates and Effluents

A basic principle of an ionic surfactant adsorption at air–water interface is the electroneutrality at the air–water interface and the sum of the negative charges of the adsorbed surfactant headgroups and the positive charges of the adsorbed counterions is equal to zero [17,26]. For the studied ion foam fractionation system consisting of SDS and cadmium ion, Cd^{2+} , it can be described by Equation 3.7:

$$2\Gamma_{\text{Cd}^{2+}} + \Gamma_{\text{Na}^+} = \Gamma_{\text{DS}^-} \quad (3.7)$$

For Cd removal, since the Cd^{2+} exhibits higher apparent surface activity than the Na^+ , as discussed in the previous section, the adsorption of Na^+ with DS^- at the air–water interface can be neglected. Therefore, the $\Gamma_{\text{DS}^-}/\Gamma_{\text{Cd}^{2+}}$ ratio is equal to 2/1. Hence, the Cd^{2+} is removed only as $\text{Cd}(\text{DS})_2$ via the adsorption on the bubble surface. The concentration of SDS in foamate can be related to that of cadmium in foamate by Equation 3.8 [17]:

$$\begin{aligned} [\text{DS}^-] &= m[\text{Cd}^{2+}] \\ \text{and } \log[\text{Cd}^{2+}] &= \log[\text{DS}^-] - \log m \end{aligned} \quad (3.8)$$

where m is a molar ratio of DS^- to Cd^{2+} adsorbing onto the air–water interface of foam. Figure 3.5 shows the correlation of Cd and SDS concentrations in the foamate and effluent of the studied multistage ion foam fractionation unit operated at different feed SDS/Cd molar ratios (≥ 2), foam heights (30–90 cm), feed flow rates (25–100 mL/min) and air flow rates (40–100 L/min). The experimental data of foamate in the optimum zone and low foam flux region were successfully fitted with Equation 3.8 ($R^2 \approx 0.96$) by using the linear regression, and the calculated values of m were 2.14 and 1.95, respectively. These values of the $[\text{SDS}]/[\text{Cd}]$ molar ratios in the foamate were very much close to 2/1, indicating that the adsorption of negative surfactant ions at the interface is totally neutralized by the adsorption of Cd counterions when the system was operated in either the optimum zone or in the low foam flux region. However, the molar ratio of SDS to Cd in the foamate was found to be much higher than 2 when the system was operated in the excessive entrainment region. This is because at high feed SDS/Cd molar ratios, the generated foam contained a high fraction of liquid, which will be discussed later.

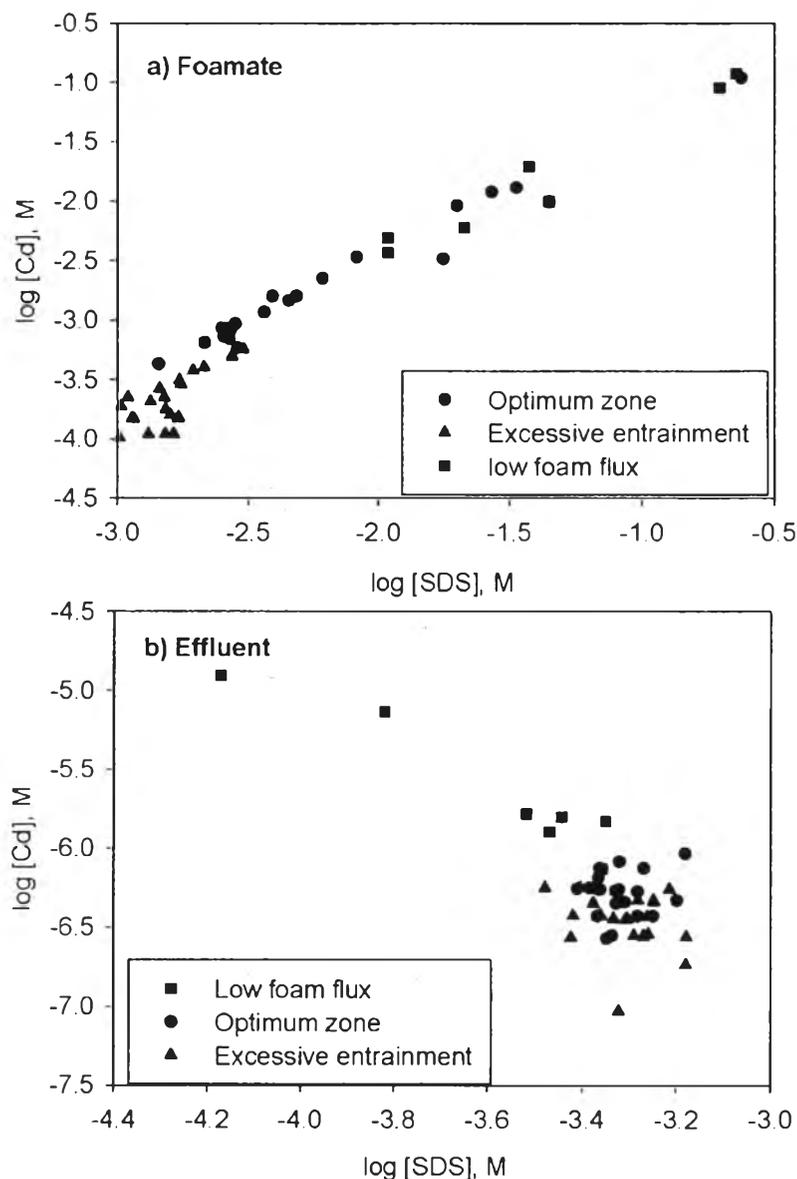


Figure 3.5 Correlations between Cd and SDS concentration (a) in the foamate and (b) in the effluent at a number of stages equal to 5 with different feed flow rates, air flow rates, and feed SDS/Cd molar ratios (≥ 2).

As shown in Figure 3.5b, the SDS/Cd molar ratio in the effluent is lower in the low foam flux region due to low Cd removal; whereas in the excessive entrainment condition, the system tends to show a higher SDS/Cd molar ratio in the effluent because a sufficiently large bubble surface is provided for Cd adsorption.

The effect of feed SDS/Cd molar ratio on the SDS/Cd molar ratio of the effluent will be discussed in detail in the next section.

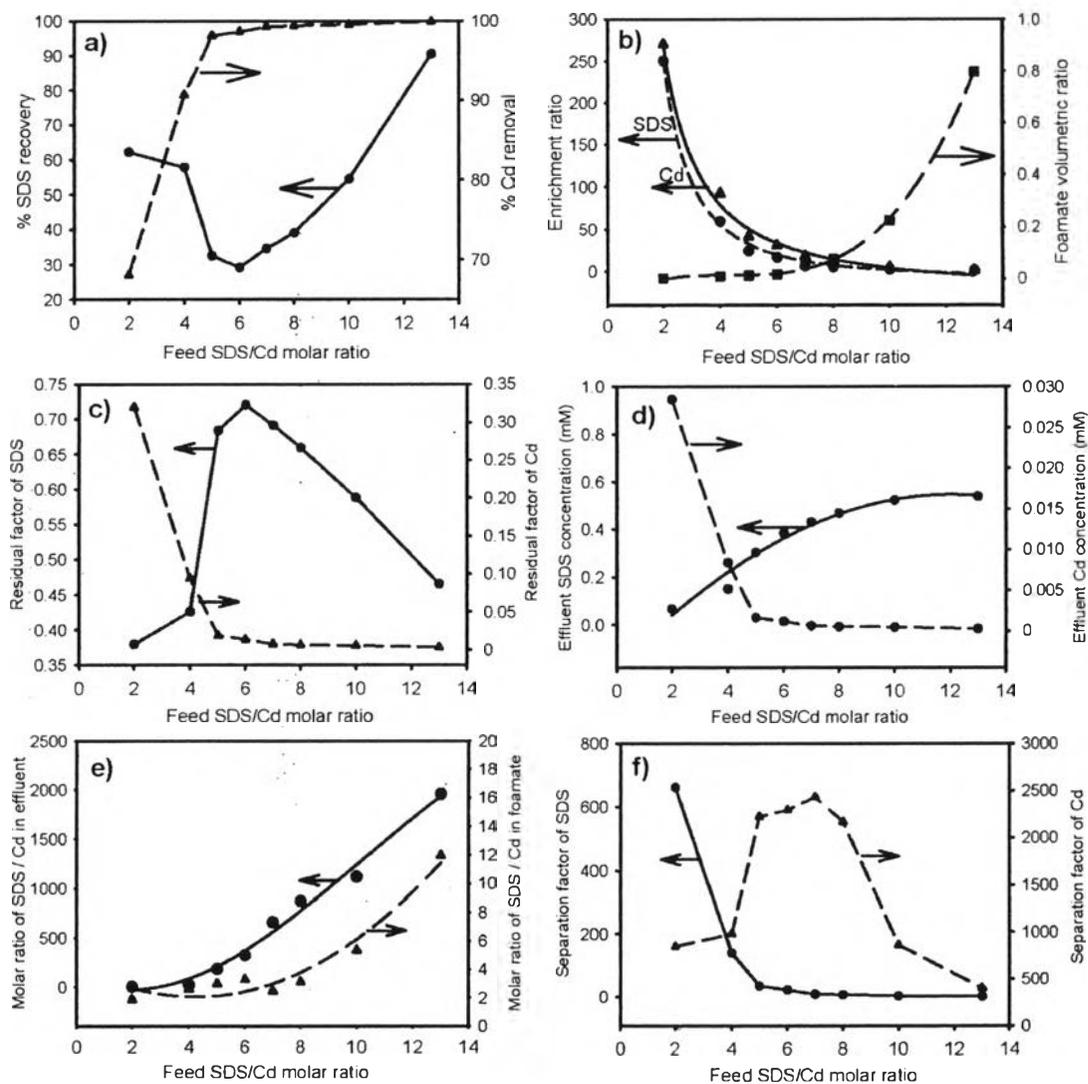


Figure 3.6 Effect of feed SDS/Cd molar ratio on (a) % SDS recovery and Cd removal, (b) enrichment ratios of SDS and Cd and foamate volumetric ratio (V_f/V_i), (c) residual factors of SDS and Cd, (d) effluent concentrations of SDS and Cd, (e) molar ratios of SDS/Cd in the foamate and effluent, and (f) separation factors of SDS and Cd at an air flow rate of 60 L/min, a feed flow rate of 40 mL/min, a foam height of 30 cm, a feed Cd concentration of 10 mg/L, and the number of trays equal to 5.

3.4.4 Effect of Feed SDS/Cd Molar Ratio

In a foam fractionation operation, it is necessary that both the enrichment ratios and the removals of SDS and Cd are as high as possible. An increase in surfactant concentration results in increasing removal but wet foam can be undesirably produced, resulting in lowering enrichment ratios [22]. Hence, the effect of feed SDS/Cd molar ratio was investigated in this study. The molar flow rate of a component in a foamate, which is related to the removal of Cd or the SDS recovery, is governed by both adsorptive transport and bulk liquid transport. The adsorptive transport and bulk liquid transport refer to the material transfer by the adsorption on the bubble surface and the entrained liquid in the foam lamella, respectively. The former is an upward stream of the adsorbed materials without carrying liquid while the latter is an upward stream of the lamella liquid with unadsorbed materials. The adsorptive transport can be expressed as $A\Gamma$, the product of flow area (cm^2/min) and surface excess concentration (mol/cm^2). The increase in bulk liquid transport can be affected directly by an enhancement in liquid entrainment in the foam, which is characterized by an increase in the foamate volumetric ratio. This mechanism can reduce both the enrichment ratios and the residual factors. However, if there is an insignificant amount of a component in the foam lamellae, the residual factors cannot be reduced by the bulk liquid transport.

Figure 3.6a shows that an increase in feed SDS/Cd molar ratio increases the Cd removal and reaches a plateau ($\approx 97\%$) at a feed SDS/Cd ratio of 8/1. For 100% Cd removal, the feed SDS/Cd molar ratio was found to be around 13/1. This might be attributed to an increase in the adsorptive transport of Cd resulting from both an increase in the ability for foam formation and the increase in the adsorption density of the SDS-Cd complex with increasing feed SDS/Cd molar ratio. As shown in Figure 3.6b, the foamate volumetric ratio is low at low feed SDS/Cd molar ratios but abruptly increases at a feed SDS/Cd molar ratio greater than 7/1, suggesting that the bulk liquid transport is low at low feed SDS/Cd molar ratios but is high at high feed SDS/Cd molar ratios. The sharp increase in foamate volumetric ratio (V_f/V_i) associated with an insignificant reduction in the residual factor of Cd (Figure 3.6c) beyond a feed SDS/Cd molar ratio of 8/1 suggests that the

increasing bulk liquid transport has an insignificant effect on the residual factor of Cd because the Cd^{2+} ions preferentially adsorb at the air–water interface of foam, leading to the small amount of unadsorbed Cd in the foam lamellae, as previously discussed.

The enrichment ratio of either SDS or Cd decreases substantially with increasing feed SDS/Cd molar ratio and approaches unity at a very high feed SDS/Cd molar ratio (13/1), as shown in Figure 3.6b. This is because of the dilution effect by the entrained liquid, which is increased with increasing feed SDS/Cd molar ratio, as indicated by an increasing foamate volumetric ratio. At the highest SDS/Cd molar ratio of 13/1, entrainment flooding was observed, as indicated by the extremely high fraction of liquid distributed into the foam (foamate volumetric ratio = 0.8), leading to both the enrichment ratios approaching unity.

The SDS separation efficiency in terms of recovery and residual factor showed opposite trends as compared to those of Cd. The SDS recovery shows a minimum whereas the residual factor of SDS reaches a maximum at a feed SDS/Cd molar ratio of 6/1, as shown in Figures 3.6a and 3.6c, respectively. The effluent SDS concentration was also found to increase with increasing feed SDS/Cd molar ratio, as shown in Figure 3.6d. Because the bulk liquid transport is low at feed SDS/Cd molar ratios below 6/1 as mention above, the separation performance of the SDS should be dominantly governed by the adsorptive transport. These results suggest that the adsorptive transport of the SDS does not increase proportionally to the increasing feed molar flow rate of the SDS, although the adsorption density increases with increasing initial SDS concentration. Similar results were also reported in the literature for single-stage foam fractionation [13]. From a visual observation of the experiments, it was found that, at any feed SDS/Cd molar ratio below 6/1, the solution in tray 3 could not generate a sufficiently stable foam to pass through the bubble caps of the upper tray due to the very low SDS concentration in the solution in tray 3, indicating that at a SDS/Cd molar ratio lower than 6/1, the maximum separation performance of the studied multistage ion foam fractionation column is achieved at a number of trays equal to 3 and an increase in the number of trays beyond 3 cannot enhance the separation efficiency. The results also suggest that to lower surface tension and to obtain stable foam throughout the ion foam fractionation

column, a feed SDS/Cd molar ratio greater than 6/1 is needed. Beyond a feed SDS/Cd molar ratio of 6/1, bulk liquid transport is promoted, as indicated by the large increase in foamate volumetric ratio, leading to decreasing the residual factor of SDS (see Figure 3.6c).

As shown in Figure 3.6e, the molar ratio of SDS/Cd in the foamate is approximately equal to 2/1 at a feed SDS/Cd molar ratio below 7/1. The results also confirm the interaction between SDS and the Cd ions at the air–water interface of foam with a theoretical ratio approaching 2/1. Beyond this feed SDS/Cd molar ratio, the molar ratio of the SDS/Cd in the foamate and the foamate volumetric ratio further increased remarkably with increasing feed SDS/Cd molar ratio. The increase in the molar ratio of the SDS/Cd in the foamate is attributed to the increase in the bulk liquid transport, as indicated by the increase in the foamate volumetric ratio.

As shown in Figure 3.6e, the molar ratio of the SDS/Cd in the effluent increases drastically with increasing feed SDS/Cd molar ratio. This is because an increase in the feed SDS/Cd molar ratio simply increases the SDS concentration in the system. The results of the molar ratio of SDS/Cd in the effluent and the effluent Cd concentration suggest that the effluent Cd concentration decreased abruptly with increasing the feed SDS/Cd molar ratio up to 5/1. However, it only slightly decreased with increasing the feed SDS/Cd molar ratio beyond 5/1. Hence, an increase in the feed molar ratio of SDS/Cd beyond 7/1 is useless, causing increasing effluent SDS concentration, as shown in Figure 3.6d. It is worth mentioning that a high feed SDS/Cd molar ratio of 7/1 is necessary to obtain the saturated surface excess concentration (Γ_m) of the SDS-Cd complex and to lower the surface tension. The first is required for obtaining maximum cadmium removal per surface area flux. The second is required to reduce the energy required to create bubbles, leading to an increasing foam production rate. To achieve more than 99 % Cd removal and to meet an allowable limit of Cd for effluent discharged into a watercourse (≤ 0.1 mg/L) [33], the studied multistage ion foam fractionation unit has to be operated at a feed SDS/Cd molar ratio not less than 7/1 (not less than 180 mg/L of SDS for 10 mg/L of Cd in feed).

Figure 3.6f shows that the separation factor of SDS declines sharply with increasing feed SDS/Cd molar ratio at low feed SDS/Cd molar ratios; but it

slightly decreases at high feed SDS/Cd molar ratios. This is because of the strong decrease in the enrichment ratio and the sharp increase in the residual factor for SDS, resulting from the increases in the bulk liquid transport, as indicated by the increase in foamate volumetric ratio. Interestingly, the separation factor of Cd increased with increasing feed SDS/Cd molar ratio and reached a maximum at a feed SDS/Cd molar ratio of 6/1. Beyond this optimum feed molar ratio for the SDS/Cd, the separation factor of Cd decreased remarkably with increasing feed SDS/Cd molar ratio. The results can be explained in that the foamate volumetric ratio only slightly increased with increasing feed SDS/Cd molar ratio at low feed SDS/Cd molar ratios but increased significantly at high feed SDS/Cd molar ratios. However, regarding the requirement of high Cd removal to meet the effluent discharge standards for Cd, a small excess of the feed SDS/Cd molar ratio might be needed to ensure a low residual factor of Cd. By trading off very low Cd and reasonably low SDS concentrations in the effluent, an optimum feed molar ratio of SDS/Cd should be around 8/1 for the studied ion foam fractionation system, which can achieve a very low Cd concentration of 0.06 mg/L. In addition, the effect of feed SDS/Cd molar ratio at a higher foam height (60 cm) also showed similar trends (results not shown here). The effects of other operational parameters will be reported in Part II of this series.

3.5 Conclusions

This study demonstrated the ability of ion foam fractionation to remove Cd²⁺ ions from simulated wastewater at a very low feed Cd concentration of 10 mg/L. In the present work, a multistage ion foam fractionator was found to be a promising technique for heavy metal removal at low heavy metal concentrations in the ppm (mg/L) level. An increase in feed SDS/Cd molar ratio was found to promote Cd removal. This is due to an increase in the ability for foam formation, and the adsorption density of Cd-SDS complex at the bubble surface. However, a very high feed SDS/Cd molar ratio results in producing wetter foam, leading to a lowering of enrichment ratios and separation factors of both Cd and SDS. The studied multistage ion foam fractionation unit—operated at the optimum feed SDS/Cd molar ratio of

8/1, an air flow rate of 60 L/min, a feed flow rate of 40 mL/min, a foam height of 30 cm, a number of trays equal to 5, and a feed Cd concentration of 10 mg/L— provided a very low concentration of Cd in effluent of 0.06 mg/L with a high Cd enrichment ratio of 13.

3.6 Acknowledgements

Financial support from the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program (Grant No, PHD/0059/2550) to the first author is greatly acknowledged. The Research Unit of Applied Surfactant for Separation and Pollution Control under the Ratchadapisak Somphot Fund, Chulalongkorn University, is acknowledged for providing financial support for this research.

3.7 References

- [1] A.B. Mukherjee, A. Kabata-Pendias, Trace Elements From Soil to Human, Springer, New York, 2007.
- [2] R. Gupta, P. Ahuja, S. Khan, R. Saxena, H. Mohapatra, Microbial biosorbents: Meeting challenges of heavy metal pollution in aqueous solutions, *Curr. Sci.* 78 (2000) 967-973.
- [3] T. Kurniawan, G. Chan, W. Lo, S. Babel, Physico-chemical treatment techniques for wastewater laden with heavy metals, *Chem. Eng. J.* 118 (2006) 83-98.
- [4] B.R. Fillipi, J.F. Scamehorn, S.D. Christian, R.W. Taylor, A comparative economic analysis of copper removal from water by ligand-modified micellar-enhanced ultrafiltration and by conventional solvent extraction, *J. Membr. Sci.* 145 (1998) 27-44.
- [5] A.E. Elsherief, Removal of cadmium from simulated wastewaters by electrodeposition on spiral wound steel electrode, *Electrochim. Acta* 48 (2003) 2667-2673.
- [6] M. E. Prudich, Alternative Solid/Liquid Separations, in: R.H. Perry, D.W. Green (Eds.), *Perry's Chemical Engineers' Handbook*, Eighth ed., McGraw-Hill Professional, New York, 2007.

- [7] J. Rubio, M. Souza, R. Smith, Overview of flotation as a wastewater treatment technique, *Miner. Eng.* 15 (2002) 139-155.
- [8] C. Wong, M. Hossain, C. Davies, Performance of a continuous foam separation column as a function of process variables, *Bioprocess Biosyst. Eng.* 24 (2001) 73-81.
- [9] C. Yapijakis, L.K. Wang, Treatment of Soap and Detergent, in: L.K. Wang, Y. Hung, H.H. Lo, C. Yapijakis (Eds.), *Waste Treatment in the Process Industries*, first ed., CRC Press, New York, 2005, pp 307-362.
- [10] P. Stevenson, X. Li, G.M. Evans, A mechanism for internal reflux in foam fractionation, *Biochem. Eng. J.* 39 (2008) 590-593.
- [11] F. Doyle, Ion flotation - Its potential for hydrometallurgical operations, *Int. J. Miner. Process.* 72 (2003) 387-399.
- [12] N. Lazaridis, E. Peleka, T. Karapantsios, K. Matis, Copper removal from effluents by various separation techniques, *Hydrometallurgy* 74 (2004) 149-156.
- [13] Y. Qu, G. Zeng, J. Huang, K. Xu, Y. Fang, X. Li, Recovery of surfactant SDS and Cd^{2+} from permeate in MEUF using a continuous foam fractionators, *J. Hazard. Mater.* 155 (2008) 32-38.
- [14] I. Scorzelli, A. Fragomeni, M. Torem, Removal of cadmium from a liquid effluent by ion flotation, *Miner. Eng.* 12 (1999) 905-917.
- [15] H. Polat, D. Erdogan, Heavy metal removal from waste waters by ion flotation, *J. Hazard. Mater.* 148 (2007) 267-273.
- [16] H. Zheng, Y. Jing, Z. Wu, Study on removal of trace Fe^{3+} from aqueous solution by foam fractionation, *J. Biotechnol.* 136 (2008) S498-S499.
- [17] Z. Liu, F. Doyle, A thermodynamic approach to ion flotation. II. Metal ion selectivity in the SDS-Cu-Ca and SDS-Cu-Pb systems, *Colloids Surf., A* 178 (2001) 93-103.
- [18] S. Choi, K. Kim, The improvement of the removal efficiency of foam flotation by the synergistic effect of mixed surfactant solutions, *Environ. Technol.* 19 (1998) 1151-1156.
- [19] M. Moussavi, M. Javidnejad, Separation of Hg(II) by foam fractionation in the acidic range: Effect of complexation, *J. Hazard. Mater.* 144 (2007) 187-193.
- [20] Q. Li, Z.-L. Wu, Y.-L. Zhao, G.-M. Liu, L. Wang, Removal of trace Cu^{2+} from aqueous solution by foam fractionation, *Chin. J. Process. Eng.* 7 (2007) 679-683.

- [21] T. Kinoshita, S. Akita, Y. Ishigaki, K. Yamaguchi, Y. Yamada, S. Nii, Continuous Foam Separation of Metals Enhanced by Down-Flowing Surfactant Solution from Column Top, *Chem. Eng. Res. Des.* 85 (2007) 229-233.
- [22] S. Boonyasuwat, S. Chavadej, P. Malakul, J.F. Scamehorn, Surfactant Recovery from Water Using a Multistage Foam Fractionator: Part I Effects of Air Flow Rate, Foam Height, Feed Flow Rate and Number of Stages, *Sep. Sci. Technol.* 40 (2005) 1835-1853.
- [23] J. Müslehiddinoglu, Y. Uludag, H. Ozbelge, L. Yilmaz, Determination of heavy metal concentration in feed and permeate streams of polymer enhanced ultrafiltration process, *Talanta* 46 (1998) 1557-1565.
- [24] H. Tsubomizu, R. Horikoshi, K. Yamagiwa, K. Takahashi, M. Yoshida, A. Ohkawa, Effect of perforated plate on concentration of poly(vinyl alcohol) by foam fractionation with external reflux, *J. Chem. Eng. Jpn.* 36 (2003) 1107-1110.
- [25] H.Z. Kister, *Distillation Design*, first ed., McGraw-Hill Professional, New York, 1992
- [26] M.J. Rosen, *Surfactants and Interfacial Phenomena*, third ed., Wiley-Interscience, New York, 2004
- [27] R. Matuura, H. Kimizuka, K. Yatsunami, The study of the adsorption of detergents at a solution-air interface by radiotracer method. III. The effect of inorganic electrolytes on the adsorption of Sodium dodecyl sulfate, *Bull. Chem. Soc. Jpn.* 32 (1959) 646-650.
- [28] K. Kubota, S. Hayashi, Y. Takubo, Fundamental studies of foam fractionation of cadmium: Effect of the addition of monovalent ions on surface excess of cadmium, *Can. J. Chem. Eng.* 57 (1979) 591-598.
- [29] K. Marinova, E. Basheva, B. Nenova, M. Temelska, A. Mirarefi, B. Campbell, I. Ivanov, Physico-chemical factors controlling the foamability and foam stability of milk proteins: Sodium caseinate and whey protein concentrates, *Food Hydrocolloids* 23 (2009) 1864-1876.
- [30] T.F. Svitova, M.J. Wetherbee, C.J. Radke, Dynamics of surfactant sorption at the air/water interface: Continuous-flow tensiometry, *J. Colloid Interface Sci.* 261 (2003) 170-179.

- [31] S. Pandey, R. P. Bagwe, D. O. Shah, Effect of counterions on surface and foaming properties of dodecyl sulfate, *J. Colloid Interface Sci.* 267 (2003) 160-166.
- [32] G. Para, E. Jarek, P. Warszynski, The Hofmeister series effect in adsorption of cationic surfactants-theoretical description and experimental results, *Adv. Colloid Interface Sci.* 122 (2006) 39-55.
- [33] Code of Practice on Pollution Control (2000 Edition) (with amendments in Feb 2001, Jun 2002 and Feb 2004)