

CHAPTER IV
REMOVAL OF TRACE Cd²⁺ USING CONTINUOUS MULTISTAGE ION
FOAM FRACTIONATION: PART II—THE EFFECTS OF OPERATIONAL
PARAMETERS

4.1 Abstract

A multistage ion foam fractionation column with bubble-cap trays was employed to study the removal of cadmium ions from simulated wastewater having low Cd concentrations (10–30 mg/L), examining the effects of foam height, air flow rate, feed flow rate, and feed Cd concentration. Sodium dodecyl sulfate (SDS) was used to generate foam in this study. An increase in foam height, which reduces liquid hold-up in the generated foam, resulted in the enhancement of the enrichment ratios of both SDS and Cd while the removal and residual factor of Cd showed insignificant change. An increase in air flow rate increased the foam generation rate, foamate volumetric ratio, and the removal efficiency of Cd but decreased the enrichment ratios of both Cd and SDS. The separation factors of both Cd and SDS decreased with increasing feed flow rate, which is mainly attributable to both the effects of the enhancement of foamate volumetric ratio and the increases in both SDS and Cd input rates. An increase in feed Cd concentration was found to increase Cd effluent concentration and SDS removal but to decrease the enrichment ratios of both Cd and SDS because of the increasing liquid entrainment in the produced foam.

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

4.2 Introduction

Ion foam fractionation is an adsorptive bubble separation process in which a surface active compound adsorbs preferentially at the air–water interface or the bubble surface of the foam, and the generated foam is subsequently separated from the bulk liquid (1). Hence, the removal of dissolved substances involves the differences in their distribution or partitioning between the air–water interface and the bulk aqueous phase. The adsorption of a surface active agent on the air–water interface of foam depends on the standard free energy change (ΔG°) involved in the transfer of the surfactant molecules from the interior of the bulk liquid phase to the air–water interface, which relates to the negative logarithm of surfactant concentration in the bulk phase required to obtain a surface pressure of 20 mN/m, called surface activity (2). If a system contains any oppositely charged ions, they can co-adsorb on the air–water interface of the generated foam, depending on the ability of these ions to penetrate the surface layer (Stern layer) of the adsorbed surfactant molecules. As a result, the coadsorption of the oppositely charged ions results in the neutralization of the adsorbed surfactant molecules (3).

In an ion foam fractionation operation, air is introduced into a liquid pool to generate air bubbles. The air bubbles, with adsorbed materials (surface active agent and oppositely charged ions), then proceed upwards to the liquid surface to produce foam. This foam (froth) is carried upward to the top of the column while the interstitial liquid with small amounts of surfactant and oppositely charged ions drains out from the foam phase. The collected foam at the top of the column is collapsed into a solution termed the foamate. As a result, both the surface active agent and the attached species are separated from the bulk liquid. However, some of the entrained interstitial liquid with unadsorbed materials is also carried with the foam phase (froth). The concentration of a component in the foamate depends on the volume fraction of entrained liquid and the adsorbed amount of material on the foam surface. Due to the liquid film drainage by gravitational forces, a small fraction of liquid is generally carried with the produced foam and the concentration of any component in the foamate can be much higher than that in the feed. The molar flow rate of a component in the foamate is governed by both the adsorptive transport and the bulk

liquid transport. The adsorptive transport and bulk liquid transport are referred to as material transfers by the adsorption on the bubble surface and the entrained liquid in the foam lamella, respectively. The former is an upward stream of adsorbed material on the foam surface without carrying liquid while the latter is an upward stream of lamella liquid with unadsorbed molecules, known as the entrained liquid. The adsorptive transport can be expressed as $A\Gamma$, which is the product of the flow rate of the interfacial area (A , cm^2/min) and the surface excess concentration (Γ , mol/cm^2), and is responsible for the reduction in the residual factor of a component (concentration in effluent/concentration in feed). The bulk liquid transport can increase the amount of a component found in the foam phase only when the concentration of the unadsorbed molecules in the bulk liquid and the volumetric flow rate of foam are significantly large. However, in general, the bulk liquid transport also carries the liquid to the foam phase, reducing both the enrichment ratio (concentration in foamate/concentration in feed) and the separation factor (concentration in foamate/concentration in effluent) in contrast to the adsorptive transport (4).

The effects of operational parameters on surfactant recovery by foam fractionation were studied by several authors (5,6,7,8). An increase in the interfacial area of the generated foam, by increasing gas flow rate, causes an increase in the removal of surfactant. However, a low gas flow rate, is in general, beneficial for separation efficiency in terms of higher enrichment ratio (6). A dryer foam can be obtained by increasing the foam height. As a result, the generated foam has a longer residence time, leading to increasing liquid film drainage. Hence, at the top, the foam becomes dry while at the bottom it remains wet (7). Temperature has little effect on the separation efficiency of foam fractionation (8,9,10). However, despite many attractive features of foam fractionation, few papers on continuous ion foam fractionation for heavy metal removal have been published in the last decade (9,11).

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 a single-stage system, especially in terms of the enrichment ratio and the percent recovery of the surfactant (12). In this work, we extend the application of continuous multistage foam

fractionation with bubble-cap trays for the removal of trace heavy metals at low concentrations. The effect of feed SDS/Cd molar ratio was discussed in Part I of this work (4). The purpose of Part II of this present work was to evaluate the effects of air flow rate, foam height, feed flow rate, and feed Cd concentration on Cd removal at low feed Cd concentrations.

4.3 Experimental

4.3.1 Materials

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

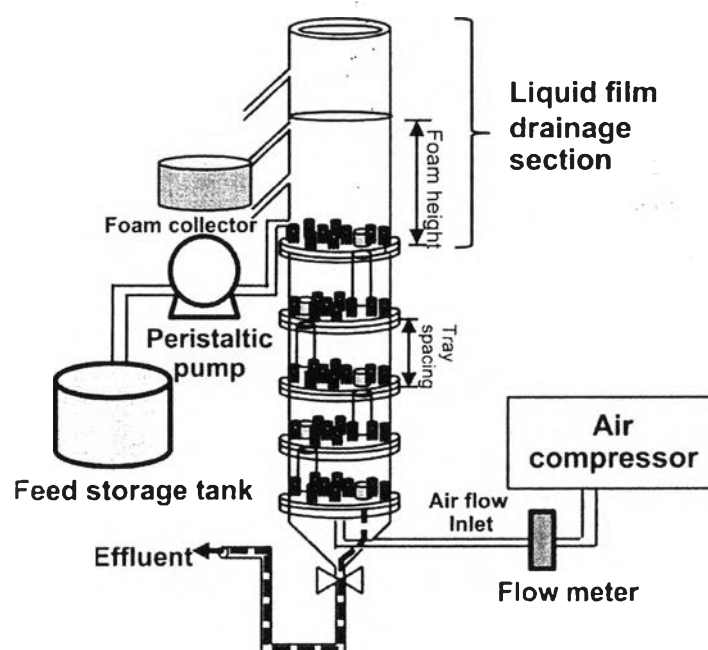


Figure 4.1 Schematic of a multistage foam fractionation unit.

4.3.2 Multistage Ion Foam Fractionation System

Figure. 4.1 shows the experimental set-up of the multistage ion foam fractionation unit used in this study. It consisted of three main parts: an air supply unit, a feed unit, and an ion foam fractionation column. The multistage foam fractionation column was made of acrylic cylinders having an inside diameter of 17.4 cm with 22 bubble caps in each tray and it was able to be assembled with up to five trays. The height of each tray (tray spacing) was 15 cm. On the top tray, the column was connected with an acrylic pipe having the same inside diameter and different outlet pipes to obtain foam heights of 30, 60, and 90 cm. In each tray, the liquid level was designed to be 3 cm by the weir height of a downcomer having a 4 cm diameter to allow liquid flow down to a lower tray. A sample port was located at the base of each tray for taking liquid samples.

4.3.3 Methodology

The ion foam fractionation system was operated in continuous mode in this study. A feed solution containing different Cd and SDS concentrations was prepared by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and SDS in deionized water. 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 range of 1–4 $\text{L}/\text{m}^2 \text{ min}$, by using a peristaltic pump. Compressed air from an air compressor was introduced under the bottom tray and was regulated by rotameter to have flow rates in the range of 30–100 L/min. The experiments were carried out at room temperature (25–27 °C) because of the insignificant influence of temperature on foam fractionation performance (9,10). The foam was collected at the top of the column at different foam heights (30, 60, and 90 cm) from the liquid pool of the top tray. The collected foam was left to collapse by itself to obtain the foamate. Samples of the feed solution, the collapsed foam, and the effluent were collected after steady state conditions (around six hours). The steady state condition was justified when all measured parameters were invariant with time. The volumetric flow rates of both foamate and effluent were also measured. All samples were acidified with concentrated nitric acid to a pH just below 2 for preservation before the determination of surfactant and Cd ion concentrations. The data obtained from at

least three runs were averaged and used to assess the process performance of the multistage ion foam fractionation system. By performing mass balances of Cd and SDS, the average error was found to be less than 10 %. Various evaluating parameters were used to assess the process performance of the studied multistage ion foam fractionation system, including the enrichment ratios of SDS and Cd, SDS recovery, Cd removal, foamate volumetric ratio, the residual factors of SDS and Cd, and the separation factors of SDS and Cd (13), as expressed below:

$$\text{Enrichment ratio} = C_f / C_i, \quad (4.1)$$

$$\% \text{ SDS recovery or } \% \text{ Cd removal} = (V_i C_i - V_e C_e) (100) / (V_i C_i), \quad (4.2)$$

$$\text{Residual factor} = C_e / C_i, \quad (4.3)$$

$$\text{Foamate volumetric ratio} = V_f / V_i, \quad (4.4)$$

$$\text{Separation factor} = C_f / C_e, \quad (4.5)$$

where C_f and C_i are the SDS or Cd concentration 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. V_i , V_f , and V_e are the volumetric flow rate of feed, foamate, and effluent, respectively.

4.3.4 Analytical Methods

The concentration of SDS was measured by using a total organic carbon analyzer (Shimadzu, TOC-VCSH). The concentration of Cd ions was determined by an atomic adsorption spectrophotometer (AAS, Varian, SpectrAA 300) at a recommended wave length of 228.8 nm. The procedure for determining Cd concentration was carried out with consideration of the effect of SDS interference, referring to the procedure reported in literature (14) and Part I of this work (4). A cadmium standard solution containing SDS at the same concentration as in the diluted sample was used for obtaining a calibration curve. The measurement range of cadmium with high accuracy is 0.02–3 mg/L, according to the AAS specification. Therefore, all sample solutions were diluted to approximately 1 mg/L Cd concentration before the determination.

4.3.5 Surface Tension Measurement

The surface tension was measured by using a drop shape analysis instrument (Kruss, DSA 10). The pendant drop 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. The adsorption density of dodecyl sulfate ions (DS^-) was calculated by using the Gibb adsorption equation (15).

4.4 Results and Discussion

4.4.1 Effect of Foam Height

Both air and liquid flow rates must be in appropriate ranges in order to successfully operate an ion foam fractionation system. The operational zone of the studied unit for multistage ion foam fractionation was determined and presented in Part I of this work (4). In the present study, an air flow rate of $60 \text{ dm}^3/\text{min}$ and a feed flow rate of $40 \text{ mL}/\text{min}$, located in the operational zone, were selected to run the multistage ion foam fractionation column in order to observe the effect of foam height on separation efficiency. A lowest feed SDS/Cd molar ratio of 8/1 was found to be necessary to produce a sufficiently stable foam capable of reaching to reach a foam height of 90 cm (4). The effect of the feed SDS/Cd molar ratio on the separation performance of both Cd and SDS was explained in our previous work (4).

For any given feed SDS/Cd molar ratio, an increase in foam height results in an enhancement in the enrichment ratios of both SDS and Cd, especially at the highest foam height (90 cm), as shown in Figure 4.2a. This is because the increase in foam height increases the foam residence time, which allows more drainage of the liquid in the foam films, as indicated by the large decrease in foamate volumetric ratio with increasing foam height (see Figure 4.2b). This decrease suggests that the bulk liquid transport is reduced with increasing foam height. In a comparison between the two feed SDS/Cd molar ratios, different degrees of liquid film drainage and different enrichment ratios were observed. It was found that the

foamate volumetric ratio at a foam height of 30 cm was much larger for the system with the higher feed SDS/Cd molar ratio, suggesting that wetter foam is created at a higher feed SDS/Cd molar ratio of 10/1. The effect of feed SDS/Cd molar ratio on the reduction in the enrichment ratios was much more profound at the higher foam height of 90 cm as compared to the lower foam height of 30 cm and 60 cm. The results can be explained by the fact that the foamate volumetric ratio decreased significantly with increasing foam height (Figure 4.2b). Interestingly, the slope of the foamate volumetric ratio versus foam height (foam residence time) relationship was found to be steeper for the system with the higher feed SDS/Cd molar ratio, suggesting a higher rate of liquid film drainage with decreasing feed SDS/Cd molar ratio. This is most likely because Gibbs–Marangoni effects are suppressed at high bulk surfactant concentrations, leading to a very high liquid drainage rates in the produced foam (16).

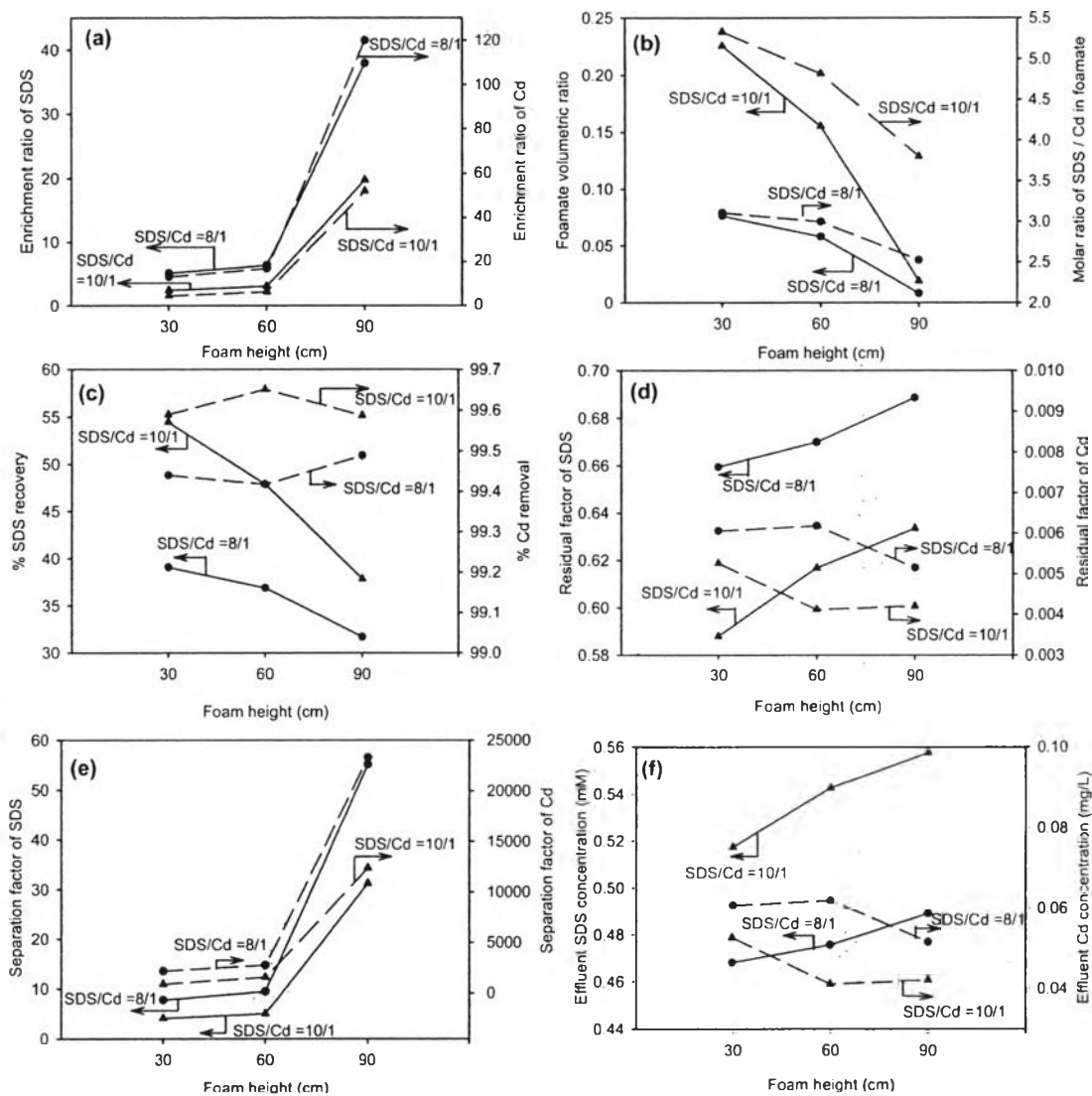


Figure 4.2 Effect of foam height on (a) the enrichment ratios of Cd and SDS; (b) foamate volumetric ratio and molar ratio of SDS/Cd in foamate; (c) SDS recovery and Cd removal; (d) the residual factors of SDS and Cd; and (e) the separation factors of SDS and Cd; and (f) effluent SDS and Cd concentration at air flow rate = $60 \text{ dm}^3/\text{min}$, feed flow rate = $40 \text{ mL}/\text{min}$, number of trays = 5, feed Cd concentration = $10 \text{ mg}/\text{L}$, and two feed SDS/Cd molar ratios of 8/1 and 10/1.

An increase in foam height leads to a significant decrease in SDS recovery for any given feed SDS/Cd molar ratio, as shown in Figure 4.2c. This is because of the loss of a significant amount of SDS with the downward draining

liquid (the decrease in bulk liquid transport with increasing foam height), as indicated by the increase in the SDS concentration in the effluent with increasing foam height, as shown in Figure 4.2f. This explanation can be also supported by the fact that the SDS recovery mirrors the foamate volumetric ratio for both feed SDS/Cd molar ratios, as shown in Fig(s). 2b and 2c. The reduction in SDS recovery was found to be more pronounced for the system with the higher feed SDS/Cd molar ratio because of the larger decrease in foamate volumetric ratio.

An increase in foam height increases the residual factor of SDS for both feed SDS/Cd molar ratios, as shown in Figure 4.2d. This is because an increase in the drainage rate of the liquid from the produced foam simply increases the SDS concentration in the effluent. However, the Cd removal and the residual factor of Cd almost remain unchanged with increasing foam height, as shown in Figures 4.2c and 4.2d. These results indicate that the draining liquid contains an insignificant amount of unadsorbed Cd while most Cd ions co-adsorb with the SDS onto the foam interface (17,18), as mentioned before in our previous work (4). Hence, a reduction of the bulk liquid transport does not decrease the molar flow rate of Cd in the foamate and does not significantly increase the concentration of Cd in the effluent. From the results, it can be concluded that the molar flow rate of Cd in the foamate and the residual factor of Cd are mainly governed by adsorptive transport.

Figure 4.2b shows the effect of foam height on the molar ratio of SDS/Cd in the foamate. For both feed molar SDS/Cd molar ratios, the molar ratio of SDS/Cd in the foamate decreased with increasing foam height. This suggests that, with increasing foam height, a decrease in the contribution of the bulk liquid transport of SDS to the molar flow rate of SDS in foamate becomes prominent. At the lowest foam height of 30 cm, the system generated wet foam, which contains a larger amount of bulk liquid with relatively high SDS concentration and a lower Cd concentration than those of dry foam. At the highest foam height of 90 cm, the foam is extremely dry and the effect of the bulk liquid transport on the molar ratio of SDS/Cd in the foamate is less pronounced. The molar ratio of SDS/Cd in the foamate at a foam height of 90 cm and a feed SDS/Cd molar ratio of 8/1 was found to be 2.5, suggesting that most free DS^- sites at the bubble surface are occupied by Cd^{2+} ions, and the adsorbed surfactant ions are totally neutralized by the Cd counterions,

whereas the value of the molar ratio of SDS/Cd in the foamate are much larger than 2 (the theoretical ratio) for the system with a feed SDS/Cd molar ratio of 10/1 at any foam height, suggesting that, beside the co-adsorption of cadmium ions, some sodium ions also co-adsorb at the interface due to excess sodium ions in the system with the high feed SDS/Cd ratio of 10/1.

Figure 4.2e shows the effects of foam height on the separation factors of SDS and Cd at two feed molar ratios of SDS/Cd. The separation factors showed to have the same trend as the enrichment ratios for both Cd and SDS. The separation factors of both were enhanced with increasing foam height due to the increase in liquid film drainage (the reduction of bulk liquid transport). The effect of foam height became more prominent as the foam height increased from 60 to 90 cm. These results suggest that the liquid film drainage is an important mechanism for enhancing separation efficiency in a foam fractionation process.

Figure 4.2f shows the effect of foam height on both SDS and Cd concentrations in the effluent. For both feed SDS/Cd molar ratios, the SDS concentration in the effluent increased with increasing foam height. This is because an increase in foam height causes an increase in foam residence time, leading to increasing liquid film drainage. In contrast, the Cd concentration in the effluent slightly decreased with increasing foam height. The result can be also explained by the fact that most Cd^{2+} ions co-adsorb with DS^- ions on the air–water interface of the produced foam.

4.4.2 Effect of Air Flow Rate

The effect of air flow rate on the separation efficiency of the studied multistage ion foam fractionation system was investigated by varying the air flow rate in the range of 40 to 100 dm^3/min , while the other operational parameters were fixed at a feed flow rate of 40 mL/min, a foam height of 60 cm, the number of trays at 5, and two levels of feed molar ratios of SDS/Cd (7/1 and 10/1). The lowest feed SDS/Cd molar ratio of 7/1 was used to operate the studied multistage ion foam fractionation unit because it could produce sufficiently stable foam. For any given feed SDS/Cd molar ratio, the enrichment ratios of both SDS and Cd decrease with increasing air flow rate, as shown in Figure 4.3a. The results can be explained by the

fact that the foamate volumetric ratio increased with increasing air flow rate (Figure 4.3b). This increase in foamate volumetric ratio indicates an increase in the bulk liquid transport. As a consequence, the foamate contained more water fraction and less SDS and Cd concentrations, leading to lowering enrichment ratios.

As shown in Figure 4.3c, both SDS recovery and Cd removal increase with increasing air flow rate for both feed SDS/Cd molar ratios. The large increase in Cd removal with increasing air flow rate from 40 to 60 dm³/min is due to the increase in the adsorptive transport, as supported by the results of Cd residual factor, which decreased significantly with increasing air flow rate from 40 to 60 dm³/min (Figure 4.3d). The small increase in Cd removal with increasing air flow rate beyond 60 dm³/min, indicating the increase in the bulk liquid transport, as supported by the increase in foamate volumetric ratio (Figure 4.3b) and the unchanged residual factor of Cd at air flow rates beyond 60 dm³/min (Figure 4.3d). However, the large increase in SDS recovery with increasing air flow rate is due to both mechanisms. This explanation can be also supported by the fact that the profile of SDS recovery mirrors that of the foamate volumetric ratio for both feed SDS/Cd molar ratios, as shown in Figures 4.3b and 4.3c. The molar ratio of SDS/Cd in the foamate increased with increasing air flow rate and it mirrored the foamate volumetric ratio, suggesting that an increasing air flow rate can increase both adsorptive and bulk liquid transport and, at very high air flow rates, the bulk liquid transport becomes predominantly. However, at an extremely high air flow rate, the system cannot produce stable foam (as explained later), causing the system to reach a maximum separation performance.

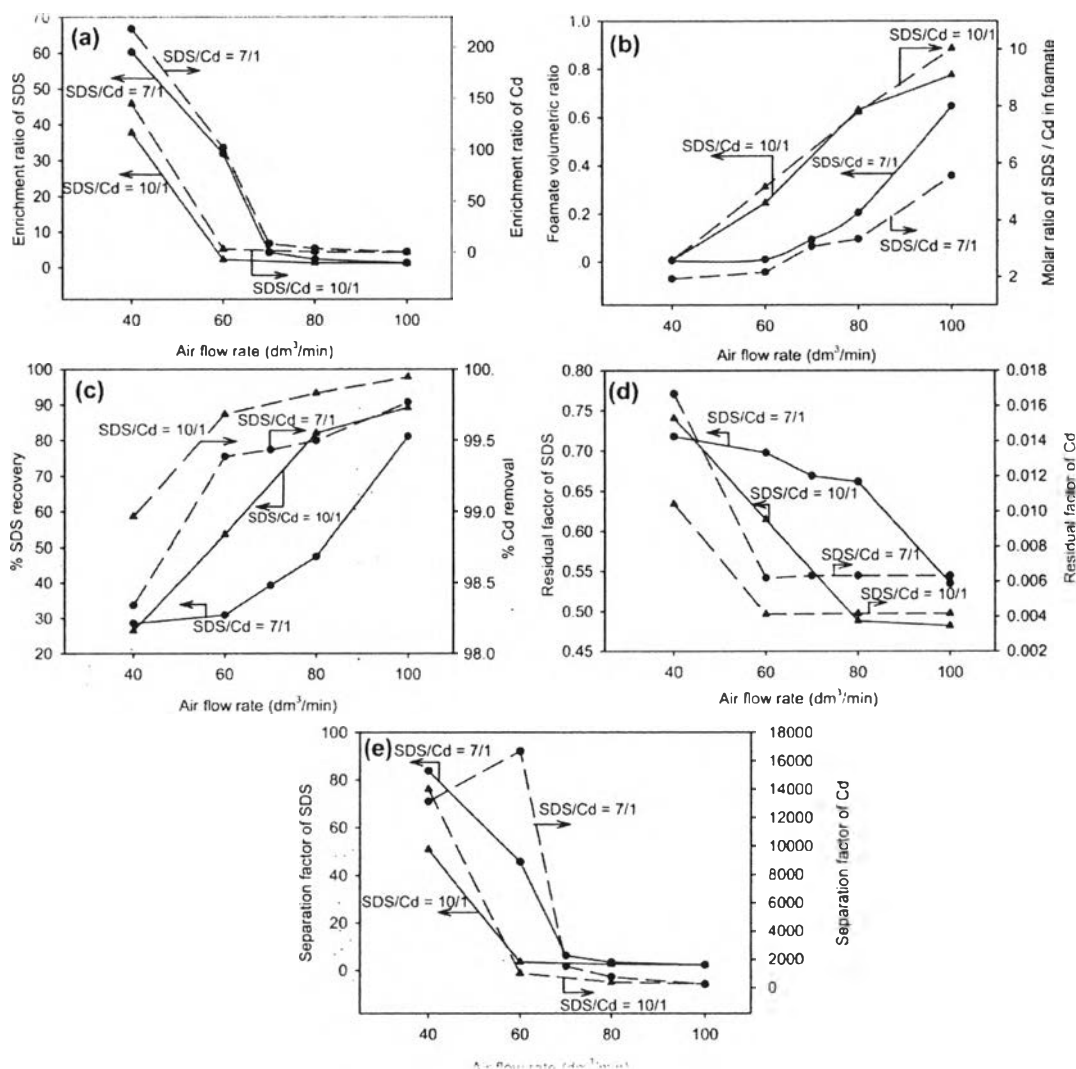


Figure 4.3 Effect of air flow rate on the enrichment ratios of Cd and SDS (a); foamate volumetric ratio and molar ratio of SDS/Cd in foamate (b); SDS recovery and Cd removal (c); the residual factors of SDS and Cd (d); and the separation factors of SDS and Cd (e) at foam height = 60 cm, feed flow rate = 60 mL/min, number of trays = 5, feed Cd concentration = 10 mg/L, and two feed molar ratios of SDS/Cd of 7/1 and 10/1.

The residual factor of Cd decreases significantly with increasing air flow rate from 40 to 60 dm³/min and levels off at air flow rates beyond 60 dm³/min for any given feed SDS/Cd molar ratio, as shown in Figure 4.3d. The rapid decrease in the residual factor of Cd with increasing air flow rate from 40 to 60 dm³/min is

mainly due to the increase in bubble surface area flow rate, leading to the increase in the adsorptive transport. When the air flow rate was further increased beyond 60 dm³/min, the residual factor of Cd remained unchanged. This is because, at higher air flow rates (more than 60 dm³/min), the surface flow rate of the produced foam reached a maximum, leading to the minimum of Cd residual factor. In comparisons between two feed SDS/Cd molar ratios, the higher the feed SDS/Cd molar ratio, the lower the residual factor of Cd. This is because the system with a higher feed SDS/Cd molar ratio can provide more adsorption sites for Cd ions to co-adsorb onto the foam surface.

Similarly, the residual factor of SDS decreases significantly with increasing air flow rate for any given feed SDS/Cd molar ratio, as shown in Figure 4.3d. The decrease in the residual factor of SDS with increasing air flow rate is attributed to the increase in adsorptive transport as confirmed by the increase in foam generation rate (as visually observed). However, the residual factor of SDS almost reached a minimum at an air flow rate above 80 dm³/min for the system with a feed SDS/Cd molar ratio of 10/1. This is because the system was operated at a very high air flow rate to remove most of SDS and so the system contained a very low SDS concentration, which could not produce stable foam, as visually observed that both tray 3 and tray 4 could not produce stable foam.

Figure 4.3e shows the effect of air flow rate on the separation factors of SDS and Cd. Similar to the residual factor, the separation factors of SDS and Cd tended to decrease with increasing air flow rate and reached minimum at high air flow rates. The separation factor (Equation 4.5) can be derived from the term of the enrichment ratio (Equation 4.1) divided by the residual factor (Equation 4.3) of either SDS or Cd. Therefore, the same explanation for the effect on the residual factors and enrichment ratios can be also used for that on the separation factor. As shown in Figure 4.3e, with focusing on Cd removal, the air flow rate of 60 dm³/min, corresponding to an air flow flux of 2500 L/ m² min, seems to provide both reasonably high Cd removal with a low residual factor of Cd and high SDS recovery for both studied feed SDS/Cd molar ratios even though the enrichment ratios and separation factors were low. Hence, this air flow rate of 60 dm³/min was selected to investigate the effect of feed flow rate.

4.4.3 Effect of Feed Flow Rate

The effect of feed flow rate on separation efficiency was investigated under two different conditions. For the first condition (A), representing wet foams (low liquid film drainage), indicating that the system separation performance is governed by the bulk liquid transport, the studied system was operated at a foam height of 60 cm (a low foam height), an air flow rate of 60 dm³/min, a feed molar ratio of SDS/Cd of 10/1, the number of trays at 5, and various feed flow rates in the range of 25–100 mL/min. For the second condition (B), representing dry foams (high liquid film drainage), indicating that the system is controlled by the adsorptive transport, the studied system was operated under the same conditions except that the foam height was increased to 90 cm (a high foam height).

Under the wet foam condition (A), an increase in feed flow rate decreases the enrichment ratios of both SDS and Cd, as shown in Figure 4.4a. This is mainly due to an increase in the bulk liquid transport, causing a dilution of adsorbed molecules on the air–water interface of the produced foam, as indicated by the increase in foamate volumetric ratio with increasing feed flow rate (see Figure 4.4b). In contrast, for the dry foam condition (B), the enrichment ratios of both SDS and Cd changed slightly with increasing feed flow rate. This is because the foamate volumetric ratio decreases slightly with increasing feed flow rate, as shown in Figure 4.4b. The results suggest that, in the case of wet foam, an increase in feed flow rate increases the bulk liquid transport, leading to increasing water content in the foam. When the foam height was increased from 60 to 90 cm, the system produced dry foams (B). As a result, the enrichment ratios of both SDS and Cd did not change with feed flow rate, indicating that the system performance is governed by adsorptive transport. These two studied conditions, wet foam (A) and dry foam (B), can be easily differentiated by the difference in the foamate volumetric ratio, as shown in Figure 4.4b.

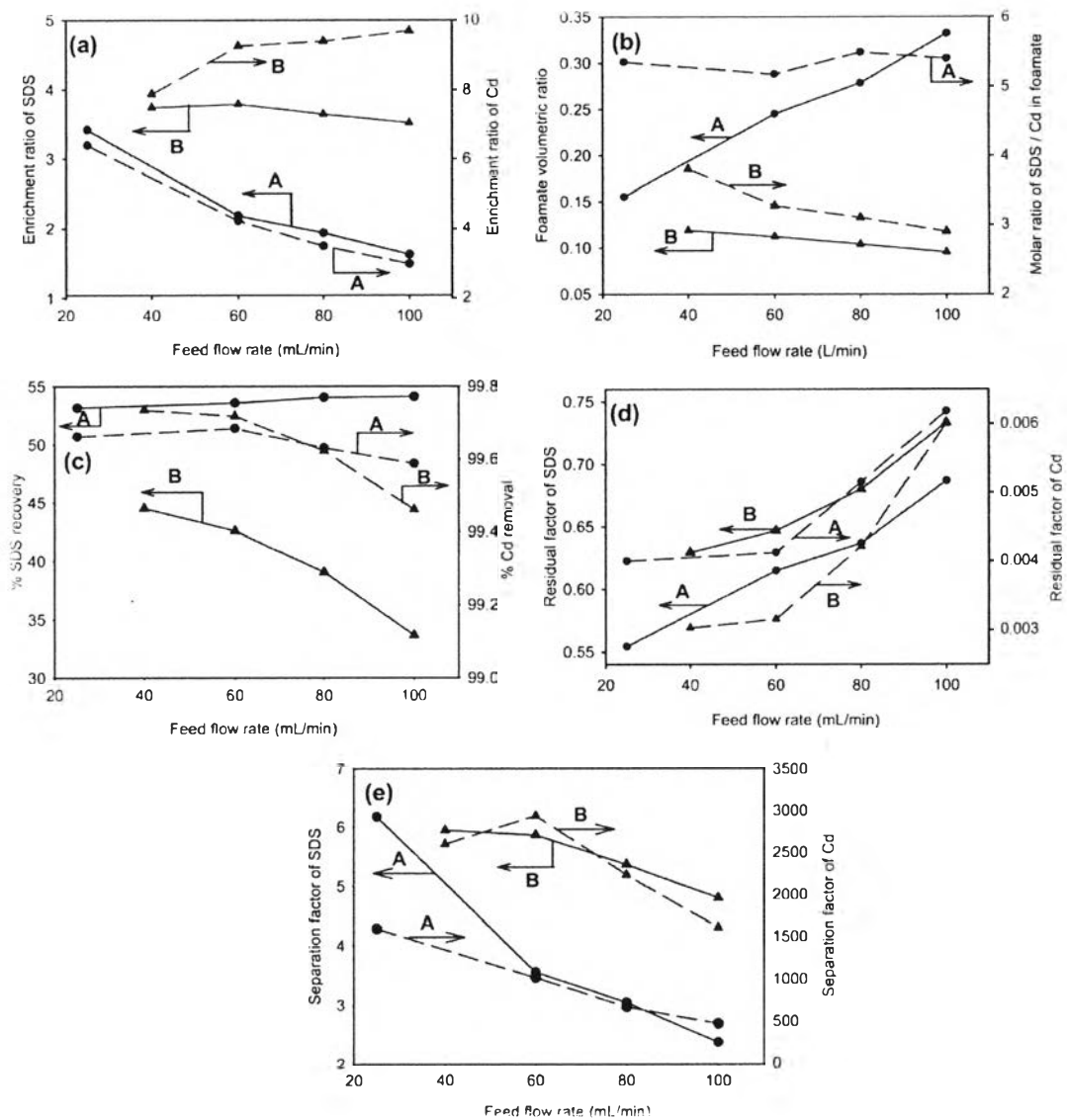


Figure 4.4 Effect of feed flow rate on the enrichment ratios of Cd and SDS (a); foamate volumetric ratio and molar ratio of SDS/Cd in foamate (b); SDS recovery and Cd removal (c); the residual factors of SDS and Cd (d); and the separation factors of SDS and Cd (e) at two conditions. (Condition A (wet foam): foam height = 60 cm, air flow rate = 60 dm³/min, SDS/Cd = 10/1, feed Cd concentration = 10 mg/L, and number of trays = 5 and Condition B (dry foam): foam height = 90 cm, air flow rate = 60 dm³/min, SDS/Cd = 10/1, feed Cd concentration = 10 mg/L, and number of trays = 5).

As shown in Figure 4.4b, the molar ratio of SDS/Cd in the foamate remains almost unchanged with increasing feed flow rate for wet foam condition (A), suggesting that the increase in feed flow rate leads to increasing liquid content in produced foam, which does not increase the concentrations of both SDS and Cd in foamate. This explanation can be supported by the equal reduction of the enrichment ratios of both SDS and Cd and the increase in foamate volumetric ratio with increasing feed flow rate. However, in the case of the dry foam condition (B), the molar ratio of SDS/Cd in the foamate decreased slightly with increasing feed flow rate which well corresponded with the slight decrease in foamate volumetric ratio.

Under steady state condition, the Cd removal and SDS recovery can be related to the molar flow rates of Cd and SDS in foamate, respectively, resulting from both adsorptive and bulk liquid transports. The SDS recovery increases slightly with increasing feed flow rate, whereas the Cd removal decreases slightly for the system under the wet foam condition (low liquid film drainage), as shown in Figure 4.4c. However, in the case of the system with dry foam (B), both SDS recovery and Cd removal significantly decreased with increasing feed flow rate. These results suggest that the increasing bulk liquid transport (wet foam condition) provides an unequal degree of bulk liquid transport between Cd and SDS, especially at high feed flow rates. The SDS recovery is promoted predominantly by the increase in bulk liquid transport as compared with the Cd removal because the entrained liquid contains predominantly SDS with a very small amount of Cd and most Cd ions adsorb preferentially at the foam surface. In other word, the Cd removal is not promoted by the increasing bulk liquid transport (wet foam condition) but is mainly governed by the adsorptive transport, as further discussed below.

Figure 4d shows the effect of feed flow rate on the residual factors of both SDS and Cd under wet and dry foam conditions. The Cd removal and the residual factor of Cd remained unchanged at low feed flow rates (not higher than 60 mL/min) for both wet and dry foam conditions. However, the Cd removal decreased with increasing feed flow rate beyond 60 mL/min whereas the residual factor of Cd increased significantly for both wet foam (A) and dry foam (B). These results suggest that the surface area flow rate is sufficiently available for the Cd adsorption at feed flow rates below 60 mL/min, whereas it is not sufficient at high feed flow

rates. On the other hand, the residual factors of SDS increased significantly with increasing feed flow rate for both studied foam conditions, suggesting that the surface area flow rate is not sufficient for SDS adsorption, in the studied range of feed flow rate. Thus it can be concluded that the adsorptive transport is not promoted by increasing the feed flow rate.

As shown in Figure 4.4e, the separation factors of both SDS and Cd decrease markedly with increasing feed flow rate for both studied foam conditions (A and B). This suggests that the reduced separation factors are influenced mainly by an increase in the residual factors of SDS and Cd. In comparisons between the two foam conditions, dry and wet, the dry foam system (B) provides much higher separation factors for both SDS and Cd than the wet foam system (A), suggesting that the bulk liquid transport has to be minimized in order to achieve maximum separation factors of both SDS and Cd. A feed flow rate of 80 mL/min was selected for further investigation because it was the highest feed flow rate to provide sufficiently high Cd removal.

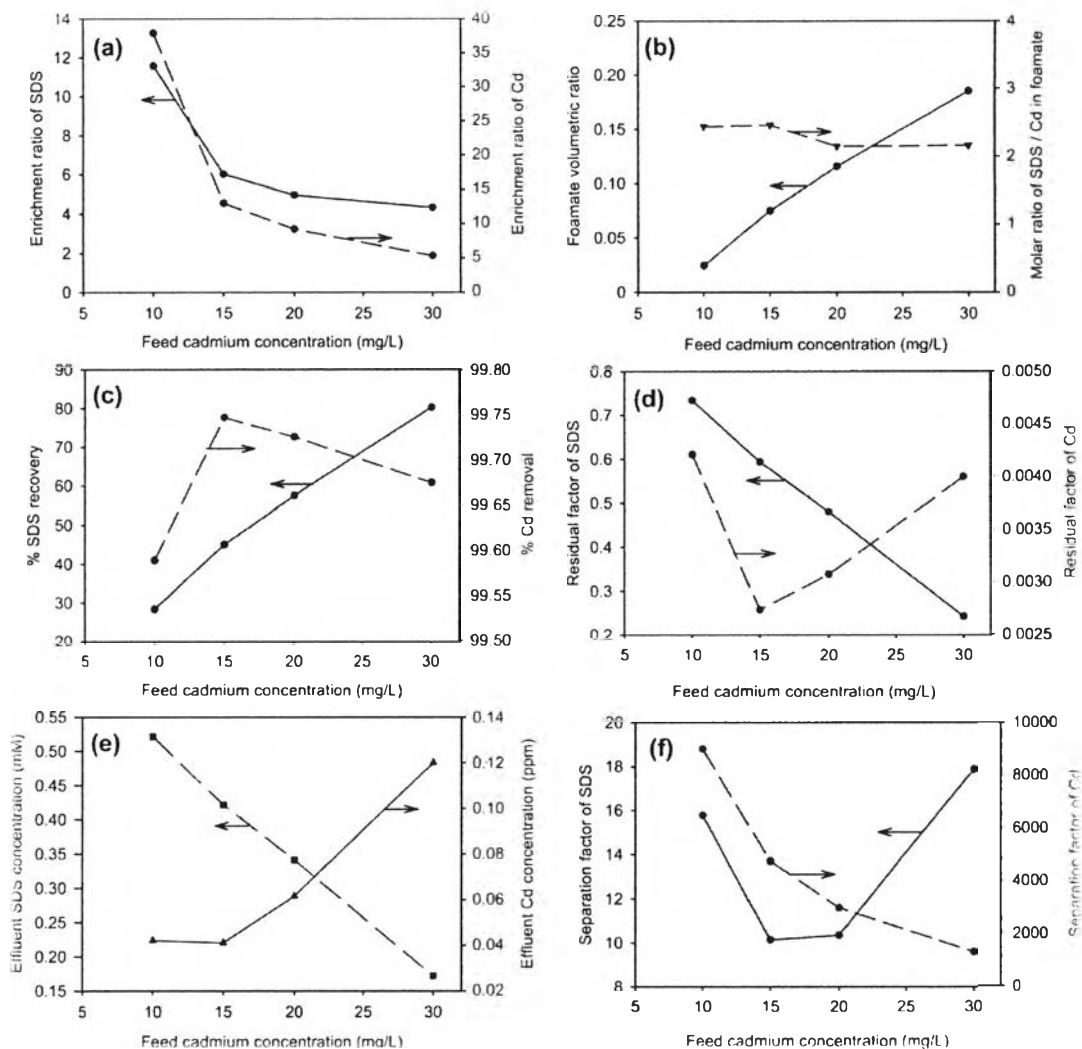


Figure 4.5 Effect of feed Cd concentration on the enrichment ratios of Cd and SDS (a); foamate volumetric ratio and molar ratio of SDS/Cd in foamate (b); SDS recovery and Cd removal (c); the residual factor of SDS and Cd (d); effluent Cd and SDS concentration (e); and the separation factor of SDS and Cd (f) at foam height = 90 cm, feed flow rate = 80 mL/min, air flow rate = 60 dm³/min, feed SDS concentration = 0.71 mM, and number of trays = 5.

4.4.4 Effect of Feed Cd Concentration

The effect of feed Cd concentration was investigated under the following conditions: a feed SDS concentration of 0.71 mM (corresponding to an optimum feed SDS/Cd molar ratio of 8/1 at a feed Cd concentration of 10 mg/L), a

foam height of 90 cm, an air flow rate of 60 dm³/min, a feed flow rate of 80 mL/min, and the number of trays at 5. These base conditions used in the experiment were selected according to the present results and from our previous work (4). An increase in feed cadmium concentration decreases sharply the enrichment ratios of both SDS and Cd, as shown in Figure 4.5a. This is because an increase in feed Cd concentration increases the foam production rate, as indicated by an increasing foamate volumetric ratio, as shown in Figure 4.5b. The increase in foamate volumetric ratio with increasing feed concentration will be discussed in detail later. Interestingly, the residual factor of SDS linearly decreases to be less than 0.3 and the % SDS recovery increases almost linearly with increasing feed Cd concentration, as shown in Figures 4.5d and 4.5c, respectively. The effluent SDS concentration also decreases linearly with increasing feed Cd concentration, as shown in Figure 4.5e. These results suggest that the ability of the SDS solution to form a sufficiently stable foam to pass through the column, foamability, is promoted significantly with increasing the Cd concentration (19). Without the addition of Cd, it was found that the SDS solution (0.71 mM) could not generate even 1 cm of steady foam height, and thus no separation occurred in the studied foam fractionation column (results not shown here). Under the presence of Cd in feed at approximately 10 mg/L, it was found that the minimum SDS concentration required to provide a steady-state foam to pass through all of the trays of the studied multistage ion foam fractionation column was about 0.4–0.5 mM at any air and feed flow rates (4). As a result, a significant amount of SDS was found in the effluent. The enhancement in foamability with increasing feed Cd concentration can be explained by the fact that the addition of an electrolyte to an SDS solution can promote both surfactant adsorption and adsorption kinetics on the air–water interface because it can decrease the free energy for forming a charged monolayer (20) and can enhance the Gibbs free energy of adsorption (pC_{20}), leading to a higher tendency for SDS and Cd to adsorb at the air–liquid interface because of the reduction of electrostatic repulsion between the ionic hydrophilic groups of the Cd²⁺ and the dodecyl sulfate ion (DS⁻) (2). This is supported by the increase in pC_{20} with increasing Cd concentration, as shown in Figure 4.6a. Consequently, the foamability of SDS increases with increasing feed Cd concentration.

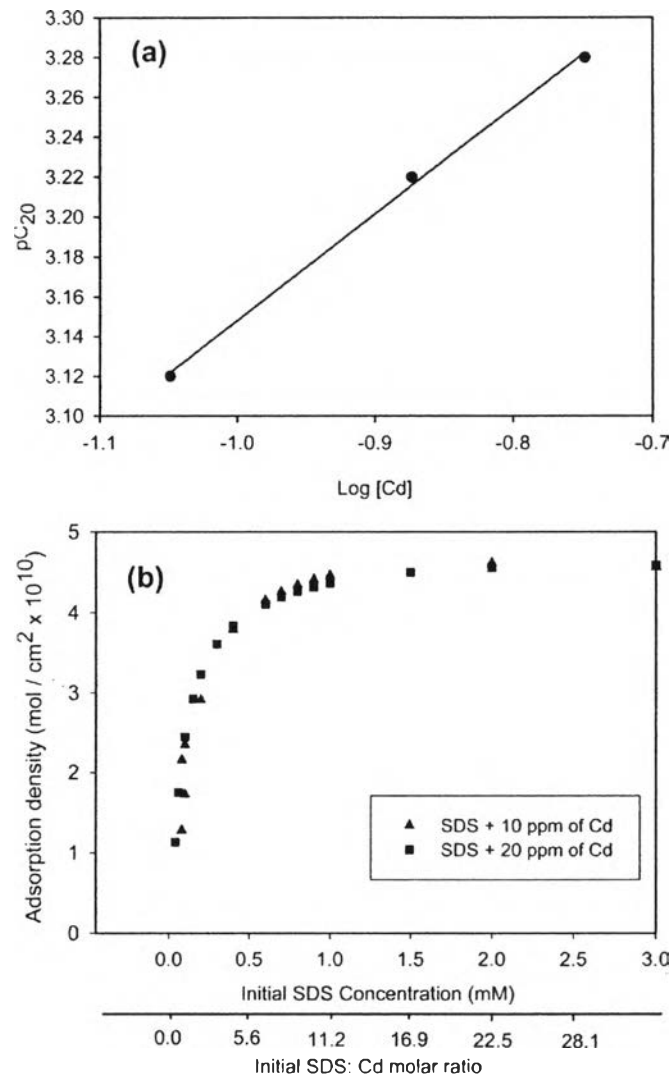


Figure 4.6 The measured values of pC_{20} (a) and the adsorption density of SDS (b) of SDS from surface tension isotherm in the presence of cadmium ion as a function of cadmium ion concentration.

The Cd removal increases with increasing feed Cd concentration and reaches a maximum at a feed Cd concentration of 15 mg/L; but the Cd removal decreases with further increasing the feed Cd concentration, as shown in Figure 4.5c. The opposite trend was observed for the residual factors of Cd, as shown in Figure 4.5d. Interestingly, the effluent Cd concentration insignificantly changes with

increasing the feed Cd concentration from 10 to 15 mg/L, but it remarkably increases with further increasing the feed Cd concentration, as shown in Figure 4.5e. The results suggest that, under the studied conditions, the adsorption site of free dodecyl sulphate ion are large enough for most Cd ions to be adsorbed and carried with the foam at low feed Cd concentrations. Beyond a Cd feed concentration of 15 mg/L, both bubble surface area and free dodecyl sulphate ion sites are no longer sufficient for Cd coadsorption, which can be explained by the model described below.

According to the ion binding model (21), the adsorption of counterions with the adsorbed surfactant ions is characterized by an equilibrium exchange reaction between the mobile counterions far from the surface and the adsorbed surfactant ions on the air–water interface. For Cd^{2+} counterions and dodecyl sulphate ions (DS^-), the reaction can be expressed as in Equation 4.6, where NDS^- and NDS_2Cd stand for the adsorbed dodecyl sulphate ions and for the bound complex of dodecyl sulphate and Cd at the air–water interface, respectively. Since Cd^{2+} ions exhibit higher apparent surface activity than Na^+ ions, the coadsorption of Na^+ with DS^- at the air–water interface can be neglected (4,22):



K_{Cd} is the corresponding equilibrium constant. The equilibrium reaction suggests that the partition of Cd between at the air–water interface and in the bulk solution depends on the surface concentration of free DS^- and bubble surface area. Moreover, the adsorption density of dodecyl sulfate ions (DS^-) insignificantly changes with increasing the feed Cd concentration from 10 to 20 mg/L as shown in Figure 4.6b. Hence, an increase in the effluent Cd concentration can imply that the system has relatively insufficient sites of adsorbed DS^- ions and/or low bubble surface area, as compared to the amount of Cd^{2+} ions in the system needed to be adsorbed.

As shown in Figure 4.5f, the SDS separation factor decreases with increasing feed Cd concentration up to 20 mg/L and then increases with further increasing feed Cd concentration. The decrease in SDS separation factor with increasing the feed Cd at low feed Cd concentrations is due to an increase in liquid hold-up in the foam, as indicated by the increasing foamate volumetric ratio (see

Figure 4.5b). The increase in SDS separation factor beyond a feed Cd concentration of 20 mg/L is more likely due to the enhancement in foaming ability by the co-adsorption of Cd ions, leading to increasing SDS adsorption, as supported by the reduction of residual factor of SDS. The separation factor of Cd decreased markedly with increasing the feed Cd concentration. This is because of both the reduction of the enrichment ratio of Cd and the increase in effluent Cd concentration with increasing feed Cd concentration, as shown in Figure 4.5e.

In ion foam fractionation operation for Cd removal, the optimum condition can be obtained by trading off between the enrichment ratio of Cd and the Cd removal. This is because complete Cd removal requires a large volume of foam for Cd to adsorb, resulting in wet foam with a very low enrichment ratio and a large volume of foamate. From the results, the optimum foam height and air flow rate were found to be 90 cm and 60 dm³/min, corresponding to an air flow flux of 2500 dm³/m² min. Under these optimum air flow rate and foam height, and a feed Cd concentration of 10 mg/L, the maximum feed flow rate should not be larger than 80 mL/min, corresponding to an feed flow flux of 3.3 dm³/m² min. The highest level of feed Cd concentration which the studied multistage ion foam fractionation system can produce an effluent Cd concentration below 0.1 mg/L (to meet the effluent discharge standards) should not be higher than 20 mg/L.

4.5 Conclusions

The effects of the operational parameters (foam height, air flow rate, feed flow rate, and feed Cd concentration) on the separation performance of continuous multistage ion foam fractionation were investigated in this study. With increasing foam height, the enrichment ratios of both SDS and Cd were enhanced due to the reduction of liquid hold-up in the produced foam while the removal and the residual factor of Cd showed an insignificant change. An increase in air flow rate increased the foam generation rate and foamate volumetric ratio, leading to decreasing the enrichment ratios of both SDS and Cd, but increasing Cd removal. The separation factors of both SDS and Cd decreased with increasing feed flow rate because of both the effects of the enhancement of foamate volumetric ratio and the increases in both

SDS and Cd input rates. An increase in feed Cd concentration increased % SDS recovery but decreased the enrichment ratios of both Cd and SDS because of the increasing foamability. In the low Cd range of 10–30 mg/L, the studied unit of multistage ion foam fractionation was demonstrated to provide a very high cadmium removal greater than 99.5 %.

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4.7 References

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