

# Foam Fractionation as an Efficient Method for the Separation and Recovery of Surfactants and Surface-Inactive Agents: State of the Art

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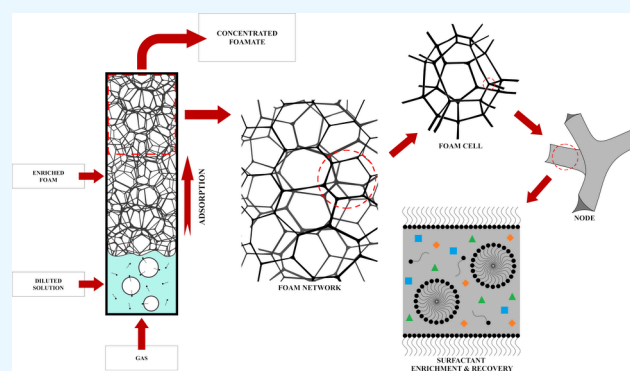
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**ABSTRACT:** Surface-active agents are widely used in industrial processes and products for daily use. Surfactants are essential in consumer products, although they are environmentally harmful. Consequently, new technologies are being sought to address the surfactant waste problem effectively. Foam fractionation is a multifunctional method of removing or purifying surface-active and inactive agents. This environmentally friendly technology enables foam separation of many compounds based on adsorption at the gas–liquid interface. The technology has been employed in wastewater treatment, remediation, metallurgy, biotechnology, pharmacy, and the cosmetics and food industries. This review highlights process handling and equipment design in terms of the enrichment and recovery of many proteins, surfactants, metal ions, and pollutants. Furthermore, the mode of action, basic laws, and mechanisms of the technology are explained, and relevant examples of the application of foam fractionation will be provided.



## 1. INTRODUCTION

Surfactants are widely used in industry and can be found in many consumer products, including detergents, hygiene products, cosmetics, food, paper, paints, and pharmaceuticals.<sup>1–3</sup> The surface activity translates to various practical properties used in foaming, cleansing, wetting, antifogging, deinking, emulsifying, and solubilizing agents.<sup>4,5</sup> Surfactants have a firmly established market position, although their application adversely impacts the environment.<sup>6,7</sup> Surfactant discharge contaminates water and soil, creating land and aquatic organism hazards.<sup>8,9</sup> Effective waste treatment or replacing synthetic surfactants with natural alternatives may provide a solution to the above-mentioned issues, and foam fractionation can be successfully utilized for that purpose.<sup>10,11</sup>

Foam fractionation provides an effective method of separating various compounds from aqueous solutions by bubble-based foam generation.<sup>12,13</sup> High selectivity of surfactant separation permits high recovery, reaching above 90% of total species removed. Selectivity allows for obtaining high enrichment values, reaching a 50-fold increase in the initial concentration of surfactant.<sup>14–16</sup> Typically, high recovery is desired in the removal of surface-active species, where high enrichment values are sought during the purification of multicomponent solutions.<sup>17,18</sup> The process is characterized by simplicity, environmental friendliness, and low energy consumption.<sup>19,20</sup> The foam fractionation phenomenon

involves selective surfactant adsorption on the gas–liquid interface.<sup>21</sup> The adsorption is driven by reducing Gibbs free energy of the system due to the amphiphilic properties of the molecules.<sup>22–24</sup> During foam fractionation, controlled gas dispersion into the surfactant solution introduces gas bubbles that expand the gas–liquid interface, forcing surfactant adsorption.<sup>25,26</sup> Bubbles emerge from the liquid, forming a surfactant stabilized and enriched foam.<sup>27</sup> The foam fractionation procedure involves two types of liquid flow distinguished within the column. The bulk liquid is entrained, carried, and enclosed between gas bubbles, forming foam that travels up the column. An opposite movement of interstitial liquid is caused by forces acting on the liquid content in the foam, leading to a gradual foam drainage.<sup>28–31</sup> As the liquid fraction diminishes, the bubble film thickness is reduced, and the foam becomes richer in surface-active species.<sup>32–34</sup> The overflowing foam is extracted from the column and broken down into enriched foamate.<sup>35,36</sup> Depending on the operating mode and parameters assumed, the fractionation process can

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extract various compounds from aqueous solutions, including surface-active and inactive species, through adsorption and collector–colligend interactions.<sup>37–39</sup>

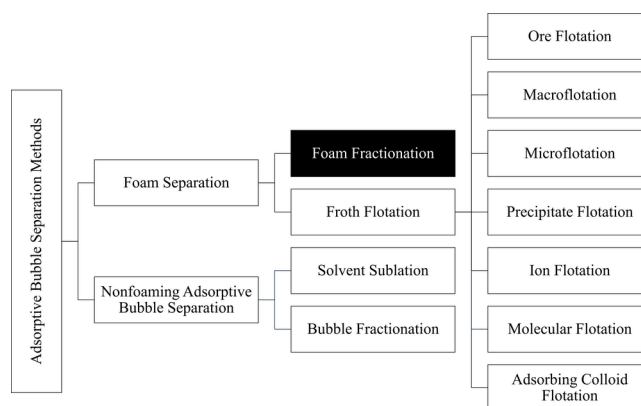
Foam fractionation has been used for over 100 years. The first publications on this subject concerned the discovery and study of the processes occurring during surfactant foaming. The overview work by Lemlich provides a closer look at the fundamentals and includes multiple examples of applications for adsorptive bubble separation methods.<sup>40</sup> Other review studies concerned more complex subjects, including the separation, concentration, and purification of compounds from aqueous solutions. The authors also explained many issues frequently encountered when exploiting adsorptive bubble separation methods.<sup>41,42</sup> A comprehensive book by Rubin et al. summarized the previous studies on the development and practical use of surfactant adsorption.<sup>36</sup> An overview prepared by Lockwood et al. addressed the theoretical aspects and the application of foam fractionation in protein isolation, particularly emphasizing the purification of products intended for pharmaceutical purposes.<sup>43</sup> Burghoff's publication concerned the biotechnological aspect in the context of separating biosurfactants, proteins, metal ions, and plant metabolites, taking into account various related processes and design parameters.<sup>31</sup> In their paper, Oraby et al. addressed the issue of foam generation occurring during aerobic fermentation, emphasizing the theoretical and design aspects of protein fractionation.<sup>44</sup> Fractionation of pollutants from wastewater is the subject of an overview prepared by Buckley et al. These authors elaborated on the subject by including the technique's historical, theoretical, and process aspects.<sup>23</sup> Stevenson et al. published books titled 'Foam Engineering' and 'Foam Fractionation Principles and Process Design', which contain fundamental knowledge concerning the foam forming process and separation methods, including foam fractionation. Furthermore, these books also elaborated on the methods' theoretical, design, and practical aspects.<sup>18,39</sup> An overview by Dolman et al. addressed the context of the production and purification of biosurfactants. The paper concerns numerous surfactant purification methods, including an integrated system that combines bioreactors with a foam fractionation column, enabling the direct removal of products by foaming.<sup>45</sup> The latest review paper by We et al. involved removal of harmful perfluoroalkyl and polyfluoroalkyl substances (PFAS) from aqueous matrices using foam fractionation technology. The authors highlighted current development, industrial implementation, and future research opportunities based on current challenges.<sup>46</sup>

Due to the rapid development of foam fractionation, it is finding a growing number of new applications. The present overview is a compendium of knowledge on foam fractionation, including basic definitions and mechanisms and a description of the processes occurring as part of the phenomenon. An effort is made to provide a thorough understanding of how the process is maintained, including the selection of process variables and efficiency parameters. Further stages of the review also cover the practical aspects of foam fractionation of numerous surface-active and inactive agents, emphasizing their industrial applications, which are supported by the latest scientific research. Considering the current interest in natural products, the use of the method in the production and purification of surfactants, which provide an alternative and environmentally friendly detergent source, is

also covered. The overview also attempts to present the latest trends for future industrial development of the method.

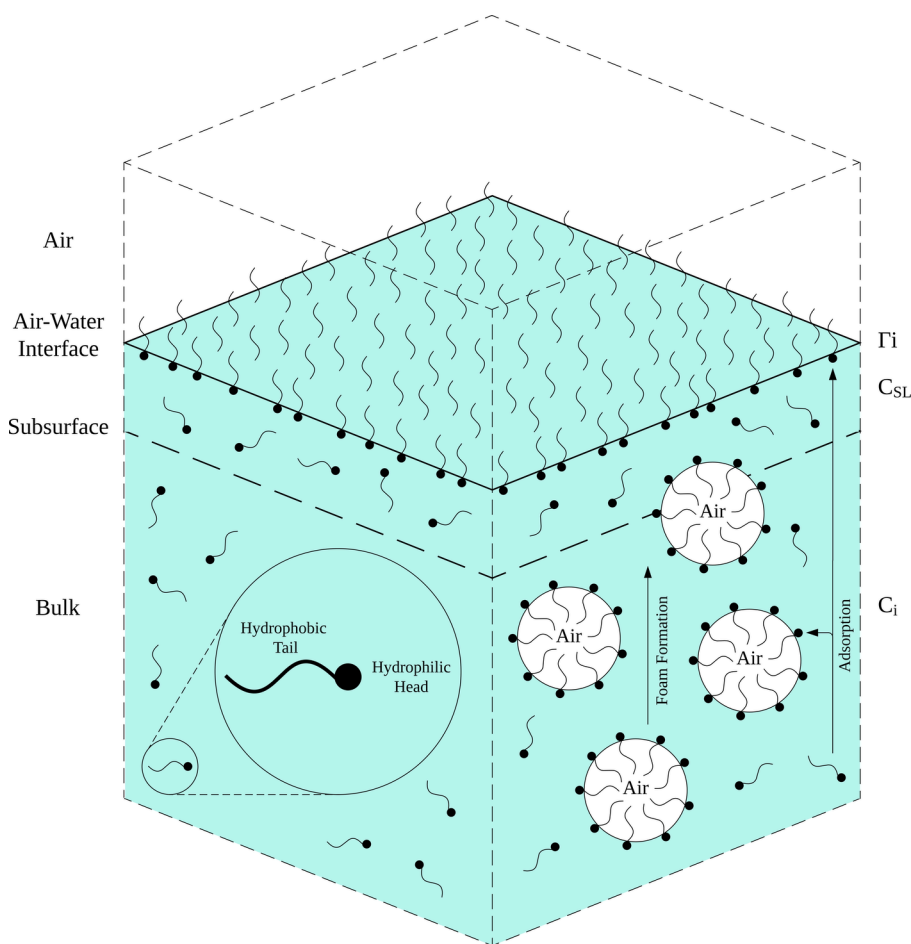
## 2. BRIEF BACKGROUND OF FOAM FRACTIONATION

The foam fractionation technique's birth date is the early 20th century, when fractionation was used to verify the Gibbs adsorption equation. According to the classification proposed by Lemlich (Figure 1), foam fractionation belongs to the group of adsorptive bubble separation methods and is placed in the foam separation subgroup.<sup>40</sup>



**Figure 1.** Classification of adsorptive bubble separation methods.

During this period, a rapid development of foam separation methods, particularly froth flotation, could be observed. The interest in flotation stemmed from its easier practical application in the mining industry for removing particulates while extracting crude oil, ores, or coal.<sup>47–49</sup> On the other hand, foam fractionation was dedicated for separating surface-active agents, such as proteins, biosurfactants, numerous metabolites, and organic compounds and for wastewater treatment.<sup>50–52</sup> The practical use of fractionation is, at present, much more limited compared to froth flotation.<sup>18,41</sup> The commercially available fractionators, called protein skimmers or protein fractionators, are used for purifying communal and animal (including zoological and fishkeeping) wastewater and contaminated soil.<sup>53–56</sup> The most commonly known industrial-scale application of fractionation is nisin extraction from the fermentation broth of *Lactococcus lactis* strains.<sup>39</sup> The latest overview by Buckley et al. provides the time frame and a more detailed description of the development of foam fractionation.<sup>23</sup> According to statistics compiled using such databases as Web of Science, Scopus, and Wiley Online Library, the first scientific publications on foam fractionation date back to around 1950. Their numbers increased significantly after 1960, when foam fractionation became globally known. Since 2000, interest in the practical use of fractionation has been observed again. Based on the Web of Science database, during the 1944–2023 period, just over 1,000 publications emerged that contained the phrase “foam fractionation”. An analysis of the data reveals that the latest studies concern chemical engineering, food technology, and biotechnology, as well as chemical and environmental sciences. The titles of the papers often reference isolation of bacterial, plant, and animal metabolites, as well as wastewater treatment, environmental protection, and remediation. A significant portion of the papers concerns the latest technological solutions that further improve the well-established technology of foam fractionation.



**Figure 2.** Mechanism of surfactant adsorption at the air-water interface during foam fractionation.

### 3. PRINCIPLES OF FOAM FRACTIONATION

The gas–liquid interface plays a crucial role in foam fractionation. Natural transport of surface-active molecules from the bulk solution toward the gas–liquid interface occurs via surface adsorption.<sup>57,58</sup> The movement is spontaneous and driven by the reduction of system free energy.<sup>3,59</sup> Due to amphiphilicity, surfactants arrange in an ordered manner at the interface, typically creating an organized surface monolayer (Figure 2).<sup>60</sup> As a result, the surface tension decreases, reducing the additional energy present on the surface of the liquid.<sup>61–63</sup> The process follows several steps and involves the movement of molecules from the bulk of the solution  $C_i$ , diffusion toward the subsurface layer  $C_{sl}$ , and formation of a surfactant monolayer at the interface.<sup>64</sup> The final stage proceeds until surface saturation and surface tension stabilization at the thermodynamic equilibrium point.<sup>65</sup> Above the CMC (critical micelle concentration), the remaining surfactant monomers begin to form micellar structures on the surface and within the bulk solution.<sup>66,67</sup> Within the context of foam fractionation, micelles are usually absent in the initial solution due to a low surfactant concentration. However, during foam fractionation, surfactant concentration within the foam increases, enabling micelles to form.<sup>31,68</sup>

In foam fractionation and other adsorptive bubble separation methods, gas is fed into the solution mechanically.<sup>42</sup> The introduced bubbles expand the gas–liquid interface, facilitating surfactant adsorption.<sup>69,70</sup> Gas bubbles “attract” and “capture”

surfactant molecules from the solution. Surfactant-enriched bubbles travel toward the surface.<sup>71</sup> The simplest example of such a process can occur in a shaken vessel of aqueous surfactant solution.<sup>72</sup> Surfactants adsorbed on the gas–liquid interface stabilize the normally unstable foam.<sup>71</sup> The foam is significantly enriched in surfactants compared with the bulk concentration. A practical example is beer foam, where the protein and water content are 73% and 10% w/w, respectively. In the beer bulk, the protein content amounts to only 0.3% w/w. The foam generated by diffusing  $\text{CO}_2$  gas concentrates the protein approximately 240-fold.<sup>39</sup> This phenomenon is especially useful in industrial branches, where the concentration of the diluted solution is usually problematic.

**3.1. Mathematical Model of Adsorption.** Isotherms can provide an important tool used for evaluating surfactant adsorption systems.<sup>73,74</sup> Adsorption isotherms typically address the mass transfer of surfactant molecules at the air-water interface, which can be associated with effective adsorption in foam fractionation. Such measurements can help predict the motion of surfactants from bulk to the foam layer, granting insight into the molecular enrichment mechanism.<sup>18,75</sup> Adsorption isotherm refers to an equilibrium correlation of bulk  $C_i$  and surface surfactant concentration of the solution called surface excess  $\Gamma$ .<sup>76,77</sup> From the extensive group of adsorption functions, only a limited number of isotherms are practically applied in foam fractionation studies.<sup>40</sup> Typically, foam fractionation procedures involve highly diluted solutions containing chemically diverse surface-active species.<sup>78,79</sup>

Therefore, certain isotherms will have greater practical applications, particularly those that take into account intermolecular or electrostatic interactions.<sup>80</sup>

The primary Gibbs isotherm is well suited for nonionic surfactant solutions of concentrations not exceeding CMC. The surface excess  $\Gamma$  of component  $i$  can be determined according to eq 1.<sup>81</sup> The practical implementation of the Gibbs equation is heavily limited when intermolecular interactions require activity coefficients to be considered or when the function loses linearity in a specific concentration range.<sup>40,82</sup> The equation also assumes the existence of a single surfactant monolayer on the solution surface. If there are no interactions between micelles and the surface layer, the equation can be applied in a broader concentration range and for determining the CMC.<sup>59</sup>

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln C_i} \quad (1)$$

The surface excess  $\Gamma$  of component  $i$  requires the values of equilibrium surface tension  $\gamma$  and surfactant concentration  $C_i$  to plot a curve and to obtain a  $\gamma(C_i)$  function. A correct function should have a linear relation to the CMC value.<sup>81–83</sup> Based on the function slope, the surface excess value  $\Gamma$  can be calculated, and consequently, the effectiveness of adsorption at the gas–liquid interface at equilibrium can be determined.<sup>74,84</sup> Large deviations in the calculated surface excess  $\Gamma_i$  value between the ionic and nonionic surfactant forms can be observed. This rule applies in particular to all types of intermolecular interactions as well as the presence of electrolytes and other surface-active agents. If present, appropriate correction factors need to be applied.<sup>77,84,85</sup> Different isotherms were created by carefully modifying the basic Gibbs equation to improve their applicability. The following isotherms are commonly used for thermodynamic calculations in foam fractionation systems: Gibbs, Langmuir, and Henry isotherms.<sup>86</sup>

**3.2. Thermodynamic Model.** The processes of surfactant adsorption and aggregation lead to a reduction in Gibbs free energy  $\Delta G$  (eq 2), resulting in the change in enthalpy and entropy at temperature  $T$ .<sup>87</sup> Adsorption and micellization take on negative values and occur spontaneously at room temperature for aqueous solutions.<sup>88,89</sup> Based on empirical observations, system free energy reduction is driven mostly by entropic gain.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, T\Delta S^\circ \gg |\Delta H^\circ| \quad (2)$$

Dissolved surfactant molecules present in an air–water system disrupt the water structure and limit the solvent's freedom of movement. The system's response is to limit unfavorable intermolecular interactions by sending surfactant molecules toward the liquid surface to form an organized monolayer via adsorption. Surface adsorption translates to a positive change in entropy, which is positive in most cases, while enthalpy change varies depending on the type of surfactant.<sup>74,90</sup> A simple example of determining the thermodynamic parameters of adsorption is the use of the Langmuir isotherm given by eq 3, which describes adsorbent monolayers, where  $\Gamma_\infty$  means the value of saturated surface excess, and  $K_L$  is the Langmuir constant. The organization of surfactant molecules on the surface is described using the standard adsorption energy  $\Delta G_{\text{ads}}^\circ$  at equilibrium in accordance with eq 4. A simple substitution of eq 2 and transformation

yields eq 5, which relates the thermodynamic equilibrium of adsorption to enthalpy and entropy changes in the system.<sup>85</sup>

$$\Gamma_i = \Gamma_\infty \left( \frac{K_L C_i}{1 + K_L C_i} \right) \quad (3)$$

$$\Delta G_{\text{ads}}^\circ = -RT \ln K_L \quad (4)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

As in the case of the Gibbs isotherm, eq 5 needs to be plotted in order to obtain a relationship between the surface tension and surfactant concentration  $\gamma(C_i)$ . The determined function enables determining the constants of the Langmuir isotherm, which provides information on the energetic nature of adsorption. The equation can be further exploited to calculate standard thermodynamic parameters of the adsorption process at equilibrium.<sup>85,91</sup> The Langmuir isotherm is frequently used in foam fractionation studies due to its simplicity and a good representation of the character of adsorption isotherms under a high surface excess of surfactants.<sup>18</sup>

**3.2.1. Thermodynamic Parameters.** Calculations on surfactant adsorption were conducted by Zdziennicka et al. In this example, the authors used several functions of state to determine standard adsorption entropy, enthalpy, and Gibbs energy of many popular ionic and nonionic surfactants at different temperatures. In this case, standard free enthalpy values suggest highly spontaneous adsorption of all surfactants investigated.<sup>92</sup> A similar analysis was performed for bio-surfactants using various methods to determine the basic thermodynamic parameters. The values obtained were consistent for rhamnolipid and surfactin and were subsequently compared with synthetic surfactants, which provided a clear overview of the adsorption process.<sup>93</sup> Two studies by Mańko et al. present a similar analysis of rhamnolipid and SDS adsorption. The authors determined the standard free energy of surfactant adsorption and micellization, taking into account molecular interactions between the surface layer and the micelles in the bulk solution.<sup>87,94</sup> The negative values of Gibbs energy demonstrate that adsorption, aggregation, and micellization are spontaneous.<sup>61,66,74</sup> Knowledge of thermodynamic parameters provides insight into molecular-level thermodynamic processes and is often indispensable when designing adsorption-based processes.<sup>62,95</sup>

### 3.3. Mass Transport Barrier in Foam Fractionation.

Selective adsorption of surface-active agents on the surface of air bubbles develops an enriched foam.<sup>96</sup> Surfactant adsorption progresses dynamically through the molecular movement of surfactant toward the surface of the liquid. Equilibrium surface tension is achieved after a specific time  $t$ , which results from the existence of kinetic barriers to mass transfer. The stage with the lowest speed restricts the kinetics of the adsorption process, also affecting the foam stability and the effectiveness of foam separation. Surface adsorption at the gas–liquid interface is divided into two major stages. The surface-active agents dissolved in the liquid are transported to the subsurface layer by diffusion. In the next stage, adsorption transports the molecules from the subsurface layer to the surface layer. The speed of the process can be limited by either diffusion or adsorption. The presence of micelles can additionally alter this process.<sup>77,97–100</sup> During foam fractionation of highly diluted

solutions, the phenomenon of micellization does not occur and consequently can be ignored. However, in the case of concentrated foam, it is worth considering this phenomenon for any possible transport barriers. From the practical standpoint, the process of micellization has a negative effect on foam stabilization, as micelles alone do not form a layered structure on the surface, unlike monomers.<sup>101</sup> The process of desorption/adsorption and micelle formation itself is complicated, and foam analysis requires complex testing methods, particularly for foams with three-dimensional structures.<sup>97,102</sup> As a result, this problem is rarely addressed by the authors. Even so, surface studies can provide the necessary information to determine the limiting stage of surfactant adsorption.<sup>103,104</sup>

**3.3.1. Practical Example: Diffusion-Controlled Adsorption.** One frequently encountered problem in separation sciences and technologies is the mass transport limitations resulting from poor molecular diffusion.<sup>77,105</sup> The subsurface layer  $C_{SL}$  and surface layer  $\Gamma$  exist in a local equilibrium. In this case, molecular transport from the bulk solution toward the subsurface layer is the diffusion-limited stage, which determines the local equilibrium conditions.<sup>18,64</sup> A modified Ward and Tordai diffusion model describes change  $\Gamma(t)$  for the surface of a surfactant solution initially free of surfactant, where according to eq 6,  $D$  is the diffusion coefficient and  $\tau$  the dummy variable with the units of time.<sup>97</sup>

$$\Gamma(t) = 2C_i \sqrt{\frac{Dt}{\pi}} - 2\sqrt{\frac{D}{\pi}} \int_0^{\sqrt{t}} C_{SL}(t - \tau) d\sqrt{\tau} \quad (6)$$

The above equation is problematic because it requires knowledge of the subsurface concentration value. Furthermore, to calculate the integer, it is necessary to assume an adsorption isotherm, which makes the equation more complicated and forces the use of iterative numerical methods.<sup>18</sup> The  $W-T$  equation comprises two terms, the first describing diffusion to the subsurface layer and the second describing desorption from the surface boundary. At short time intervals, when  $C_{SL}(t) = 0$ , the equation becomes simplified according to eq 7.

$$\Gamma(t) \cong 2C_i \sqrt{\frac{Dt}{\pi}} \quad (7)$$

After a longer time  $t_i$  concentration  $C_{SL}$  will tend toward equilibrium values. Calculations should, therefore, be split into two parts:  $0 \rightarrow t_i$  and  $t_i \rightarrow t$ , and then the two terms are added together.<sup>100</sup> The  $W-T$  equation works well for diluted solutions of nonionic surfactants below the CMC. It is also possible to apply suitable modifications to the  $W-T$  equation, replacing planar adsorption with spherical, which is observed in foam fractionation, in accordance with eq 8, where  $b$  is the gas bubble radius.<sup>64</sup>

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}} \left[ C_i \sqrt{t} - \int_0^{\sqrt{t}} C_{SL}(t - \tau) d\sqrt{\tau} \right] + \frac{D}{b} \left[ C_i t - \int_0^t C_{SL}(\tau) d\tau \right] \quad (8)$$

Simplifications are commonly used to make calculations easier by combining equations with the Gibbs isotherm. For short times, when surface excess  $\Gamma$  is small and no transport barriers to the subsurface layer exist, substituting the isotherm into eq 7 yields eq 9. In this case, the limiting stage is molecular diffusion to the subsurface layer. When the system is close to reaching equilibrium, simplifications, as in eq 10, can

be made.<sup>97</sup> The equation term responsible for molecule desorption from the subsurface layer was omitted.

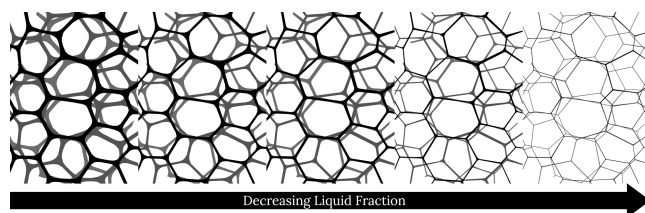
$$\gamma - \gamma_w \sim 2RTC_i \sqrt{\frac{Dt}{\pi}} \quad (9)$$

$$\gamma - \gamma_{eq} \sim \frac{2RT\Gamma^2}{C_i} \sqrt{\frac{\pi}{4Dt}} \quad (10)$$

Depending on the process, many more or less significant limiting factors may be encountered in foam fractionation, including complex adsorption of natural macromolecules, proteins, enzymes, and lipids. These molecules often exhibit denaturation by conformational changes, and their size imposes an activation barrier on the process. Another example are ionic molecules, which are associated with the presence of a double electrical layer, where electrostatic interactions, repelling of co-ions, and attraction of counterions can be observed.<sup>18</sup>

## 4. FOAM STRUCTURE

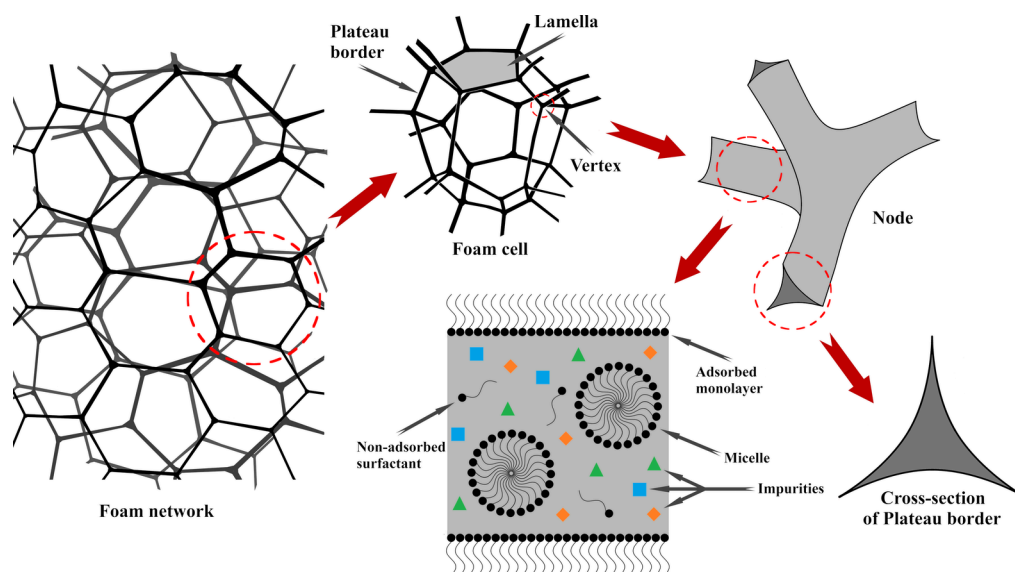
Liquid foam is a complex gas and liquid dispersion system, typically air-water. Surfactant transport and enrichment are feasible through a foam system. Foam is produced by enclosing gas between thin layers of liquid. The difference in pressure between the liquid and gas creates a force that acts evenly on the surface of gas bubbles. Excess surface energy reduces the bubble's interfacial area, resulting in a spherical shape.<sup>106</sup> The liquid fraction  $\varepsilon$  of the foam determines its behavior and stability.<sup>107</sup> Foam drainage reduces the liquid fraction due to the interstitial film rupture, coalescence, and coarsening of gas bubbles.<sup>108,109</sup> When the liquid content drops to a critical value  $\varepsilon_c$ , which is referred to as jamming transition, the bubbles are compressed in the surroundings and begin to lose their spherical shape and independent movement. For ordered and disordered foams, the threshold values  $\varepsilon_c$  are 25 and 36% w/w, respectively. Above this value, the bubbles no longer are in contact with each other, forming a so-called "bubbly liquid". Adding surfactant reduces the surface tension, prolonging the foam stability above the jamming transition. Reduction in the liquid fraction minimizes the surface area of the bubbles, creating a honeycomb-shaped structure (Figure 3). Wet foam



**Figure 3.** Change in the foam structure caused by decreasing content of the liquid fraction  $\varepsilon$ .

with a 10–20% liquid fraction value begins to take on a specific cellular structure. The honeycomb structure is observed for dry foam with a liquid fraction value of less than 10%.<sup>110</sup>

Dry foam is composed of honeycomb-like cells with a polyhedral structure as a result of low liquid fraction, which reduces the length of the Plateau border cross-section. A single cell consists of faces (lamellas) connected by thin channels (Plateau borders).<sup>111</sup> The tetrahedral junction of four borders surrounded by the four faces is called a vertex (node) (Figure



**Figure 4.** Mechanism of surfactant enrichment by adsorption on the surface of the interstitial liquid.

4).<sup>47,112</sup> Adsorbed surfactants form monolayers on the surface of the film that partially enclose the liquid inside the film and maintain film tension. The film's curvature results from lower pressure at the Plateau border than at the lamella surface.<sup>113</sup> This force drives the movement of the liquid from the lamella toward the border, reducing the wall thickness until the film ruptures. This is the cause of the rapid breakdown of nonstabilized liquid foam.<sup>110</sup> In the presence of surfactants, the lifetime of the foam increases significantly, and destabilization through drainage, coalescence, and coarsening occurs more slowly.<sup>34</sup> However, other factors may contribute to a further reduction in the stability of the metastable foam.<sup>108,114</sup> If there is an uneven distribution of the thickness of the film separating two cells, rupture may occur at the thinnest point and shortest path, resulting in coalescence.<sup>32</sup> The distribution of Laplace pressure inside the foam may cause gas to flow from smaller to larger bubbles, resulting in coarsening.<sup>107,115</sup>

**4.1. Foam Decay.** A high liquid fraction is preferred when removing surface-active species from solutions, which can be achieved via foam stabilization.<sup>111</sup> On the other hand, impurities present in the liquid pool may be transferred within interstitial liquid, resulting in low foamate purity.<sup>52</sup> A low liquid fraction results in a higher content of surface-active species in the surface layers; thus, greater purity can be achieved by enhancing foam drainage, as shown in Figure 3 and Figure 4.<sup>39</sup>

In practice, the foam structure is chaotic and often deviates from the ideal. By application of the Plateau law, the foam structure can be averaged according to the following guidelines:

- (1) Three and only three films meet at an edge at a 120° angle.
- (2) Four and only four Plateau borders meet at a point at a 109° angle.

The description above applies to an ideal foam cell, although it does not differ substantially from real structures. Such assumptions can be used to further describe the phenomenon of foam drainage. The film surface forms a Plateau border channel by curving the film edge. Because of the curvature, the

pressure at the edge is lower than in the center of the channel, causing the radial flow of the interstitial liquid and consequently draining the channels over time.<sup>32,116</sup> The liquid flow is driven by capillary and gravity forces while being resisted by viscous damping. Under gravity-free drainage, with increasing foam height, the liquid fraction decreases and slowly approaches a steady state. Higher foam layers become drier, less stable, and prior to the effects of coarsening and coalescence, resulting in ruptures.<sup>34,108,117</sup> Movement of this type is described by the drainage equation, which is a complex function and will be described in only a simplified manner. Depending on the initial and boundary conditions, many different drainage equations exist and can be used to predict loss in liquid content within the foam.<sup>117–119</sup>

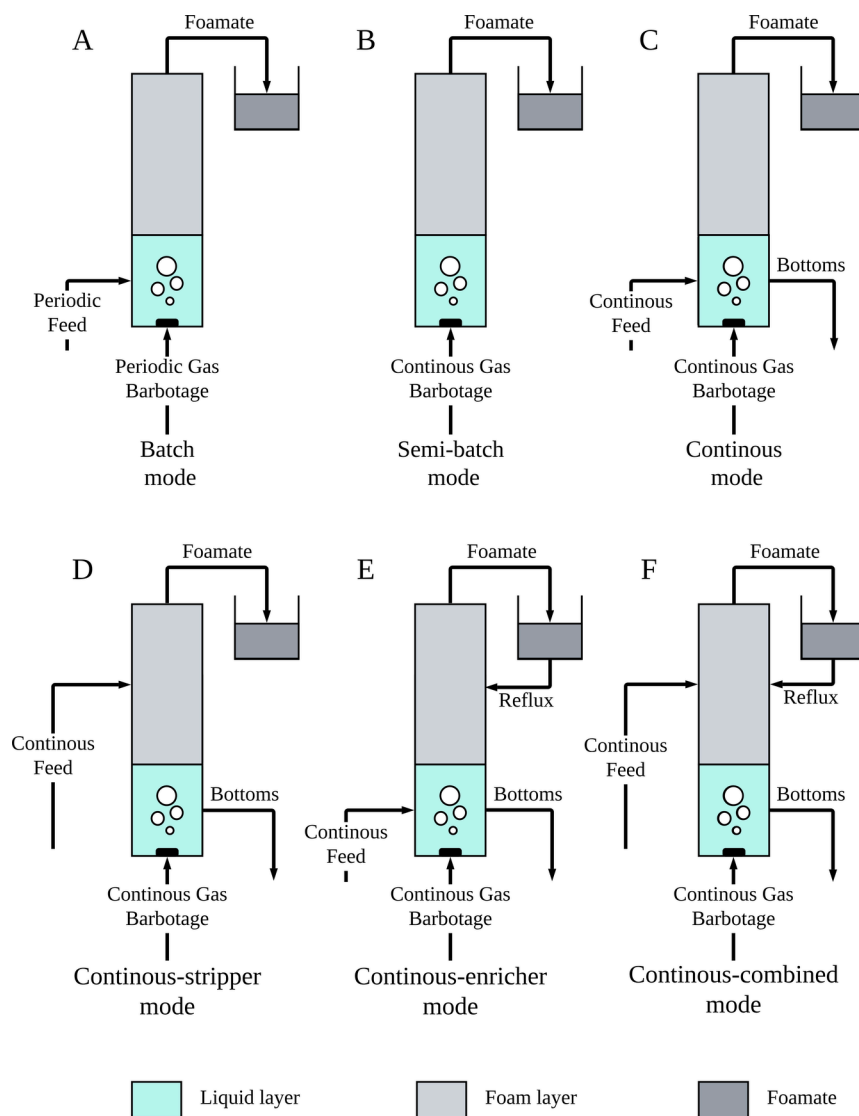
**4.1.1. Practical Example: Foam Drainage Equation.** An example of drainage equation developed by Verbist et al. describes a network of Plateau borders with a surface cross-section  $A(x,t)$  that depends on vertical position  $x$  and time  $t$ . The continuity equation of an incompressible fluid is in this case:

$$\frac{\partial A}{\partial t} + \frac{\partial(A\nu)}{\partial x} = 0 \quad (11)$$

$$\text{Gravity force: } \rho g, \quad \text{Capillary force: } -\left(\frac{\partial}{\partial x}\right)p_g - \frac{C\gamma}{\sqrt{A}},$$

$$\text{Dissipation force: } -\frac{\eta\mu}{A} \quad (12)$$

where  $\nu$  is the average velocity of the liquid in the downward direction. Assuming that capillary and gravity forces balance each other out, eq 11 is derived from the Laplace–Young law and Darcy's law. The L–Y law describes the relation between the pressure difference at the edge and inside the Plateau channel, while Darcy's law provides the relation of driving pressure gradient to liquid permeability in the medium. The above equation can be further transformed using dimensionless coordinates  $\xi = x/x_0$  and  $\tau = t/t_0$  and conversion of the transverse cross-section area to the dimensional variable value of  $\alpha = A/x_0$ .<sup>2</sup> Next, physical parameters such as surface tension  $\gamma$ , liquid density  $\rho$ , gravitational acceleration  $g$ , or effective liquid viscosity  $\eta$  are established, which allow  $x_0$  and  $t_0$  to be



**Figure 5.** Various operating modes of foam fractionation.

determined. The cross-section surface area  $A$  is proportional to liquid fraction content  $\varepsilon$  in the foam, the number of Plateau borders  $N$ , and the column cross-section  $S$ . The transformations yield a vertical foam density distribution function from the dimensional  $A(x,t)$  to the dimensionless form  $\alpha(\xi,\tau)$ .

$$\frac{\partial A}{\partial t} + \frac{1}{\eta} \frac{\partial}{\partial x} \left( \rho g A^2 - \frac{C\gamma}{2} \sqrt{A} \frac{\partial A}{\partial x} \right) = 0 \quad (13)$$

$$A = \alpha x_0^2 \quad (14)$$

$$\varepsilon = \frac{NA}{S} \quad (15)$$

$$\frac{\partial \alpha}{\partial \tau} + \frac{\partial}{\partial \xi} \left( \alpha^2 - \frac{\sqrt{\alpha}}{2} \frac{\partial \alpha}{\partial \xi} \right) = 0 \quad (16)$$

Numerical solving of eq 16 enables estimation of the position of foam corresponding to a given liquid fraction content and consequent assessment of the effectiveness of foam drainage. Unfortunately, the equation requires the input of boundary conditions, which cannot always be achieved in practice. The present drainage equation assumes no

coalescence and coarsening, which affect foam cell size. In practice, a uniform foam structure is never achieved. The equation is applicable for dry foam. Normally, the lower foam layers that remain in contact with the liquid pool are often too wet. High liquid fraction causes the loss of polyhedral cell structure, in favor of circular shape as shown in Figure 3. In such cases, correction factors resulting from cell size distribution against time  $t$  and position  $x$  need to be included in the equations.<sup>117,120,121</sup> Despite its complexity, the drainage equation can be successfully employed in foam fractionation to model and predict foam draining over time.<sup>26</sup>

## 5. PERFORMANCE OF FOAM FRACTIONATION

Foam fractionation efficiency is based on performance factors, including the enrichment ratio (eq 17) and recovery percentage (eq 18). The enrichment ratio  $E$  is a relationship between the concentration of the  $i$  component in the foamate  $C_f$ , compared to the concentration in the initial solution  $C_i$ . Recovery percentage  $R$  represents the total recovery of the  $i$  component from the initial solution  $V_i$  into the foamate  $V_f$ .

$$E = \frac{C_f}{C_i} \quad (17)$$

$$R = \frac{C_f V_f}{C_i V_i} \times 100\% \quad (18)$$

Performance factors behave contrarily, meaning that a trade-off exists between high enrichment and high recovery. High enrichment values are typically obtained during the fractionation of highly diluted solutions. The amount of extracted material is significantly reduced due to the low foam stabilizing capacity of the surfactant system. Improved foam drainage minimizes the liquid fraction content, which favors a high concentration of surface-active agents while reducing their total recovery. The opposite effect is observed for foam systems with improved stability and diminished drainage. Therefore, it becomes necessary to balance the process parameters to modify the physicochemical properties of the foam and achieve the intended performance.<sup>17,18,122</sup>

## 6. MODES OF OPERATION

The primary operating mode of foam fractionation is the batch mode. The gas is fed periodically, usually until a predefined foam height is achieved. Then, the foam is left to drain (Figure 5A). The sparging process is repeated several times to extract the dry foam, and the depleted liquid can be replenished with a fresh solution. The batch mode is the simplest method, but due to low surfactant recovery and high time consumption, it is only used for laboratory-scale processes. A more practical approach, also used on the industrial scale, is the semibatch mode. Differences in operation are in the gas feeding duration since the process is usually run until the adsorbing species are depleted or a predetermined time elapses (Figure 5B). Unfortunately, batch modes have fundamental drawbacks in the context of their practical application. Depletion of the surface-active species in the liquid pool diminishes the enrichment ratio and foam stability over time. Batch modes are often preferred for practical reasons when the adsorbed components have a limited expiry time, which is observed, especially for enzymes that undergo denaturation. In continuous modes, the liquid pool is replenished using a feed and the bottom stream. These modes are more complex but allow the process to be run in a steady state at constant surfactant concentration in the liquid pool (Figure 5C). In stripper mode, the feed is dosed into the foam layer, forcing additional adsorption and improved recovery (Figure 5D). Another modification of the continuous mode uses external reflux, which further concentrates the foam with foamate to improve the enrichment (Figure 5E). The combined continuous mode couples both stripper and enricher modes, dispensing reflux and feed streams straight into the foam layer (Figure 5F). Unfortunately, the combined mode is rarely used in practice due to the complexity of its internal processes. Depending on the assumed scale of operation, both batch and continuous modes are considered. Laboratory and pilot-scale processes often utilize batch mode due to process simplicity. In the context of performance, continuous mode is carried out in a steady state and can be operated on a larger scale, often required in many industries.<sup>18,30,36,40,41,123</sup>

## 7. OPERATING PARAMETERS

The operating parameters affecting the foam fractionation performance can be divided into two primary groups: chemical

and physical or dependent and independent.<sup>124</sup> The effect of variables is evaluated based on performance factors and may differ depending on the nature of the process. Certain variables have a universal effect on the foam fractionation performance.<sup>125–127</sup>

**7.1. Temperature Effect.** Temperature causes numerous changes in surfactant behavior. At low concentrations, temperature amplifies the surface activity of the surfactant, resulting in a decrease of liquid surface tension and foam formation. The effects occurring in surfactant solutions at higher concentrations are more unpredictable and are heavily dependent on their chemical structure and interactions.<sup>91,123</sup> An increase in the temperature intensifies the evaporation effect while reducing liquid viscosity. This effect improves molecular diffusion and foam drainage and enhances bubble coalescence.<sup>17,41</sup> The above effects reduce the liquid fraction, favoring greater enrichment and reducing the total recovery of surface-active species due to lower foam stability.<sup>25,123,128</sup> The reduction of foam stability with increasing temperature should be considered, as it can prevent the foam from being extracted from the column.<sup>10,129</sup>

**7.2. Solute Effect.** Foam fractionation rarely involves the separation of single-component solutions. Separation of wastewater, fermentation broths, or plant extracts is more complex since it includes multicomponent mixtures.<sup>70,130,131</sup> Effects of solute intermolecular interactions on foam formation and stability are often addressed in the literature, confirming their individual impact on a particular system.<sup>123,124,130,132</sup> Performance factors are highly sensitive to changes in the surfactant concentration. Foam stability and viscosity are improved by increasing the surfactant concentration, which reduces the rate of coalescence and bubble rupture but increases the recovery rate. The opposite effect is observed at low surfactant concentrations, which supports foam drainage and, thus, a high enrichment ratio.<sup>129,133</sup>

**7.3. Solution Acidity.** Solution acidity can be modified to benefit the foam fractionation performance. However, this impact is ambiguous, complex, and often system-specific.<sup>134</sup> At the isoelectric point, protein solubility is minimal, and as a result, they more readily adsorb on the gas–liquid interface, as observed for albumin.<sup>101,125,131</sup> At the isoelectric point for cellulase, surface tension reaches its minimum, which improves adsorption and protein recovery.<sup>135</sup> A similar effect can be observed for ionic and nonionic surfactants, which can be controlled by pH adjustment. In the presence of an electrical double layer, the net charge increases with rising pH, which causes repelling between the molecules. The electrical layer increases foam film thickness by slowing drainage, thus improving surfactant recovery.<sup>21,122</sup> Solution acidity also impacts metal ion separation, where for higher pH values ions more readily discharge themselves from the solution and react with adsorbed collectors, improving their enrichment. This effect is due to the differential dissociation of compounds into ionic form resulting from the solution's acidity.<sup>136,137</sup>

**7.4. Flow Rate.** Surfactant removal is strongly related to the gas flow rate and the bubble–liquid contact time in the liquid pool. The volumetric gas flow rate affects the velocity of bubbles and residence time in the liquid pool as well as the foaming rate. An increased gas flow rate produces greater gas–liquid surface area, promoting foam stability with higher liquid fraction.<sup>96,138</sup> Due to the shorter foam residence time in the column, high recovery at the cost of low enrichment is expected.<sup>139</sup> Liquid residence time is a parameter specific to



continuous modes resulting from the presence of a feed stream. As the feed flow rate increases, the liquid residence time decreases, resulting in a slower upward foam flow rate and, thus, longer foam drainage.<sup>140</sup> At constant solute concentration, more surfactant molecules can adsorb due to the turbulences caused by the more vigorous flow, favoring greater enrichment.<sup>136</sup> The liquid residence time can also be modified by changing the liquid height while maintaining a constant feed flow rate or changing the feed flow while maintaining a constant liquid height.<sup>124,141</sup>

**7.5. Bubble Size.** Bubble size affects gas–liquid surface area, which is directly related to interfacial adsorption.<sup>142,143</sup> Foam structures with nonuniform cell sizes are more susceptible to the effects of foam decay, whereas larger cells have a thinner film, which results in faster coalescence, ripening, and ruptures.<sup>32,39</sup> Smaller bubbles are more stable and provide a greater surface area for adsorption.<sup>124</sup> On the other hand, more frequent ruptures of larger bubbles enhance foam drainage through the release of interstitial liquid.<sup>13,144,145</sup> According to Grassia et al., bubble size increases with foam height due to foam decay effects. The formation of nonuniform foam with different cell sizes may provide improved stability and drainage.<sup>33,133</sup>

**7.6. Column Diameter.** Column dimensions are defined by diameter and height, which may affect the process performance. Foam rising velocity decreases with increasing column diameter while maintaining the exact column height. Increased foam residence time improves the enrichment ratio through longer drainage.<sup>44</sup> The column walls support the growing foam layers. As column diameter increases, the wall stabilizing effect diminishes. According to Kown, in columns of great diameter the surfactant-rich interstitial liquid is not collected effectively and is returned to the liquid pool due to poor foam stability resulting from an insufficient wall supporting effect.<sup>146</sup> According to Stevenson et al., the foam fractionation process has no minimum limit on the column diameter beyond the diameter of the delivered bubbles. Small-diameter columns will sometimes perform better due to the effects of walls promoting foam drainage. The upper diameter limit is associated with the foamate collection method. Greater diameters require specific receivers, as collecting such foam may be problematic. The other reason is the decreasing supporting effect of the walls on foam stability with increasing column diameter.<sup>18</sup> According to Crofcheck et al., stability in larger columns is insufficient to maintain a stable foam layer despite the beneficial impact on drainage and enrichment ratio.<sup>147</sup> The diameter needs to be specifically chosen to fit a particular system.

**7.7. Column Height.** The effective column height is measured from the sparger position to the column top and consists of foam and a liquid layer.<sup>146</sup> The upward movement of the foam layer is directly linked with its residence time in the column. Longer foam residence time indicates longer drainage and interfacial adsorption, which improves surfactant enrichment.<sup>69,129</sup> Crofcheck et al. found that taller columns provide higher enrichment while having only a minor effect on recovery.<sup>147</sup> Stevenson et al. emphasized that a greater column height improves enrichment, not through foam drainage itself but by the following bubble rupture. Stevenson described a detailed mechanism affecting enrichment ratio during vertical foam flow: a foam system with uniform and nonuniform bubble size distribution. If the adsorption equilibrium is not achieved in the bubbly liquid, it is not achieved in the foam

layer either, when the bubble size distribution in the foam layer is uniform. In such systems, drainage does not occur; the liquid in the foam remains stagnant; and foam height does not improve enrichment. An increase in enrichment is possible through the foam decay mechanism, which occurs when the bubble size distribution changes with height due to bubble rupture. Foam decay and rupture release the interstitial liquid, enabling improved adsorption through the introduced internal reflux. A reduction in liquid fraction favors the formation of dryer, more enriched foam at the column top. In practice, additional absorption in the foam layer can be achieved even for systems with uniform bubble size distribution by employing an external reflux.<sup>18</sup>

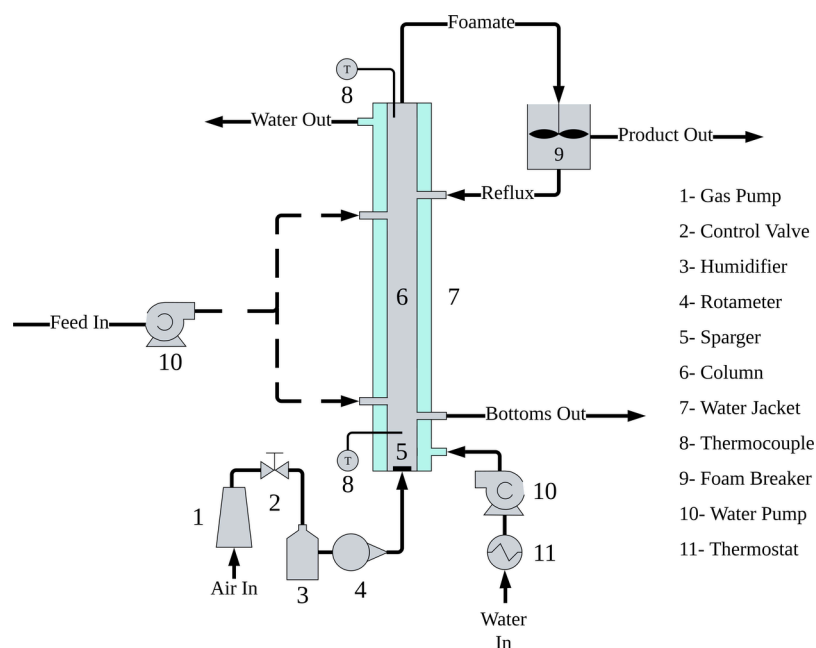
The liquid height is responsible for bubble contact time with surface-active molecules present in the liquid.<sup>136</sup> Increasing liquid height has a positive effect on adsorption as the bubbles have more time to emerge from the liquid, capturing more molecules from the solution. In this case, the adsorption equilibrium is established sooner, resulting in more stable foam and improved recovery.<sup>35,42,148</sup> The influence of variables on process performance has been summarized in Table 1.

**Table 1. Influence of Process Variables on Foam Fractionation Performance**<sup>13,18,21,25,32,33,35,39,44,69,101,122–124,128,129,131,133–141,146–148</sup>

Increasing operating parameter	Enrichment <i>E</i> of Solute	Recovery <i>R</i> of Solute
Temperature	↑	↓
Solute Type	Dependent	Dependent
Solute Concentration	↓	↑
Gas Type	Dependent	Dependent
pH	Dependent	Dependent
Column Diameter	↑	↓
Liquid Height	↓	↑
Foam Height	↑	↓
Gas Flow Rate	↓	↑
Feed Flow Rate	↑	↓
Reflux Flow Rate	↑	↓
Bubble Size	↑	↓
Operating Mode	Dependent	Dependent
Flow Pattern	Dependent	Dependent

## 8. APPARATUS DESIGN

The foam fractionation setup comprises several components, which are often necessary to run and operate the process. Figure 6 shows typical elements of a fractionation column. Gas pumps ensure a constant gas flow rate, necessary to generate uniform foam.<sup>122</sup> Depending on the intended separation, different gas types can be used, including air in wastewater treatment and surfactant isolation or inert gases (N<sub>2</sub>, Ar<sub>2</sub>, or CO<sub>2</sub>) in biological purification to prevent potential oxidation.<sup>19,149–151</sup> Continuous modes employ peristaltic or centrifugal pumps to dose feed or reflux streams at a constant flow rate.<sup>69,152–154</sup> Depending on the operation mode used, the number of pumps may differ, especially when more stages are considered.<sup>18,155</sup> Appropriate valves must be installed along the gas stream to stabilize and control the gas flow. Humidifiers moisturize the flowing gas and limit water evaporation from the foam surface.<sup>156</sup> Volumetric flow rate is controlled by rotameters. Through the water jacket, both liquid and foam layers are heated to a specific temperature, as



**Figure 6.** Typical foam fractionation setup.

measured by the thermocouples installed at the bottom and top of the column, respectively. Gas is fed into the column through a sparger, which consists of a porous material with a specific pore size or a perforated material with a system of nozzles. The most common are glass or quartz disc spargers formed into a porous network with a standardized average porosity. Such materials are commonly available commercially in different sizes and porosities. More versatile are perforated discs made of ceramics or metal and which are usually custom.<sup>79,143,148</sup> Typically, in foam fractionation of diluted solutions or surfactants of low foamability, materials with numerous fine pores should be selected. A smaller number of larger pores is preferred for processes where foam stability is not an issue.<sup>18</sup> The foam extracted from the column is transported to the foam breaker, where it can be reduced to a concentrated foamate. Vacuum, mechanical stirrers, or an addition of an antifoaming agent are typically used for this purpose.<sup>23,96,157</sup>

## 9. APPLICATIONS OF FOAM FRACTIONATION

Surfactants are essential foaming agents called collectors, which are used to generate and stabilize foam.<sup>12,158</sup> Collectors, in addition to their own enrichment, enable the separation and concentration of surface inactive species called colligends.<sup>51,68,159</sup> Surfactants adsorbed on bubble surface bind surface-inactive species and form collector–colligend complexes via physicochemical interactions. Foam fractionation has been employed to separate many surfactants and surface inactive compounds.<sup>36,46,125</sup>

**9.1. Fundamental Studies.** Fundamental studies in this area utilize synthetic surfactants due to their ready availability, high purity, and surface activity. Generally, they are used to assess the performance of the experimental setup, separation mechanism, and other theoretical aspects of foam fractionation. The latest studies focus on the effects of impurities, additives, specific process variables, and equipment designs on process performance (Table 2).

**Table 2.** Summary of the Performances Obtainable in Foam Fractionation Practical Studies

Surfactant	Operating Variables	Highest Performance under Optimal Conditions		Ref
		Enrichment $E$	Recovery $R$	
SDS	SC <sup>d</sup> , SGV <sup>e</sup> , LH <sup>f</sup> , PD <sup>g</sup>	$E^a = 28.0$	$R^b = 94.2\%$	160
SDS	SC, SGV, LV <sup>h</sup>	$E = 15.7$	$R = \sim 24\%$	13
SDBS	Additive, SC, GFR <sup>i</sup>	$E = \sim 50$	$R = 77\%$	130
SDBS	Additive, SC, GFR	-	$R = \sim 65\%$	12
CTAB	Additive, SC, GFR,	-	$R = \sim 60\%$	145
CPC, SDS	GFR, SC, NT <sup>j</sup> , LFR <sup>k</sup> , FH <sup>l</sup>	$E \sim 240$	RF <sup>c</sup> = 100%	69
CPC, SDS, Span80	GFR, SC, NT, LFR, FH,	$E = \sim 55$	RF = $\sim 85\%$	129
ETS, UDD-079	LH, FH, SGV, SC,	$E = 362$	RF = 93%	161
PGE	SC, GFR,	-	$R = 100\%$	162

<sup>a</sup>Enrichment ratio. <sup>b</sup>Removal/recovery percentage. <sup>c</sup>Removal fraction. <sup>d</sup>Solute concentration. <sup>e</sup>Superficial gas velocity. <sup>f</sup>Liquid height. <sup>g</sup>Pore diameter. <sup>h</sup>Liquid volume. <sup>i</sup>Gas flow rate. <sup>j</sup>Number of trays. <sup>k</sup>Liquid flow rate. <sup>l</sup>Foam height.

In their study on foam separation, Li et al. determined the minimum applicable concentration of the SDS surfactant in the range of 20–50 mg/dm<sup>3</sup>, also analyzing multiple parameters in the semibatch and continuous mode. The lowest SDS feed concentration was 50 mg/dm<sup>3</sup> for the two-stage mode. The authors depleted the concentration of the initial liquid to 6 mg/dm<sup>3</sup>, enriching the SDS to 168 mg/dm<sup>3</sup> and removing 94.2% of the surfactant.<sup>160</sup> Liu et al. also used SDS within the concentration range 0.2–1 g/dm<sup>3</sup> to determine the defoaming percentage of the novel foam breaker with perforated plates. The defoaming percentage increased from 19 to 63% compared to a breaker without any plates.<sup>157</sup> Yang et al. also used SDS in the process of improving foam drainage using an internal spiral component. The novel column equipped with

internal spiral enhanced foam decay, thus resulting in a significant decrease of liquid holdup in the foam phase. The examined concentration ranged from 0.15 to 0.35 g/dm<sup>3</sup>, increasing surfactant enrichment to 15.7, which was 2.5-fold greater in relation to the comparison column.<sup>13</sup> SDBS was used in a study of surfactant recovery within the 0.5–3 g/dm<sup>3</sup> concentration range in the presence of methanol and ethanol. In the process, 77% of the surfactant was recovered as a solid paste, as well as 95% of water.<sup>130</sup> In a study by Srinet et al. SDBS was also isolated in paste form from an aqueous solution containing an addition of NaCl.<sup>12</sup> A similar study conducted by Kumar et al. assessed the extraction of CTAB surfactant at high concentrations, reaching 5-fold CMC. The authors thus forced surface adsorption of micelles, recovering the surfactant in a paste form in the presence of sodium salts.<sup>145</sup> A study by Boonyasuwat et al. concerned a separation of CPC and SDS using a multistage continuous foam fractionator equipped with a bubble-cap trayed column. The authors achieved an enrichment ratio as high as 120.23 and 100% of surfactant recovery.<sup>69</sup> In addition to ionic surfactants (CPC and SDS), the authors also isolated nonionic Span80 within the 0.5- and 1-fold CMC range. The study assessed the separation efficiency depending on the surfactant chemical structure.<sup>129</sup> Another example is AEO alkyl ethoxylates, used in a study by Morgan et al. Eumulgin ET5 and Genapol UDD-079 are a mixture of nonionic surfactants with hydrocarbon chains of varied lengths. The authors assessed the performance of a multistage setup for isolating the above surfactants.<sup>161</sup> Another study concerned foam fractionation of PGE surfactant at the cloud point. An experiment at the cloud point temperature provided better separation efficiency in terms of the volume reduction ratio than at room temperature.<sup>162</sup>

**9.2. Recovery of Proteins and Enzymes.** Biotechnological processes used for protein production encounter difficulties with concentrating diluted solutions. The most common purification methods are labor-intensive and are characterized by a low efficiency of substance isolation and often lead to deactivation of the product. A method without the aforementioned disadvantages is foam fractionation, which can exploit the surface activity of proteins.<sup>31</sup> Crofcheck et al. assessed the use of fractionation for separation and concentration of BSA (Bovine Serum Albumin) based on various operating variables that affect performance. Analyzing the issues arising from the increased scale of the production, the authors demonstrated that recovery of proteins from a pilot-scale column can be predicted based on the performance of a laboratory-scale column.<sup>147</sup> *Mimosa pudica* L. plant contains surface-active proteins separated by Jeong et al. from aqueous seed extract using foam fractionation in semibatch mode. In the process of determining the optimum process parameters, protein enrichment increased from 1.11 to 2.46, while recovery dropped from 9.9 to 3.7%. The authors explained this low result with the high initial protein concentration.<sup>131</sup> Liu et al. assessed the effects of denaturation during enzyme fractionation, which is a significant problem when the protein comes into contact with oxygen. Trypsin and catalase were subjected to fractionation using different types of sparging gases at different pH values of the initial solution. By selection of the optimum parameters, the trypsin activity decay was reduced to below 10%, while for catalase it was completely eliminated. In addition, satisfactory foam fractionation performance was achieved.<sup>149</sup> Li et al. assessed the application of foam separation in the industrial process of purifying whey

soy proteins (WSP) from soy whey wastewater. The initial studies were performed to adjust the process variables and study the effects of the addition of different concentrations of preservatives. Next, the authors analyzed the impact of scaling the setup to pilot-scale size and obtained a product that contained numerous proteins and enzymes.<sup>163</sup> A study conducted by Nakabayashi et al. concerned the purification of chicken lysozymes and  $\alpha$ -amylase mixtures from *Bacillus subtilis* while assessing changes in the optical and enzymatic changes due to foaming. The authors noted that pH-dependent foam separation allowed us to selectively isolate proteins close to the isoelectric point.<sup>150</sup> Wang et al. extracted nisin from *Lactococcus lactis subspecies lactis* W28 broth by foam fractionation. The effect of variables and trehalose addition was evaluated with regard to the efficiency and degree of peptide deactivation. In optimal conditions, nisin deactivation was reduced to below 6%. The authors concluded that temperature variation and an addition of trehalose can promote the application of foam fractionation technology in biological and chemical industries.<sup>128</sup> Thermal denaturation of proteins was used to modify the surface tension of  $\beta$ -lactoglobulin aqueous solutions. This change was then used by Koop et al. to enhance the foam fractionation performance. The denaturation had a positive effect on the reduction of surface tension, which resulted in greater foaming ability of  $\beta$ -lactoglobulin. However, denaturation had a minor effect on protein extraction.<sup>156</sup> In another study on proteins, laccase (*Trametes spec.*) was isolated using foam fractionation by the team of Linke et al. The authors used synthetic surfactants as an additive to enhance the foam stability (CTAB, *Quillaja* saponin, Triton X-100, Brij 35 and SDS). The CTAB addition increased protein recovery while maintaining 89% enzymatic activity.<sup>164</sup> Mukhopadhyay et al. conducted a similar study on the recovery of proteins from whey waste using the semibatch mode. An addition of SDS and optimization of various parameters provided highly satisfactory results, which demonstrate that foam fractionation is a suitable method for protein recovery.<sup>16</sup> Among the commercial applications of protein separation, the technology of nisin production must be emphasized. This antibacterial peptide is produced by semibatch fermentation in liquid medium using *Lactococcus lactis* strains. The postfermentation broth is aerated, and if the generated foam is insufficient, a collector addition is required. Nisin is then precipitated by pH adjustment and then freeze-dried. The process is described in detail by Stevenson et al. in their book "*Foam Fractionation Principles and Process Design*" in the chapter Case Study: The Production of Nisin.<sup>18</sup> Based on the above examples (Table 3), protein foam fractionation technology can be successfully applied to protein recovery, although a proper approach is required.

**9.3. Waste Treatment and Remediation.** In addition to purifying fermentation broths of excess proteins, an important subject is the removal of harmful waste pollutants from various chemical and food industries or the recovery of valuable components for reuse. In this context, foam fractionation has also found numerous applications.<sup>10</sup> Oil industry waste, particularly from the processing of olives, contains large quantities of phenolic compounds that inhibit natural microbiological processes. Matavos-Aramyan et al. attempted the purification of olive mill wastewater (OMW) using a single-stage semibatch mode. With adequately adjusted variables, the authors achieved over 80% removal of COD (Chemical Oxygen Demand) from the feed solution using the CTAB

**Table 3. Summary of Performance Obtained in Foam Fractionation of Proteins**

Protein	Operating Variables	Highest Performance under Optimal Conditions		Ref
		Enrichment	Recovery	
A–D, H	pH, SC <sup>d</sup>	$E^a = 2.46$	$R^b = 3.7\%$	131
BSA	SGV <sup>e</sup> , PS <sup>f</sup> , CH <sup>g</sup> , CV <sup>h</sup>	$E = 6.20$	$R = 98.0\%$	147
Trypsin, Catalase	pH, GC <sup>i</sup>	$E = \sim 26$	$R = \sim 78\%$	149
WSP	Additive, SC, SGV, T <sup>j</sup>	$E = 2.85$	$R = 35.8\%$	163
Lysozyme, $\alpha$ -Amylase	pH, SC	$E = 4.5$	$R = \sim 100\%$	150
Nisin	Additive, SC, T, GFR <sup>k</sup> , LV <sup>l</sup>	$E = 23.7$	$R = 84.1\%$	128
$\beta$ -Lactoglobulin	ST <sup>m</sup>	$E = \sim 2$	$R = \sim 95\%$	156
Laccase	Additive, SC, SGV, pH, Ft <sup>n</sup> , T	$E^c = 2.3$	$R = 94\%$	164
WP	Additive, pH, SC, GFR, SGV, GH <sup>o</sup> , BS <sup>p</sup> , BT <sup>q</sup> , SR <sup>r</sup>	$E = 48.19$	$R = 96.38\%$	16

<sup>a</sup>Enrichment ratio. <sup>b</sup>Removal/recovery percentage. <sup>c</sup>Purification ratio. <sup>d</sup>Solute concentration. <sup>e</sup>Superficial gas velocity. <sup>f</sup>Pore size. <sup>g</sup>Column height. <sup>h</sup>Column volume. <sup>i</sup>Gas composition. <sup>j</sup>Temperature. <sup>k</sup>Gas flow rate. <sup>l</sup>Liquid volume. <sup>m</sup>Surface tension. <sup>n</sup>Foaming time. <sup>o</sup>Gas hold up. <sup>p</sup>Bubble size. <sup>q</sup>Foam breaking time. <sup>r</sup>Solute ratio.

surfactant.<sup>165</sup> Perfluoroalkyl and polyfluoroalkyl compounds (PFAS) are a group of toxic pollutants that often accumulate in landfill leachate, wastewater, and contaminated groundwater. A study by McCleaf et al. concerned the removal of PFAS using an innovative method combining nanofiltration and foam fractionation on a laboratory and pilot scale. A wastewater concentrate obtained from nanofiltration was subjected to fractionation, which enabled removing 90% and 94% PFAS without and with the addition of the cationic cosurfactant Montaline C40, respectively.<sup>166</sup> Smith et al. used the continuous and comparative semibatch modes of foam fractionation at the pilot scale to remove PFAS from landfill leachate. The authors conducted a series of experiments with many variables, also expanding the setup into the enricher and stripper modes.<sup>167</sup> Jia et al. applied the method to recover nanoparticles (NPs) from wastewater using CTAB. The authors thoroughly assessed the impact of gas bubble size on the generated foam at the bottom and top of the column. Based on these results, the authors were able to recover more than 90% of silica nanoparticles (SNPs) and carbon nanotubes (CNTs).<sup>133</sup> Pyridine and its derivatives are a group of harmful organic compounds that show acute toxicity and teratogenic effects. Huang et al. used three cationic surfactants (AES, SDS, and AOS) to conduct a study on removing pyridine from wastewater. The authors used a modified column with a vertical sieve tray and a floating tongue type tray to enhance interfacial adsorption and foam drainage, respectively. Experimentally, the authors selected SDS as the model surfactant and then determined the optimum process parameters and removed over 90% of pyridine.<sup>168</sup> Another study involved creatine-contaminated wastewater, which is a valuable and poorly water-soluble  $\beta$ -guanidinoacetic acid. A two-stage foam fractionation setup was used to remove creatine from the wastewater using SDS, and then the collector was separated from creatine by pH modification. Total creatine

recovery was 59.3% under the optimal conditions.<sup>169</sup> Li et al. conducted research on the recovery of silk sericin (SS), which is a waste product of the silk industry in Asia. The processing of silkworm cocoons generates wastewater that contains valuable sericin protein. In their study, the authors used an innovative column with a groined internal component (GIC) to improve process performance at room temperature. Under optimum experimental conditions, the authors recovered over 80% of the protein.<sup>170</sup> Qu et al. processed wastewater containing heavy Cd<sup>2+</sup> ions using the technique of micellar-enhanced ultrafiltration (MEUF) combined with foam fractionation. The authors used anionic SDS at low CMC values to determine the influence of MEUF-FF on the separation performance. A MEUF permeate contained the surfactant and trace amounts of metal ions, making it ideally suited for further foam fractionation to remove the remaining impurities. Compared to the MEUF technique, the combination with foam fractionation enabled improved ion recovery from 80% to 100%, significantly reducing surfactant consumption.<sup>171</sup> The food processing industry is burdened by large volumes of wastewater generated during the preparation of tomatoes. The lycopene contained in wastewater is a valuable metabolite with broad health benefits. Liu et al. used rhamnolipid to produce a stable foam and conduct foam fractionation of the metabolite, recovering over 94% RL and over 83% lycopene under optimal conditions.<sup>172</sup>

Foam fractionation can be a powerful tool for the efficient removal of harmful and toxic impurities from solutions, as described above (Table 4). An undisputed commercial

**Table 4. Summary of Performance Obtained in the Foam Fractionation of Wastewater**

Waste	Operating Variables	Highest Performance under Optimal Conditions		Ref
		Enrichment	Recovery	
OMW	SC <sup>c</sup> , Pt <sup>d</sup> , pH, GFR <sup>e</sup>	-	$R^a = \sim 80\%$	165
PFAS	CT <sup>f</sup> , GFR, FF <sup>g</sup> , LFR <sup>h</sup>	-	$R = 60\%$	167
PFAS	Additives, SC, CH <sup>i</sup> , WV <sup>j</sup> , GFR, CT	-	$R = 94\%$	166
NP	SC, GFR, BS <sup>k</sup>	$E^b = 9.9$	$R = 94.5\%$	133
Pyridine	pH, NT <sup>l</sup> , TS <sup>m</sup> , GFR, LFR	$E = 34.5$	$R = 90.2\%$	168
Creatine	SC, pH, T <sup>n</sup> , GFR	$E = 3.1$	$R = 70.6\%$	169
SS	CD <sup>o</sup> , pH, PD <sup>p</sup> , GFR	$E = 6.77$	$R = 80.29\%$	170
MEUF Permeate	SC	-	$R = 100\%$	171
Lycopene	SC, T, pH, GFR, LV <sup>q</sup> , RT <sup>r</sup>	$E = 4.42$	$R = 83.43\%$	172

<sup>a</sup>Removal/recovery percentage. <sup>b</sup>Enrichment ratio. <sup>c</sup>Solute concentration. <sup>d</sup>Process time. <sup>e</sup>Gas flow rate. <sup>f</sup>Contact time. <sup>g</sup>Foam fraction. <sup>h</sup>Liquid flow rate. <sup>i</sup>Column height. <sup>j</sup>Water volume. <sup>k</sup>Bubble size. <sup>l</sup>Number of trays. <sup>m</sup>Tray spacing. <sup>n</sup>Temperature. <sup>o</sup>Component dimensions. <sup>p</sup>Pore size. <sup>q</sup>Liquid volume. <sup>r</sup>Reusing time.

achievement in this area is SAFF technology. The technology was tested for PFAS removal from landfill leachate at the Telge recycling plant in Sweden for ten months, processing 80,000 m<sup>3</sup> of wastewater without pretreatment. SAFF was able to remove  $\geq 98.7\%$  PFOS,  $\geq 99.7\%$  PFOA, and  $\geq 98.8\%$  PFHxS without using chemical or physical additives.<sup>173</sup> Such an undertaking clearly indicates that further industrial applications of foam fractionation for the remediation of postindustrial sites can be expected in the near future.

**9.4. Removal of Metal Ions.** Many heavy metals harm the environment and living organisms, causing adverse and chronic health effects. Heavy metal ions, such as arsenic, chromium, copper, lead, nickel, or zinc, reach the environment through soil erosion, industrial and municipal wastewater discharges, mining, incineration, or the use of fertilizers and pesticides.<sup>174</sup> Foam separation is widely used for the treatment and removal of various heavy metal ions from wastewater and contaminated soils.<sup>34,172,173</sup> Applications in metal recovery from waste electronic equipment or catalytic systems are also possible.<sup>23</sup>

Kinoshita et al. used a nonionic surfactant PONPE20 at a 0.5% w/w concentration to separate metal ions from electroplating industrial effluent using continuous mode foam fractionation. The authors achieved a highly selective recovery of Au(III) from a solution of multiple metals.<sup>140</sup> Lu et al. used a mixture of the biosurfactant from washnut (*Sapindus mukorossi* Gaertn.) and the cationic CTAB at a ratio of 1:1 to remove Cr(VI) ions from aqueous solutions. This surfactant mixing procedure was intended to reduce the mass of the model surfactant and replace it with an environmentally friendly alternative. The authors achieved an ion recovery of 94.05%, enriching the solution 48.15-fold. CTAB alone reduced total recovery, increasing ion enrichment by 38.6%.<sup>138</sup> Biosurfactants have also been used as collectors in ion fractionation. Chen et al. conducted Hg(II) ion separation from contaminated water using surfactin, anionic SDS, and nonionic Tween 80, analyzing various process parameters. The biosurfactant provided the best ion separation at high concentrations (10 CMC) compared to those of the other surfactants. The highest ion recovery was 10.4% at 1.53-fold enrichment.<sup>137</sup> A similar study on this subject was conducted by Maity et al. Harmful heavy metal ions (Cu, Pb, and Zn) present in contaminated soil were removed using biosurfactants (surfactin and saponins from *Sapindus mukorossi*) by foam fractionation. The authors also assessed the effects of soil washing with the above-mentioned surfactant solutions. Based on varying parameters, ion fractionation effectiveness was 98%, 95%, and 56%, respectively, for Pb, Cu, and Zn ions. The results indicated that foam separation is more effective than ion leaching.<sup>139</sup> The team of Huang et al. conducted another study on purifying a MUEF permeate using foam fractionation. The authors assessed the effects of the Triton X-100/SDS mixture on the performance of Cd(II) ion removal. Under optimal conditions, the technology removed almost all the cadmium ions from the solution.<sup>122</sup> Fractionation has also been employed by Shao et al. to remove bivalent nickel Ni(II) ions from aqueous solutions of two surfactants (SDS and DBSA). In their study, the authors selected the optimum parameters for process operation, achieving a 12-fold enrichment and 98% ion removal from the initial solution, which indicates that foam separation is a promising method for purifying electroplating wastewater.<sup>175</sup> Trace cadmium Cd(II) was also removed at 99.8% from highly diluted aqueous solutions using the novel anionic–nonionic AEC (sodium trideceth-4 carboxylate) surfactant.<sup>176</sup> Tabibi et al. were the first to remove cobalt ions from an industrial effluent using SDS as the collector, achieving 99.4% recovery under the optimal experimental conditions.<sup>177</sup> Matsuoka et al. also performed alkali metal ion fractionation using the anionic SDS, removing 47%, 73%, 77%, and 80% of Li, K, Rb, and Cs content, respectively.<sup>178</sup> A wide range of the metal ions separated emphasizes the versatility of the foam fractionation

method. Most results of the above studies maintain the total ion recovery above 90% (Table 5).

**Table 5. Summary of Performance Obtained in Foam Fractionation of Metal Ions**

Metal Ion	Operating Variables	Highest Performance under Optimal Conditions		Ref
		Enrichment	Recovery	
Au(III)	t <sup>c</sup> , LFR <sup>d</sup> , FH <sup>e</sup> , LH <sup>f</sup>	E <sup>a</sup> = 4.5	R <sup>b</sup> = 54%	140
Cr(VI)	SC <sup>g</sup> , pH, GFR <sup>h</sup>	E = 48.15	R = 94.05%	138
Hg(II)	SC, FT <sup>i</sup> , GFR, pH	E = 1.53	R = 10.4%	137
Cu(II), Pb(II), Zn(II)	SC, T <sup>j</sup> , GFR	-	R = 98%	139
Cd(II)	SC, pH	-	R = 99.1%	122
Ni(II)	SC, LV <sup>k</sup> , GFR, t	E = 12	R = 98%	175
Cd(II)	SC	-	R = 99.8%	176
Co(II)	SC, GFR, pH, t	-	R = 99.4%	177
Li, K, Rb, Cs	SC, t	-	R = 80%	178

<sup>a</sup>Enrichment ratio. <sup>b</sup>Removal/recovery percentage. <sup>c</sup>Time. <sup>d</sup>Liquid flow rate. <sup>e</sup>Foam height. <sup>f</sup>Liquid height. <sup>g</sup>Solute concentration. <sup>h</sup>Gas flow rate. <sup>i</sup>Foaming time. <sup>j</sup>Temperature. <sup>k</sup>Liquid volume.

**9.5. Isolation of Organic Compounds of Synthetic and Natural Origin.** Many organic colligends interact with collectors and can be isolated from solutions by a foam separation. This process is based on the union between the colligend and the adsorbing compound through chelation, counterionic attraction, or some other mechanism. Foam fractionation, therefore, provides a method for the isolation of many organic solutes through surfactant adsorption at the gas–liquid interface.<sup>36,52,179</sup>

Mandal used the single-stage semibatch mode column and cationic surfactants (TTAB and CTAB) to isolate captopril from aqueous solutions, achieving 90.21% drug recovery.<sup>68</sup> The zwitterionic SB3–12, cationic DTAC, and anionic SDS were used to separate two ionic dyes (cationic methylene blue and anionic Fast Green FCF). The authors concluded that dye separation performance depends on electrostatic interactions with oppositely charged surfactant.<sup>151</sup> A less conventional fractionation method was used by Patist et al. with nonionic Tween 20 and C<sub>12</sub>(EO)<sub>5</sub>. The authors generated foam by shaking the solutions and then separating the solution from the foam. The authors assessed process performance based on surface tension and dye micellization assay.<sup>72</sup> Firlbeck et al. developed a technology for separating vanillic acid as an exemplary method for isolating hydrophilic phenolic compounds from olive-mill wastewater (OMW). Employing the single-stage semibatch mode and cationic CTAB under optimal conditions, the authors enriched vanillic acid over 22-fold with a recovery of 50%.<sup>127</sup> Numerous dissolved dyes can be found in wastewater originating from the textile, tannery, pharmaceutical, cosmetic, food, and paper industries. Kumar Bharadwaj et al. conducted a separation of methylene blue in semibatch mode using anionic SDS. Adjusting parameters such as aeration time, liquid height, pH, dye, and collector concentrations, the authors removed over 95% of the total dye from the solution.<sup>35</sup> Many nonpolar compounds have been concentrated from aqueous plant extracts (*Humulus lupulus* L., *Curcuma longa* L., *Camellia sinensis* L., *Daucus carota* L., *Citrus sinensis* L., and *Citrus paradisi* Macfad.) by Backle-

Soht et al. Several biologically active compounds, such as derivatives of humulones, curcuminoids, and carotenoids, have been recovered at more than 90% yield at a minimal enrichment of 13.8.<sup>19</sup> Other metabolites were separated from *Radix Glycyrrhizae* (RG) and *Radix Scutellariae* (RS). Under optimal conditions, the authors extracted and pacificated glycyrrhizic acid from RG and baicalein and wogonin from RS by foam fractionation. The results indicate that foam fractionation extraction yield is greater than the conventional ultrasonic extraction (UE), achieving 56.67, 13.25, and 9.51 mg/g, respectively, for baicalein, glycyrrhizic acid, and wogonin.<sup>180</sup> Caffeic acid was separated using microbubble foam fractionation, and a natural surfactant, whey soy protein (WSP), was used. In this study, Wang et al. determined the optimum process conditions to ensure prolonged stability of caffeic acid while recovering over 70% of the metabolite.<sup>79</sup> The redundant use of antibiotics has resulted in pharmaceuticals being readily discharged into the environment, causing a global rise of antimicrobial resistance, contaminating surfaces and groundwater. As a result, Ghosh et al. studied the foam fractionation of fluoroquinolone (FQ) antibiotics. The authors used popular antibiotics ciprofloxacin, norfloxacin, levofloxacin, and ofloxacin as colligends and SDS and CTAB as collectors in a semibatch single-stage mode. Under optimal conditions, the highest recovery ratio for ciprofloxacin was achieved at 93.6% using SDS. The other recovery results were 97.9%, 91.7%, and 96.7%, respectively, for norfloxacin, levofloxacin, and ofloxacin.<sup>181</sup> Reactive and dispersive dyes (DB 60 and RR 241) were removed from aqueous solutions using the CTAB surfactant. The study has shown that foam separation is a suitable and efficient method for removing anionic and nonionic dyes from solutions, resulting in 99.4% and 84.8% color removal for RR 241 and DB 60, respectively.<sup>182</sup> Phenol is an important chemical substrate and a harmful contaminant for water and the soil environment. Furthermore, it easily accumulates in living organisms, causing damage to the respiratory, immune, and reproductive systems. Guo et al. conducted a study on phenol extraction from aqueous solutions using CTAB in a two-stage semibatch mode. After determining the optimum operating conditions for the developed setup, they recovered over 90% of the compound at a very high 84-fold enrichment,<sup>15</sup> again confirming the very extensive practicality of the foam fractionation method for removing or isolating organic compounds (Table 6).

**9.6. Foam Fractionation of Biosurfactants.** Due to the environmental benefits of replacing synthetic surfactants with natural substitutes, biosurfactants are becoming the object of increasing interest. The appeal of biosurfactants stems from their biodegradability, renewability, and low toxicity.<sup>44</sup> This group includes many compounds of bacterial, fungal, animal, and plant origin. In terms of structure, biosurfactants can be divided into lipoproteins, lipids, polymers, lipopolysaccharides, glycosides, bile salts, and fatty acids.<sup>183–188</sup> Only a limited amount of synthetic surfactants is used in foam fractionation, but a wide range of naturally available amphiphiles leaves the scope for further research (Table 7).

The first group consists of biosurfactants produced by microbiological organisms controlled by biotechnological processes. Bacteria, fungi, and yeasts synthesize such compounds.<sup>187</sup> Diluted postfermentation broths must be concentrated using various methods to obtain final products. Lipopeptides and glycolipids are among the best-studied biosurfactants used in many branches of industry.<sup>189</sup>

**Table 6. Summary of Performance Obtained in Foam Fractionation of Organic Compounds**

Compound	Operating Variables	Highest Performance under Optimal Conditions		Ref
		Enrichment	Recovery	
Captopril	SGV <sup>d</sup> , pH, SC <sup>e</sup> , CH <sup>f</sup> , LV <sup>g</sup>	E <sup>a</sup> = 45.11	R <sup>b</sup> = 90.21%	68
Vanillic Acid	SC, pH, GFR <sup>h</sup>	E = 22.24	R = 55.88%	127
Methylene Blue	At <sup>i</sup> , LH <sup>j</sup> , SC, pH	E = 7.49	R = 95.7%	35
Plant Metabolites	-	E = 21.4	R = 90%	19
Caffeic Acid	GFR, pH	E = 20.0	R = 73.9%	79
FQ Antibiotics	SC, pH	E = 15.7	R = 97.9%	181
DB 60, RR 241	pH, t <sup>k</sup> , GFR, SC, GT <sup>l</sup>	-	R <sup>c</sup> = 99.6%	182
Phenol	pH, SC, GFR, T <sup>m</sup>	E = 84.46	R = 94.43%	15

<sup>a</sup>Enrichment ratio. <sup>b</sup>Removal/recovery percentage. <sup>c</sup>Color reduction. <sup>d</sup>Superficial gas velocity. <sup>e</sup>Solute concentration. <sup>f</sup>Column height. <sup>g</sup>Liquid volume. <sup>h</sup>Gas flow rate. <sup>i</sup>Aeration time. <sup>j</sup>Liquid height. <sup>k</sup>Time. <sup>l</sup>Gas type. <sup>m</sup>Temperature.

**Table 7. Summary of the Performances Obtainable in the Foam Fractionation of Biosurfactants**

Biosurfactant	Operating Variables	Highest Performance under Optimal Conditions		Ref
		Enrichment	Recovery	
Surfactin	CT <sup>c</sup>	E <sup>a</sup> = 55	R <sup>b</sup> = 92.3%	14
Surfactin	CT	E = ~50	R = 28.7%	190
Rhamnolipid	GFR <sup>d</sup> , BS <sup>e</sup>	E = 3.57	R = 38%	144
Rhamnolipid, Acidic Precursor	SC	E = 17	R = 22%	154
Hydrophobin	LFR <sup>f</sup> , GFR, SGV <sup>g</sup> , RT <sup>h</sup>	E = 6.6	R = 70%	152
Trehalolipid	SC	E = 2.3	R = 23%	192
Lipopeptide	AR <sup>i</sup> , CH <sup>j</sup>	E = 3.2	R = 54%	193
Tea Saponin	T <sup>k</sup> , pH, LV <sup>l</sup> , GFR	E = 3.47	R = 80.1%	196
Tea Saponin	T, GFR, pH, LFR <sup>m</sup> , FP <sup>n</sup>	E = 4.02	R = 86.3%	21
Soybean Saponin	pH, SC, T, GFR, LFR	E = 4.45	R = 74%	50
Dioscin	SC, T, LV, GFR	E = 7.53	R = 91.08%	199, 200
Sapindus Saponin	SC, LV, GFR, PD <sup>o</sup> , T	E = 133.4	R = 36.4%	17

<sup>a</sup>Enrichment ratio. <sup>b</sup>Removal/recovery percentage. <sup>c</sup>Culture time. <sup>d</sup>Gas flow rate. <sup>e</sup>Bubble size. <sup>f</sup>Liquid flow rate. <sup>g</sup>Superficial gas velocity. <sup>h</sup>Residence time. <sup>i</sup>Aeration rate. <sup>j</sup>Column height. <sup>k</sup>Temperature. <sup>l</sup>Liquid volume. <sup>m</sup>Liquid flow rate. <sup>n</sup>Feed position. <sup>o</sup>Pore diameter.

Biosurfactant production also involves purifying postfermentation mixtures, where foam fractionation is readily employed.<sup>44</sup> Using the semibatch mode, Chen et al. produced the biosurfactant surfactin from *Bacillus subtilis* (BBK006) cultures. The authors enriched surfactin approximately 50-fold, achieving a concentration of 136 mg/dm<sup>3</sup>.<sup>14</sup> In another paper, the authors combined the continuous fermentation with foam fractionation to maintain a high steady-state concentration of surfactin reaching 18 mg/dm<sup>3</sup> and an enrichment ratio of approximately 50, with a dilution rate of 0.2/h and glucose concentration of 0.25 g/dm<sup>3</sup>.<sup>190</sup> Rhamno-

lipids produced by *Pseudomonas aeruginosa* (ATCC 9027) and *Burkholderia thailandensis* (E264) have been separated using a continuous-stripper mode. Depending on the parameters, the enrichment of the produced rhamnolipids Rha-C<sub>10</sub>-C<sub>10</sub> and Rha-Rha-C<sub>14</sub>-C<sub>14</sub> was within the 1.2–2.9 and 1.55–3.57 range, respectively. The recovery percentage was within the 96–6% and 29–38% range, as above.<sup>144</sup> Lethcoe et al. conducted foam fractionation of apolipoprotein III synthesized during a fermentation of *Locusta migratoria*. The ApoLp-III is a 164-amino acid amphipathic exchangeable apolipoprotein, which in the aqueous solution takes the form of five elongated amphipathic  $\alpha$ -helices organized as a five helix bundle. Employing continuous mode, the authors obtained a foam containing apoLp-III as the only main protein component, with a concentration of 0.15 g/dm<sup>3</sup> to 0.2 g/dm<sup>3</sup>.<sup>191</sup> Using foam fractionation and foam adsorption enables purifying postfermentation broths. The continuous-stripper mode has been used to separate a bacterial rhamnolipid (RL) and acidic precursor (HAA) produced by *Pseudomonas putida* (KT2440). The postfractionation enrichment of the biosurfactant was 7.5 g<sub>RL</sub>/dm<sup>3</sup> and 2.0 g<sub>HAA</sub>/dm<sup>3</sup>. The authors extracted the products with a mass of 4.7 g<sub>RL</sub> and 2.8 g<sub>HAA</sub> using the two-stage technology during 36 h from a 2 dm<sup>3</sup> culture volume. The process scale-up to 9 dm<sup>3</sup> improved the mass of adsorbed RL to 16 g.<sup>154</sup> Hydrophobin is an amphiphilic protein synthesized by many fungi. Hydrophobin HFBII from *Saccharomyces cerevisiae* (CBS128322) was recovered by Winterburn et al. with a continuous *in situ* foam fractionation technology. Foam fractionation was used to remove protein from the batch-fed fermentations, reducing the uncontrolled overflow of foam from the fermentation tanks. Under optimum conditions, integrated foam separation provided a recovery of 70% and enrichment of 6.6.<sup>152</sup> Bages-Estopa et al. used the marine bacteria *Rhodococcus* sp. (PML026) to produce the biosurfactant trehalolipid and subsequently performed foam fractionation on the postfermentation product. The authors evaluated the fermentation broth volume scale-up from 1 to 5 dm<sup>3</sup>, improving fermentation performance approximately 3-fold.<sup>192</sup> Another example of biosurfactant foam separation was conducted by Khondee et al. The authors used *Bacillus* sp. (GY19) immobilized on chitosan to increase cell density and facilitate lipopeptide production. The concentration observed under a steady state was 7.12 g/dm<sup>3</sup>. Next, the authors improved biosurfactant purity by selecting the right column height and aeration rate, recovering more than 50% of the product.<sup>193</sup>

Another example of biosurfactants used in the foam separation method are saponins, synthesized by plants and, in rare cases, marine organisms. These glycosides consist of a hydrophilic sugar chain and a hydrophobic aglycone. The aglycone structure classified saponins into two groups: triterpenes and steroids. Saponins exhibit surface activity and a range of biological properties.<sup>194,195</sup> In two studies by Yan et al., tea saponins were foam separated using consecutively two-stage batch and two-stage continuous modes. The two-stage batch mode yielded an enrichment of 3.47 and 80.1% total saponin recovery. The two-stage continuous mode achieved an enrichment ratio of 4.02 and a total saponin recovery of 86.3%. The low concentration result is probably the consequence of the high initial total saponin concentration (TSC) of 3.57 g/dm<sup>3</sup> and 3.10 g/dm<sup>3</sup> for the batch and continuous mode, respectively.<sup>21,196</sup> A modern technology combining extraction and fractionation has been developed by Ding et al. Total

saponins from the root of *Achyranthes bidentata* Blume (AB) were subjected to coupled extraction and separation. The powdered plant material was sealed in a nylon filter cloth with different pocket bore diameters. The technology enabled a continuous release and fractionation of saponins. Compared to the traditional technology, the coupled method provided an approximately 1,74-fold higher AB saponin concentration and over 4-fold increased extraction rate.<sup>197</sup> Soybean saponins (SS) were subjected to two-stage foam fractionation and resin adsorption technology, where the extracted foamate was adsorbed on a resin for further purification. Foam fractionation resulted in a 4.45, 74, and 67% enrichment, recovery, and purity of SS, respectively. Adsorption further improved SS purity to 88.4%.<sup>50</sup> Saponins contained in *Apostichopus japonicus* were identified by the Zhang et al. The authors performed purification by foam fractionation and microporous resin adsorption.<sup>198</sup> Two papers by Zhang et al. concerned using foam fractionation to purify extracts from *Trigonella foenum-graecum* L. and *Dioscorea zingiberensis* C. H. Wright. The authors separated dioscin (a steroid saponin) and diosgenin (a steroid sapogenin) using foam separation combined with P-HPLC to develop a technology for isolating high-purity monomers.<sup>199,200</sup> Wanschura et al. separated triterpenoid saponins from tropical tree biomass using synthetic surfactants (Tween 20 and SDS). However, the method described by the authors requires further refinement to improve performance.<sup>78</sup> In the study by Li et al., the authors compared the impact of a spiral internal component (SIC) on column performance during the separation of saponins from the *S. mukorossi* extract. In the study, the authors used a two-stage batch mode setup, optimizing the separation process to achieve a high saponin purity of 90.3%.<sup>17</sup>

## 10. CONCLUSION

Foam fractionation is a “green” technology, and due to its many advantages, it has attracted a lot of attention. The popularity stems from what it offers, including cost-effectiveness, environmental friendliness, simplicity, and versatility. The latter is described and supported with numerous examples in this overview, including successful removal, isolation, and treatment of proteins, plant metabolites, metal ions, organic compounds, waste, and biosurfactants. As many authors have noted, although considered a well-established technology, foam fractionation has not yet been industrialized. Currently, foam fractionation is mainly used in biotechnological and waste treatment branches, as highlighted by nisin and PFAS recovery. In this respect, several manufacturers already include fractionators in their product ranges, called protein skimmers. Despite many practical applications, industrial implementation of foam fractionation is currently limited on account of the high sensitivity of process variables on separation performance and limited scale-up from the laboratory to large pilot and industrial systems. Due to commercial requirements, high enrichment ratios and recovery percentages are mandatory, necessitating multicolumn systems, often operated in continuous mode. In this regard, using foam fractionation in natural saponin extraction seems to be an attractive method of obtaining natural components for the cosmetic and household chemical industry.

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### Author Contributions

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## REFERENCES

- (1) Kumar Dutta, A. Introductory Chapter: Surfactants in Household and Personal Care Formulations - An Overview. In *Surfactants and Detergents*; IntechOpen, 2019; pp 1–10. DOI: [10.5772/intechopen.89245](https://doi.org/10.5772/intechopen.89245).
- (2) Sar, P.; Ghosh, A.; Scarso, A.; Saha, B. Surfactant for Better Tomorrow: Applied Aspect of Surfactant Aggregates from Laboratory to Industry. *Res. Chem. Intermed.* **2019**, *45* (12), 6021–6041.
- (3) Farn, R. J. *Chemistry and Technology of Surfactants*; Farn, R. J., Ed.; Wiley, 2006; pp 1–315. DOI: [10.1002/9780470988596](https://doi.org/10.1002/9780470988596).
- (4) Kohli, R.; Mittal, K. L. *Surfactants in Precision Cleaning*; Elsevier, 2022; pp 1–53. DOI: [10.1016/C2019-0-03690-4](https://doi.org/10.1016/C2019-0-03690-4).
- (5) Nakama, Y. Surfactants. In *Cosmetic Science and Technology*; Sakamoto, K., Lochhead, R. Y., Maibach, H. I., Yamashita, Y., Eds.; Elsevier, 2017; pp 231–244. DOI: [10.1016/B978-0-12-802005-0.00015-X](https://doi.org/10.1016/B978-0-12-802005-0.00015-X).
- (6) Shaban, S. M.; Kang, J.; Kim, D. H. Surfactants: Recent Advances and Their Applications. *Compos. Commun.* **2020**, *22*, 100537.
- (7) Vantage Market Research & Consultancy Services. *Vantage Market Research*. <https://www.vantagemarketresearch.com/industry-report/surfactants-market-1671>. (Accessed online: 13.09.2024).
- (8) Arora, U.; Khuntia, H. K.; Chanakya, H. N.; Kapley, A. Surfactants: Combating the Fate, Impact, and Aftermath of Their Release in the Environment. *Int. J. Environ. Sci. Technol.* **2023**, *20* (10), 11551–11574.
- (9) Saxena, N.; Islam, M. M.; Baliyan, S.; Sharma, D. A Comprehensive Review on Removal of Environmental Pollutants Using a Surfactant Based Remediation Process. *RSC Sustain.* **2023**, *1* (9), 2148–2161.
- (10) Badmus, S. O.; Amusa, H. K.; Oyehan, T. A.; Saleh, T. A. Environmental Risks and Toxicity of Surfactants: Overview of Analysis, Assessment, and Remediation Techniques. *Environ. Sci. Pollut. Res.* **2021**, *28* (44), 62085–62104.
- (11) Arora, J.; Ranjan, A.; Chauhan, A.; Biswas, R.; Rajput, V. D.; Sushkova, S.; Mandzhieva, S.; Minkina, T.; Jindal, T. Surfactant Pollution, an Emerging Threat to Ecosystem: Approaches for Effective Bacterial Degradation. *J. Appl. Microbiol.* **2022**, *133* (3), 1229–1244.
- (12) Srinet, S. S.; Basak, A.; Ghosh, P.; Chatterjee, J. Separation of Anionic Surfactant in Paste Form from Its Aqueous Solutions Using Foam Fractionation. *J. Environ. Chem. Eng.* **2017**, *5* (2), 1586–1598.
- (13) Yang, Q.-W.; Wu, Z.-L.; Zhao, Y.-L.; Wang, Y.; Li, R. Enhancing Foam Drainage Using Foam Fractionation Column with Spiral Internal for Separation of Sodium Dodecyl Sulfate. *J. Hazard. Mater.* **2011**, *192* (3), 1900–1904.
- (14) Chen, C.-Y.; Baker, S. C.; Darton, R. C. Batch Production of Biosurfactant with Foam Fractionation. *J. Chem. Technol. Biotechnol.* **2006**, *81* (12), 1923–1931.
- (15) Guo, S.; Wu, Z.; Liu, W.; Huang, D.; Li, H.; Hu, N. Enrichment and Isolation of Phenol from Its Aqueous Solution Using Foam Fractionation. *J. Ind. Eng. Chem.* **2016**, *36*, 180–183.
- (16) Mukhopadhyay, G.; Khanam, J.; Nanda, A. Protein Removal from Whey Waste by Foam Fractionation in a Batch Process. *Sep. Sci. Technol.* **2010**, *45* (9), 1331–1339.
- (17) Li, R.; Wu, Z. L.; Wang, Y. J.; Li, L. L. Separation of Total Saponins from the Pericarp of Sapindus Mukorossi Gaerten. by Foam Fractionation. *Ind. Crops Prod.* **2013**, *51*, 163–170.
- (18) Stevenson, P.; Li, X. *Foam Fractionation Principles and Process Design*; CRC Press, 2014; Vol. 57, pp 1–204. DOI: [10.1201/b16483](https://doi.org/10.1201/b16483).
- (19) Backleh-Sohrt, M.; Ekici, P.; Leupold, G.; Parlar, H. Efficiency of Foam Fractionation for the Enrichment of Nonpolar Compounds from Aqueous Extracts of Plant Materials. *J. Nat. Prod.* **2005**, *68* (9), 1386–1389.
- (20) Fei, X.; Li, W.; Zhu, S.; Liu, L.; Yang, Y. Simultaneous Treatment of Dye Wastewater and Surfactant Wastewater by Foam Separation: Experimental and Mesoscopic Simulation Study. *Sep. Sci. Technol.* **2018**, *53* (10), 1604–1610.
- (21) Yan, J.; Wu, Z.; Wang, W. Separation of Tea Saponin by Two-Stage Continuous Foam Fractionation. *Sep. Sci. Technol.* **2012**, *47* (16), 2460–2466.
- (22) Miyake, M.; Yamashita, Y. Molecular Structure and Phase Behavior of Surfactants. In *Cosmetic Science and Technology*; Elsevier, 2017; pp 389–414. DOI: [10.1016/B978-0-12-802005-0.00024-0](https://doi.org/10.1016/B978-0-12-802005-0.00024-0).
- (23) Buckley, T.; Xu, X.; Rudolph, V.; Firouzi, M.; Shukla, P. Review of Foam Fractionation as a Water Treatment Technology. *Sep. Sci. Technol.* **2022**, *57* (6), 929–958.
- (24) Myers, D. *Surfactant Science and Technology*, 4th ed.; Wiley: Hoboken, NJ, USA, 2020; pp 1–151. DOI: [10.1002/9781119465829](https://doi.org/10.1002/9781119465829).
- (25) Shi, M.; Wu, Z. A Novel Three-Stage Foam Separation Technology for Recovering Sodium Dodecylbenzene Sulfonate from Its Wastewater. *J. Taiwan Inst. Chem. Eng.* **2016**, *63*, 1–5.
- (26) Tobin, S. T.; Weaire, D.; Hutzler, S. Theoretical Analysis of the Performance of a Foam Fractionation Column. *Proc. R. Soc. A Math. Phys. Eng. Sci.* **2014**, *470* (2165), 20130625.
- (27) Martin, P. J.; Dutton, H. M.; Winterburn, J. B.; Baker, S.; Russell, A. B. Foam Fractionation with Reflux. *Chem. Eng. Sci.* **2010**, *65* (12), 3825–3835.
- (28) Rosa, P. T. V.; Santana, C. C.; Carbonell, R. G. Determination of the Liquid Pool Surfactant and Protein Concentration for Semi-Batch Foam Fractionation Columns. *Brazilian J. Chem. Eng.* **2007**, *24* (1), 1–14.
- (29) Chen, S.; Timmons, M. B.; Bisogni, J. J.; Aneshansley, D. J. Modeling Surfactant Removal in Foam Fractionation: I — Theoretical Development. *Aquac. Eng.* **1994**, *13* (3), 163–181.
- (30) Narsimhan, G. FLOTATION | Foam Fractionation. In *Encyclopedia of Separation Science*; Elsevier, 2000; pp 1513–1521. DOI: [10.1016/B0-12-226770-2/05841-5](https://doi.org/10.1016/B0-12-226770-2/05841-5).
- (31) Burghoff, B. Foam Fractionation Applications. *J. Biotechnol.* **2012**, *161* (2), 126–137.
- (32) Bhakta, A.; Ruckenstein, E. Decay of Standing Foams: Drainage, Coalescence and Collapse. *Adv. Colloid Interface Sci.* **1997**, *70* (1–3), 1–124.
- (33) Grassia, P.; Torres-Ulloa, C. A Model for Foam Fractionation with Spatially Varying Bubble Size. *Chem. Eng. Sci.* **2023**, *281*, 119163.



- (34) Langevin, D. Aqueous Foams and Foam Films Stabilised by Surfactants. Gravity-Free Studies. *Comptes Rendus. Mécanique* **2017**, *345* (1), 47–55.
- (35) Kumar Bharadwaj, T.; Naresh Gupta, K. Dye Separation Using a Semi-Batch Foaming Process: Process Optimization Using Taguchi Methodology and Grey Relational Analysis. *Environ. Eng. Res.* **2021**, *26* (4), 200242.
- (36) Rubin, E.; Scherfig, J. A. N. *Adsorptive Bubble Separation Techniques*; Elsevier, 1972; pp 1–331. DOI: 10.1016/B978-0-12-443350-2.X5001-1.
- (37) Pinfeld, T. A. Adsorptive Bubble Separation Methods. *Sep. Sci.* **1970**, *5* (4), 379–384.
- (38) Rubin, A. J. *Removal of Surface Inactive Substance By Foam Separation Process*; Ohio, 1972; pp 1–50.
- (39) Stevenson, P. *Foam Engineering*; Stevenson, P., Ed.; Wiley, 2012; pp 1–530. DOI: 10.1002/9781119954620.
- (40) Lemlich, R. ADSORPTIVE BUBBLE SEPARATION METHODS—Foam Fractionation and Allied Techniques. *Ind. Eng. Chem.* **1968**, *60* (10), 16–29.
- (41) Somasundaran, P. Separation Using Foaming Techniques. *Sep. Sci.* **1975**, *10* (1), 93–109.
- (42) Grieves, R. B. Foam Separations: A Review. *Chem. Eng. J.* **1975**, *9* (2), 93–106.
- (43) Lockwood, C. E.; Bummer, P. M.; Jay, M. Purification of Proteins Using Foam Fractionation. *Pharm. Res.* **1997**, *14* (11), 1511.
- (44) Oraby, A.; Weickardt, I.; Zibek, S. Foam Fractionation Methods in Aerobic Fermentation Processes. *Biotechnol. Bioeng.* **2022**, *119* (7), 1697–1711.
- (45) Dolman, B. M.; Wang, F.; Winterburn, J. B. Integrated Production and Separation of Biosurfactants. *Process Biochem.* **2019**, *83* (May), 1–8.
- (46) We, A. C. E.; Zamyadi, A.; Stickland, A. D.; Clarke, B. O.; Freguia, S. A Review of Foam Fractionation for the Removal of Per- and Polyfluoroalkyl Substances (PFAS) from Aqueous Matrices. *J. Hazard. Mater.* **2024**, *465*, 133182.
- (47) Denkov, N. D.; Marinova, K. G. *Antifoam Effects of Solid Particles, Oil Drops and Oil-Solid Compounds in Aqueous Foams*; Cambridge University Press, 2009; pp 383–444. DOI: 10.1017/CBO9780511536670.011.
- (48) Taggart, A. F. Mineral Flotation. *J. Phys. Chem.* **1932**, *36* (1), 130–153.
- (49) Mondal, S.; Acharjee, A.; Mandal, U.; Saha, B. Froth Flotation Process and Its Application. *Vietnam J. Chem.* **2021**, *59* (4), 417–425.
- (50) Jiang, J.; Wu, Z.; Liu, W.; Gao, Y.; Guo, S.; Kang, S. Separation of Soybean Saponins from Soybean Meal by a Technology of Foam Fractionation and Resin Adsorption. *Prep. Biochem. Biotechnol.* **2016**, *46* (4), 346–353.
- (51) Hiraide, M. Foam Fractionation and Flotation. In *Encyclopedia of Analytical Science*; Elsevier, 2005; pp 195–201. DOI: 10.1016/B0-12-369397-7/00174-6.
- (52) Eldib, I. A. Foam Fractionation for Removal of Soluble Organics from Wastewater. *J. Water Pollut. Control Fed.* **1961**, *33*, 914–931.
- (53) Mat-Kuling Norwegian Ras Technology. *Protein Skimmers - Foam Fractionators*. <https://matkuling.com/equipment/protein-skimmer-fractionator-aquaculture/> (Accessed online: 13.09.2024).
- (54) Henderson Plastics Ltd. *Commercial Foam Fractionators*. [https://www.hendersons.co.uk/wms/foam\\_fractionator.html](https://www.hendersons.co.uk/wms/foam_fractionator.html) (Accessed online: 13.09.2024).
- (55) Pure Aquatics. *RK2 Freshwater Foam Fractionators*. <https://pureaquatics.com.au/rk2-systems-protein-fractionators/rk2-freshwater-foam-fractionators/> (Accessed online: 13.09.2024).
- (56) OPEC Systems. *Pfas Solutions*. <https://opecsystems.com/enviro/pfas-solutions/> (Accessed online: 13.09.2024).
- (57) Danek, V. Surface Tension. In *Physico-Chemical Analysis of Molten Electrolytes*; Elsevier, 2006; pp 271–312, Vol. 105. DOI: 10.1016/B978-044452116-3/50007-6.
- (58) Kronberg, B.; Holmberg, K.; Lindman, B. *Surface Chemistry of Surfactants and Polymers*; Wiley, 2014; pp 1–479. DOI: 10.1002/9781118695968.
- (59) Rekiel, E. A. Adsorption Effectiveness and Adsorption Efficiency of Chosen Surfactants. *Annales Universitatis Mariae Curie-Skłodowska Lublin – Polonia* **2019**, *LXXIII*, 51–60.
- (60) Ghosh, S.; Ray, A.; Pramanik, N. Self-Assembly of Surfactants: An Overview on General Aspects of Amphiphiles. *Biophys. Chem.* **2020**, *265* (July), 106429.
- (61) Sohrabi, B. Amphiphiles. In *Self-Assembly of Materials and Supramolecular Structures*; IntechOpen, 2022; pp 1–25. DOI: 10.5772/intechopen.107880.
- (62) De Angelis, P.; Cardellini, A.; Asinari, P. Exploring the Free Energy Landscape to Predict the Surfactant Adsorption Isotherm at the Nanoparticle-Water Interface. *ACS Cent. Sci.* **2019**, *5* (11), 1804–1812.
- (63) Berg, J. C. The Role of Surfactants. In *Textile Science and Technology*; Elsevier Masson SAS, 2002; pp 149–198. DOI: 10.1016/S0920-4083(02)80008-1.
- (64) Yunfei, H.; Yazhuo, S.; Honglai, L.; Dominique, L.; Anniina, S. Surfactant Adsorption onto Interfaces: Measuring the Surface Excess in Time. *Langmuir* **2012**, *28* (6), 3146–3151.
- (65) Menger, F. M.; Rizvi, S. A. A Relationship between Surface Tension and Surface Coverage. *Langmuir* **2011**, *27* (23), 13975–13977.
- (66) Gerola, A. P.; Costa, P. F. A.; Nome, F.; Quina, F. Micellization and Adsorption of Zwitterionic Surfactants at the Air/Water Interface. *Curr. Opin. Colloid Interface Sci.* **2017**, *32*, 48–56.
- (67) Danov, K. D.; Kralchevsky, P. A.; Denkov, N. D.; Ananthapadmanabhan, K. P.; Lips, A. Dynamics of Adsorption from Micellar Surfactant Solutions at Expanding Fluid Interfaces in Relation to the Emulsification Process. *Proc. 4th World Congr. Emuls. Lyon, Fr.* **2006**, No. Paper No. 2.1-376, 3–8.
- (68) Mandal, A. Foam Fractionation in Recovery of Captopril. *MARMARA Pharm. J.* **2013**, *3* (17), 170–170.
- (69) Boonyasuwat, S.; Chavadej, S.; Malakul, P.; Scamehorn, J. F. Anionic and Cationic Surfactant Recovery from Water Using a Multistage Foam Fractionator. *Chem. Eng. J.* **2003**, *93* (3), 241–252.
- (70) Brunner, C. A.; Stephan, D. G. FOAM FRACTIONATION. *Ind. Eng. Chem.* **1965**, *57* (5), 40–48.
- (71) Chang, Q. Emulsion, Foam, and Gel. In *Colloid and Interface Chemistry for Water Quality Control*; Elsevier, 2016; pp 227–245. DOI: 10.1016/B978-0-12-809315-3.00011-6.
- (72) Patist, A.; Bhagwat, S. S.; Penfield, K. W.; Aikens, P.; Shah, D. O. On the Measurement of Critical Micelle Concentrations of Pure and Technical-Grade Nonionic Surfactants. *J. Surfactants Deterg.* **2000**, *3* (1), 53–58.
- (73) Fainerman, V. B.; Miller, R. Liquid Interfaces: Adsorption Isotherms. *Encycl. Surf. Colloid Sci. Third Ed.* **2016**, 3842–3857.
- (74) Rosen, M. J.; Kunjappu, J. T. Characteristic Features of Surfactants. In *Surfactants and Interfacial Phenomena*; Wiley, 2012; pp 1–38. DOI: 10.1002/9781118228920.ch1.
- (75) Abbott, S. Surfactant Science: Principles and Practice. *Surfactant Sci. Princ. Pract.* **2015**, 1–249.
- (76) Danov, K. D.; Kralchevsky, P. A.; Ivanov, I. B. Equilibrium and Dynamics of Surfactant Adsorption Monolayers and Thin Liquid Films. In *Handbook of Detergents - 6 Vol. Set*; CRC Press, 2008; pp 319–434. DOI: 10.1201/NOE1420091625-16.
- (77) Tadros, T. *Encyclopedia of Colloid and Interface Science*; 2013; pp 1–1436.
- (78) Wanschura, R.; Windeisen, E.; Richter, K. Application of Foam Fractionation to Wood. *Wood Sci. Technol.* **2019**, *53* (2), 349–371.
- (79) Wang, T.; Huang, D.; Wang, X.; Chang, D.; Liu, H.; Zhong, C.; Wu, Z. Microbubble-Foam Fractionation Enabled Long-Term Caffeic Acid Stability in the Separation Process: Self-Assembly WSP as Collector. *J. Mol. Liq.* **2021**, *342*, 117467.
- (80) Tadros, T. F. *Applied Surfactants*; Wiley, 2005; pp 1–634. DOI: 10.1002/3527604812.

- (81) Martínez-Balbuena, L.; Arteaga-Jiménez, A.; Hernández-Zapata, E.; Márquez-Beltrán, C. Applicability of the Gibbs Adsorption Isotherm to the Analysis of Experimental Surface-Tension Data for Ionic and Nonionic Surfactants. *Adv. Colloid Interface Sci.* **2017**, *247* (April), 178–184.
- (82) Li, P. X.; Li, Z. X.; Shen, H.-H.; Thomas, R. K.; Penfold, J.; Lu, J. R. Application of the Gibbs Equation to the Adsorption of Nonionic Surfactants and Polymers at the Air-Water Interface: Comparison with Surface Excesses Determined Directly Using Neutron Reflectivity. *Langmuir* **2013**, *29* (30), 9324–9334.
- (83) Vafakish, B.; Wilson, L. D. A Review on Recent Progress of Glycan-Based Surfactant Micelles as Nanoreactor Systems for Chemical Synthesis Applications. *Polysaccharides* **2021**, *2* (1), 168–186.
- (84) Shahir, A. A.; Nguyen, K. T.; Nguyen, A. V. A Sum-Frequency Generation Spectroscopic Study of the Gibbs Analysis Paradox: Monolayer or Sub-Monolayer Adsorption? *Phys. Chem. Chem. Phys.* **2016**, *18* (13), 8794–8805.
- (85) Bera, A.; Kumar, T.; Ojha, K.; Mandal, A. Adsorption of Surfactants on Sand Surface in Enhanced Oil Recovery: Isotherms, Kinetics and Thermodynamic Studies. *Appl. Surf. Sci.* **2013**, *284*, 87–99.
- (86) Ivanov, I. B.; Danov, K. D.; Dimitrova, D.; Boyanov, M.; Ananthapadmanabhan, K. P.; Lips, A. Equations of State and Adsorption Isotherms of Low Molecular Non-Ionic Surfactants. *Colloids Surfaces A Physicochem. Eng. Asp.* **2010**, *354* (1–3), 118–133.
- (87) Mańko, D.; Zdziennicka, A.; Jańczuk, B. Adsorption and Aggregation Activity of Sodium Dodecyl Sulfate and Rhamnolipid Mixture. *J. Surfactants Deterg.* **2017**, *20* (2), 411–423.
- (88) Hinton, Z. R.; Alvarez, N. J. A Molecular Parameter to Scale the Gibbs Free Energies of Adsorption and Micellization for Nonionic Surfactants. *Colloids Surfaces A Physicochem. Eng. Asp.* **2021**, *609*, 125622.
- (89) Ebelegi, A. N.; Ayawei, N.; Wankasi, D. Interpretation of Adsorption Thermodynamics and Kinetics. *Open J. Phys. Chem.* **2020**, *10* (03), 166–182.
- (90) Danov, K. D.; Kralchevsky, P. A. The Standard Free Energy of Surfactant Adsorption at Air/Water and Oil/Water Interfaces: Theoretical vs. Empirical Approaches. *Colloid J.* **2012**, *74* (2), 172–185.
- (91) Fainerman, V. B.; Miller, R. Thermodynamics of Adsorption of Surfactants at the Fluid Interfaces. *Studies in Interface Science* **2001**, *13*, 99–188.
- (92) Zdziennicka, A.; Szymczyk, K.; Krawczyk, J.; Jańczuk, B. Activity and Thermodynamic Parameters of Some Surfactants Adsorption at the Water-Air Interface. *Fluid Phase Equilib.* **2012**, *318*, 25–33.
- (93) Zdziennicka, A.; Jańczuk, B. Thermodynamic Parameters of Some Biosurfactants and Surfactants Adsorption at Water-Air Interface. *J. Mol. Liq.* **2017**, *243*, 236–244.
- (94) Mańko, D.; Zdziennicka, A.; Janczuk, B. Thermodynamic Properties of Rhamnolipid Micellization and Adsorption. *Colloids Surfaces B Biointerfaces* **2014**, *119*, 22–29.
- (95) Hinton, Z. R.; Alvarez, N. J. A Molecular Parameter to Scale the Gibbs Free Energies of Adsorption and Micellization for Nonionic Surfactants. *Colloids Surfaces A Physicochem. Eng. Asp.* **2021**, *609*, 125622.
- (96) Merz, J.; Burghoff, B.; Zorn, H.; Schembecker, G. Continuous Foam Fractionation: Performance as a Function of Operating Variables. *Sep. Purif. Technol.* **2011**, *82* (1), 10–18.
- (97) He, Y.; Yazhgur, P.; Salonen, A.; Langevin, D. Adsorption-Desorption Kinetics of Surfactants at Liquid Surfaces. *Adv. Colloid Interface Sci.* **2015**, *222*, 377–384.
- (98) Danov, K. D.; Valkovska, D. S.; Kralchevsky, P. A. Adsorption Relaxation for Nonionic Surfactants under Mixed Barrier-Diffusion and Micellization-Diffusion Control. *J. Colloid Interface Sci.* **2002**, *251* (1), 18–25.
- (99) Borwankar, R. P.; Wasan, D. T. The Kinetics of Adsorption of Surface Active Agents at Gas-Liquid Surfaces. *Chem. Eng. Sci.* **1983**, *38* (10), 1637–1649.
- (100) LIU, J.; XU, Y.; SUN, H. Diffusion-Controlled Adsorption Kinetics of Surfactant at Air/Solution Interface. *Chin. J. Chem. Eng.* **2013**, *21* (9), 953–958.
- (101) Ahmad, S. I. Laws of Foam Formation and Foam Fractionation. I. The Effect of Different Operating Parameters on the Foam Fractionation of Albumin from a Solution Containing Organic and Inorganic Materials. *Sep. Sci.* **1975**, *10* (6), 673–688.
- (102) Pugh, R. J. Experimental Techniques for Studying the Structure of Foams and Froths. *Adv. Colloid Interface Sci.* **2005**, *114–115*, 239–251.
- (103) Moorkanikkara, S. N.; Blankschtein, D. Short-Time Behavior of Mixed Diffusion-Barrier Controlled Adsorption. *J. Colloid Interface Sci.* **2006**, *296* (2), 442–457.
- (104) Damodaran, S.; Song, K. B. Diffusion and Energy Barrier Controlled Adsorption of Proteins at the Air–Water Interface. *ACS Symp. Ser.* **1991**, *454*, 104–121.
- (105) Ahuja, S. Mass Transport and Separation. In *Sep. Sci. Technol.*; Academic Press, 2003; pp 69–79. DOI: 10.1016/S0149-6395(03)80023-5.
- (106) van Wijngaarden, L.; Vossers, G. Mechanics and Physics of Gas Bubbles in Liquids: A Report on Euromech 98. *J. Fluid Mech.* **1978**, *87* (04), 695–704.
- (107) Mikhailovskaya, A.; Chatzigiannakis, E.; Renggli, D.; Vermant, J.; Monteux, C. From Individual Liquid Films to Macroscopic Foam Dynamics: A Comparison between Polymers and a Nonionic Surfactant. *Langmuir* **2022**, *38* (35), 10768–10780.
- (108) Lazidis, A.; de Almeida Parizotto, L.; Spyropoulos, F.; Norton, I. T. Reprint of: Microstructural Design of Aerated Food Systems by Soft-Solid Materials. *Food Hydrocoll.* **2018**, *78*, 26–35.
- (109) Fereidoon, A.; Yaghoobi, H.; Davoudabadi, M. Application of the Homotopy Perturbation Method for Solving the Foam Drainage Equation. *Int. J. Differ. Equations* **2011**, DOI: 10.1155/2011/864023.
- (110) Breward, C. J. W.; Howell, P. D. The Drainage of a Foam Lamella. *J. Fluid Mech.* **2002**, *458*, 379–406.
- (111) Lee, J.; Nikolov, A.; Wasan, D. Foam Stability: The Importance of Film Size and the Micellar Structuring Phenomenon. *Can. J. Chem. Eng.* **2014**, *92* (12), 2039–2045.
- (112) Koursari, N.; Arjmandi-Tash, O.; Trybala, A.; Starov, V. M. Drying of Foam under Microgravity Conditions. *Microgravity Sci. Technol.* **2019**, *31* (5), 589–601.
- (113) Moradpour, N.; Yang, J.; Tsai, P. A. Liquid Foam: Fundamentals, Rheology, and Applications of Foam Displacement in Porous Structures. *Curr. Opin. Colloid Interface Sci.* **2024**, *74*, 101845.
- (114) Tadros, T. F. 7. Surfactants for Foam Stabilization. In *An Introduction to Surfactants*; De Gruyter, 2014; pp 121–134. DOI: 10.1515/9783110312133.121.
- (115) Briceño-Ahumada, Z.; Langevin, D. On the Influence of Surfactant on the Coarsening of Aqueous Foams. *Adv. Colloid Interface Sci.* **2017**, *244*, 124–131.
- (116) Drenckhan, W.; Hutzler, S. Structure and Energy of Liquid Foams. *Adv. Colloid Interface Sci.* **2015**, *224*, 1–16.
- (117) Koehler, S. A.; Hilgenfeldt, S.; Stone, H. A. A Generalized View of Foam Drainage: Experiment and Theory. *Langmuir* **2000**, *16* (15), 6327–6341.
- (118) El-Nabulsi, R. A.; Anukool, W. Foam Drainage Equation in Fractal Dimensions: Breaking and Instabilities. *Eur. Phys. J. E* **2023**, DOI: 10.1140/epje/s10189-023-00368-6.
- (119) Stevenson, P. Dimensional Analysis of Foam Drainage. *Chem. Eng. Sci.* **2006**, *61* (14), 4503–4510.
- (120) Cox, S. J.; Weaire, D.; Hutzler, S.; Murphy, J.; Phelan, R.; Verbist, G. Applications and Generalizations of the Foam Drainage Equation. *Proc. R. Soc. A Math. Phys. Eng. Sci.* **2000**, *456* (2002), 2441–2464.
- (121) Verbist, G.; Weaire, D.; Kraynik, A. M. The Foam Drainage Equation. *J. Phys.: Condens. Matter* **1996**, *8* (21), 3715–3731.

- (122) Huang, J.; Zhu, L.; Zeng, G.; Shi, L.; Shi, Y.; Yi, K.; Li, X. Recovery of Cd(II) and Surfactant in Permeate from MEUF by Foam Fractionation with Anionic-Nonionic Surfactant Mixtures. *Colloids Surfaces A Physicochem. Eng. Asp.* **2019**, *570* (March), 81–88.
- (123) Kumpabooth, K.; Scamehorn, J. F.; Osuwan, S.; Harwell, J. H. Surfactant Recovery from Water Using Foam Fractionation: Effect of Temperature and Added Salt. *Sep. Sci. Technol.* **1999**, *34* (2), 157–172.
- (124) Wheaton, F. W.; Lawson, T. B.; Lomax, K. M. Foam Fractionation Applied to Aquacultural Systems. *Proc. World Maric. Soc.* **1979**, *10* (1–4), 795–808.
- (125) Mandal, A. Separation of Bovine Serum Albumin (BSA) Protein by Foam Fractionation Technique. *Bov. Sci. - Challenges Adv.* **2022**, 1–15.
- (126) Bharadwaj, T.; Gupta, K. N. Foam Drainage Enhancement in Foam Fractionation for Dye Removal: Process Optimization by Taguchi Methodology and Grey Relational Analysis. *Int. J. Chem. React. Eng.* **2021**, *19* (7), 749–765.
- (127) Firlbeck, D.; Faulstich, M.; Urmann, C.; Azaizeh, H.; Tafesh, A.; Riepl, H. Central Composite Design for Optimal Technology of Concentrating Vanillic Acid Using Foam Fractionation. *Sep. Purif. Technol.* **2013**, *119*, 28–34.
- (128) Wang, Y.; Nan, F.; Zheng, H.; Wu, Z. Effects of Temperature and Trehalose on Foam Separation of Nisin from the Culture Broth Produced by *Lactococcus Lactis* Subspecies *Lactis* W28. *J. Dairy Sci.* **2012**, *95* (10), 5588–5596.
- (129) Boonyasuwat, S.; Chavadej, S.; Malakul, P.; Scamehorn, J. F. Surfactant Recovery from Water Using a Multistage Foam Fractionator: Effect of Surfactant Type. *Sep. Sci. Technol.* **2009**, *44* (7), 1544–1561.
- (130) Kumar, A. K.; Ghosh, P. Removal and Recovery of an Anionic Surfactant in the Presence of Alcohol by Foam Fractionation. *Ind. Eng. Chem. Res.* **2022**, *61* (21), 7349–7360.
- (131) Jeong, G.-T.; Park, E.-S.; Wahlig, V. L.; Burapatana, V.; Park, D.-H.; Tanner, R. D. Effect of PH on the Foam Fractionation of *Mimosa Pudica* L. Seed Proteins. *Ind. Eng. Chem. Res.* **2004**, *43* (2), 422–427.
- (132) Cho, D.; Chang, H. N. Separation of Oil Contaminants by Surfactant-Aided Foam Fractionation. *Korean J. Chem. Eng.* **1998**, *15* (4), 445–448.
- (133) Jia, L.; Liu, W.; Cao, J.; Wu, Z.; Yang, C. Recovery of Nanoparticles from Wastewater by Foam Fractionation: Regulating Bubble Size Distribution for Strengthening Foam Drainage. *J. Environ. Chem. Eng.* **2021**, *9* (4), 105383.
- (134) Du, L.; Prokop, A.; Tanner, R. D. Effect of PH on the Startup of a Continuous Foam Fractionation Process Containing Ovalbumin. *Sep. Sci. Technol.* **2003**, *38* (5), 1093–1109.
- (135) Lambert, W. D.; Du, L.; Ma, Y.; Loha, V.; Burapatana, V.; Prokop, A.; Tanner, R. D.; Pamment, N. B. The Effect of PH on the Foam Fractionation of  $\beta$ -Glucosidase and Cellulase. *Bioresour. Technol.* **2003**, *87* (3), 247–253.
- (136) Arulmozhi, M.; Begum, K. M. M. S.; Anantharaman, N. Continuous Foam Separation of Heavy Metal Ions from Electroplating Industrial Effluent. *Chem. Eng. Commun.* **2010**, *198* (4), 541–551.
- (137) Chen, H. R.; Chen, C. C.; Reddy, A. S.; Chen, C. Y.; Li, W. R.; Tseng, M. J.; Liu, H. T.; Pan, W.; Maity, J. P.; Atla, S. B. Removal of Mercury by Foam Fractionation Using Surfactin, a Biosurfactant. *Int. J. Mol. Sci.* **2011**, *12* (11), 8245–8258.
- (138) Lu, J.; Liu, Z.; Wu, Z.; Liu, W.; Yang, C. Synergistic Effects of Binary Surfactant Mixtures in the Removal of Cr(VI) from Its Aqueous Solution by Foam Fractionation. *Sep. Purif. Technol.* **2020**, *237* (Vi), 116346.
- (139) Maity, J. P.; Huang, Y. M.; Hsu, C. M.; Wu, C. I.; Chen, C. C.; Li, C. Y.; Jean, J. S.; Chang, Y. F.; Chen, C. Y. Removal of Cu, Pb and Zn by Foam Fractionation and a Soil Washing Process from Contaminated Industrial Soils Using Soapberry-Derived Saponin: A Comparative Effectiveness Assessment. *Chemosphere* **2013**, *92* (10), 1286–1293.
- (140) Kinoshita, T.; Akita, S.; Ozawa, S.; Nii, S.; Kawaizumi, F.; Takahashi, K. Continuous Recovery of Gold(III) via Foam Separation with Nonionic Surfactant. *J. Miner. Mater. Charact. Eng.* **2004**, *03* (01), 53–63.
- (141) Grieves, R. B.; Wood, R. K. Continuous Foam Fractionation: The Effect of Operating Variables on Separation. *AIChE J.* **1964**, *10* (4), 456–460.
- (142) Hofmann, A.; Schembecker, G.; Merz, J. Role of Bubble Size for the Performance of Continuous Foam Fractionation in Stripping Mode. *Colloids Surfaces A Physicochem. Eng. Asp.* **2015**, *473*, 85–94.
- (143) Du, L.; Ding, Y.; Prokop, A.; Tanner, R. D. Measurement of Bubble Size Distribution in Protein Foam Fractionation Column Using Capillary Probe with Photoelectric Sensors. *Twenty-Second Symp. Biotechnol. Fuels Chem.* **2001**, *91*, 387–404.
- (144) Diaz De Rienzo, M. A.; Kamalanathan, I. D.; Martin, P. J. Comparative Study of the Production of Rhamnolipid Biosurfactants by *B. Thailandensis* E264 and *P. Aeruginosa* ATCC 9027 Using Foam Fractionation. *Process Biochem.* **2016**, *51* (7), 820–827.
- (145) Kumar, A. K.; Rawat, N.; Ghosh, P. Removal and Recovery of a Cationic Surfactant from Its Aqueous Solution by Foam Fractionation. *J. Environ. Chem. Eng.* **2020**, *8* (2), 103555.
- (146) Kown, B. T. The Effects of Column Height and Diameter on the Effectiveness of a Continuous Bubble Fractionation System. *Water Res.* **1971**, *5* (3), 93–102.
- (147) Crofcheck, C.; Gillette, K. Evaluation Of Foam Fractionation Column Scale-up For Recovering Bovine Serum Albumin. *Trans. ASAE* **2003**, *46* (6), 1759–1764.
- (148) Tharapiwattananon, N.; Scamehorn, J. F.; Osuwan, S.; Harwell, J. H.; Haller, K. J. Surfactant Recovery from Water Using Foam Fractionation. *Sep. Sci. Technol.* **1996**, *31* (9), 1233–1258.
- (149) Liu, Z.; Liu, Z.; Wang, D.; Ding, F.; Yuan, N. On the Denaturation of Enzymes in the Process of Foam Fractionation. *Bioseparation* **1998**, *7* (3), 167–174.
- (150) Nakabayashi, T.; Takakusagi, Y.; Iwabata, K.; Sakaguchi, K. Foam Fractionation of Protein: Correlation of Protein Adsorption onto Bubbles with a PH-Induced Conformational Transition. *Anal. Biochem.* **2011**, *419* (2), 173–179.
- (151) Goto, Y.; Nema, Y.; Matsuoka, K. Foam Separation of Dyes Using Anionic, Cationic, and Amphoteric Surfactants. *J. Oleo Sci.* **2020**, *69* (6), 549–555.
- (152) Winterburn, J. B.; Russell, A. B.; Martin, P. J. Integrated Recirculating Foam Fractionation for the Continuous Recovery of Biosurfactant from Fermenters. *Biochem. Eng. J.* **2011**, *54* (2), 132–139.
- (153) Vo, P. H. N.; Buckley, T.; Xu, X.; Nguyen, T. M. H.; Rudolph, V.; Shukla, P. Foam Fractionation of Per- and Polyfluoroalkyl Substances (PFASs) in Landfill Leachate Using Different Cosurfactants. *Chemosphere* **2023**, *310*, 136869.
- (154) Blesken, C. C.; Strümpfler, T.; Tiso, T.; Blank, L. M. Uncoupling Foam Fractionation and Foam Adsorption for Enhanced Biosurfactant Synthesis and Recovery. *Microorganisms* **2020**, *8* (12), 2029.
- (155) Darton, R. C.; Supino, S.; Sweeting, K. J. Development of a Multistaged Foam Fractionation Column. *Chem. Eng. Process. Process Intensif.* **2004**, *43* (3), 477–482.
- (156) Koop, J.; Merz, J.; Wilmshöfer, R.; Winter, R.; Schembecker, G. Influence of Thermally Induced Structure Changes in Diluted  $\beta$ -Lactoglobulin Solutions on Their Surface Activity and Behavior in Foam Fractionation. *J. Biotechnol.* **2020**, *319* (May), 61–68.
- (157) Liu, Y.; Wu, Z.; Zhao, B.; Li, L.; Li, R. Enhancing Defoaming Using the Foam Breaker with Perforated Plates for Promoting the Application of Foam Fractionation. *Sep. Purif. Technol.* **2013**, *120*, 12–19.
- (158) Li, R.; Wu, Z.; Wang, L.; Yang, Q.; Zhu, H. Enhancing Foam Drainage by Spiral Internal Components of Different Thread Pitches and Inclined Angles and Their Applications to Enrichment of SDS. *Sep. Purif. Technol.* **2012**, *98*, 109–117.

- (159) Schlebusch, I.; Pott, R. W. M.; Tadie, M. The Ion Flotation of Copper, Nickel, and Cobalt Using the Biosurfactant Surfactin. *Discovery Chem. Eng.* **2023**, DOI: 10.1007/s43938-023-00023-8.
- (160) Li, L.; Zhang, Y.; Wu, Z.; Liu, Y.; Zhang, L. Separation of SDS from Its Determined Lowest Concentration by a Two-Stage Foam Separation. *Sep. Purif. Technol.* **2014**, *129*, 50–56.
- (161) Morgan, G.; Wiesmann, U. Single And Multistage Foam Fractionation Of Rinse Water With Alkyl Ethoxylate Surfactants. *Sep. Sci. Technol.* **2001**, *36* (10), 2247–2263.
- (162) Shen, Y.-H. Cloud Point Foaming Technique for Separation of Nonionic Surfactant from Solution. *Sep. Sci. Technol.* **1997**, *32* (13), 2229–2235.
- (163) Li, R.; Wu, Z.; Wang, Y.; Liu, W. Pilot Study of Recovery of Whey Soy Proteins from Soy Whey Wastewater Using Batch Foam Fractionation. *J. Food Eng.* **2014**, *142*, 201–209.
- (164) Linke, D.; Zorn, H.; Gerken, B.; Parlar, H.; Berger, R. G. Laccase Isolation by Foam Fractionation-New Prospects of an Old Process. *Enzyme Microb. Technol.* **2007**, *40* (2), 273–277.
- (165) Matavos-Aramyan, S.; Ghazi-MirSaeed, M.; Saeedi-Emadi, A.; Nemati, M.; Neysari, S. Influence of the Process Parameters on the Foam Fractionation Treatment of Olive Mill Wastewater. *Sci. Iran.* **2016**, *23* (6), 2820–2827.
- (166) McCleaf, P.; Stefansson, W.; Ahrens, L. Drinking Water Nanofiltration with Concentrate Foam Fractionation—A Novel Approach for Removal of per- and Polyfluoroalkyl Substances (PFAS). *Water Res.* **2023**, *232*, 119688.
- (167) Smith, S. J.; Wiberg, K.; McCleaf, P.; Ahrens, L. Pilot-Scale Continuous Foam Fractionation for the Removal of Per- A Nd Polyfluoroalkyl Substances (PFAS) from Landfill Leachate. *ACS Environ. Sci. Technol. Water* **2022**, *2*, 841.
- (168) Huang, D.; Liu, W.; Wu, Z.; Liu, G.; Yin, H.; Chen, Y.; Hu, N.; Jia, L. Removal of Pyridine from Its Wastewater by Using a Novel Foam Fractionation Column. *Chem. Eng. J.* **2017**, *321*, 151–158.
- (169) Huang, D.; Wu, Z. L.; Liu, W.; Hu, N.; Li, H. Z. A Novel Process Intensification Approach of Recovering Creatine from Its Wastewater by Batch Foam Fractionation. *Chem. Eng. Process. Process Intensif.* **2016**, *104*, 13–21.
- (170) Li, N.; Liu, W.; Wu, Z.; Xu, Y.; Shu, T.; Lu, K.; Zhao, Y. Recovery of Silk Sericin from the Filature Wastewater by Using a Novel Foam Fractionation Column. *Chem. Eng. Process. - Process Intensif.* **2018**, *129* (April), 37–42.
- (171) Qu, Y. H.; Zeng, G. M.; Huang, J. H.; Xu, K.; Fang, Y. Y.; Li, X.; Liu, H. L. Treatment of the Wastewater Containing Cd<sup>2+</sup> Using Micellar Enhanced Ultrafiltration Combined with Foam Fractionation. *Environ. Eng. Sci.* **2009**, *26* (4), 761–766.
- (172) Liu, W.; Wu, Z.; Wang, Y.; Li, R.; Ding, L.; Huang, D. Rhamnolipid Assisted Recovery of Lycopene from the Tomato-Based Processing Wastewater Using Foam Fractionation. *J. Food Eng.* **2015**, *164*, 63–69.
- (173) Burns, D. J.; Hinrichsen, H. M.; Stevenson, P.; Murphy, P. J. C. Commercial-Scale Remediation of per- and Polyfluoroalkyl Substances from a Landfill Leachate Catchment Using Surface-Active Foam Fractionation (SAFF). *Remediation* **2022**, *32* (3), 139–150.
- (174) Jaishankar, M.; Tseten, T.; Anbalagan, N.; Mathew, B. B.; Beeregowda, K. N. Toxicity, Mechanism and Health Effects of Some Heavy Metals. *Interdiscip. Toxicol.* **2014**, *7* (2), 60–72.
- (175) Shao, W.; Zhang, J.; Feng, A.; Pan, X.; Xiao, Z. Removal of Ni(II) in Aqueous Solutions by Foam Fractionation. *Desalin. Water Treat.* **2016**, *57* (40), 18724–18729.
- (176) Lu, J.; Li, Y.; Zhang, S.; Sun, Y. Removal of Trace Cd<sup>2+</sup> from Aqueous Solution by Foam Fractionation. *J. Hazard. Mater.* **2015**, *286*, 466–473.
- (177) Tabibi, S.; Moussavi, M.; Adlo, H. Cobalt Removal from an Industrial Effluent by Foam Fractionation. *Environ. Challenges* **2021**, *4* (April), 100135.
- (178) Matsuoka, K.; Miura, H.; Karima, S.; Taketaka, C.; Ouno, S.; Moroi, Y. Removal of Alkali Metal Ions from Aqueous Solution by Foam Separation Method. *J. Mol. Liq.* **2018**, *263*, 89–95.
- (179) Karger, B. L.; Rogers, L. B. Foam Fractionation of Organic Compounds. *Anal. Chem.* **1961**, *33* (9), 1165–1168.
- (180) Chen, C.; Li, G.; Dai, L.; Zhao, H.; Li, N.; Mi, W.; Yin, S.; Wang, S.; Zhang, J. Simultaneous Separation of Glycyrrhizic Acid, Baicalin and Wogonin from Radix Glycyrrhizae and Radix Scutellariae Using Foam Fractionation and in Vitro Activity Evaluation. *J. Sci. Food Agric.* **2022**, *102* (12), 5200–5209.
- (181) Ghosh, R.; Hareendran, H.; Subramaniam, P. Adsorption of Fluoroquinolone Antibiotics at the Gas-Liquid Interface Using Ionic Surfactants. *Langmuir* **2019**, *35*, 12839–12850.
- (182) Soylu, M.; Gökkuş, Ö.; Özyonar, F. Foam Separation for Effective Removal of Disperse and Reactive Dyes from Aqueous Solutions. *Sep. Purif. Technol.* **2020**, *247*, 116985.
- (183) Barbosa, F. G.; Ribeaux, D. R.; Rocha, T.; Costa, R. A. M.; Guzmán, R. R.; Marcelino, P. R. F.; Lacerda, T. M.; da Silva, S. S. Biosurfactants: Sustainable and Versatile Molecules. *J. Braz. Chem. Soc.* **2022**, *33* (8), 870–893.
- (184) Bezerra, K. G. O.; Silva, I. G. S.; Almeida, F. C. G.; Rufino, R. D.; Sarubbo, L. A. Plant-Derived Biosurfactants: Extraction, Characteristics and Properties for Application in Cosmetics. *Biocatal. Agric. Biotechnol.* **2021**, *34* (May), 102036.
- (185) Sobrinho, H. B. S.; Luna, J. M.; Rufino, R. D.; Porto, A. L. F.; Sarubbo, L. A. Biosurfactants: Classification, Properties and Environmental Applications. *Recent Dev. Biotechnol.* **2014**, *11*, 1–29.
- (186) Nagtode, V. S.; Cardoza, C.; Yasin, H. K. A.; Mali, S. N.; Tambe, S. M.; Roy, P.; Singh, K.; Goel, A.; Amin, P. D.; Thorat, B. R.; Cruz, J. N.; Pratap, A. P. Green Surfactants (Biosurfactants): A Petroleum-Free Substitute for Sustainability—Comparison, Applications, Market, and Future Prospects. *ACS Omega* **2023**, *8*, 11674.
- (187) Jahan, R.; Bodratti, A. M.; Tsianou, M.; Alexandridis, P. Biosurfactants, Natural Alternatives to Synthetic Surfactants: Physicochemical Properties and Applications. *Adv. Colloid Interface Sci.* **2020**, *275*, 102061.
- (188) da Silva, A. F.; Banat, I. M.; Giachini, A. J.; Robl, D. Fungal Biosurfactants, from Nature to Biotechnological Product: Bioprospection, Production and Potential Applications. *Bioprocess Biosyst. Eng.* **2021**, *44* (10), 2003–2034.
- (189) Ndlovu, T.; Rautenbach, M.; Vosloo, J. A.; Khan, S.; Khan, W. Characterisation and Antimicrobial Activity of Biosurfactant Extracts Produced by *Bacillus Amyloliquefaciens* and *Pseudomonas Aeruginosa* Isolated from a Wastewater Treatment Plant. *AMB Express* **2017**, DOI: 10.1186/s13568-017-0363-8.
- (190) Chen, C.-Y.; Baker, S. C.; Darton, R. C. Continuous Production of Biosurfactant with Foam Fractionation. *J. Chem. Technol. Biotechnol.* **2006**, *81* (12), 1915–1922.
- (191) Lethcoe, K.; Fox, C. A.; Ryan, R. O. Foam Fractionation of a Recombinant Biosurfactant Apolipoprotein. *J. Biotechnol.* **2022**, *343*, 25–31.
- (192) Bages-Estopa, S.; White, D. A.; Winterburn, J. B.; Webb, C.; Martin, P. J. Production and Separation of a Trehalolipid Biosurfactant. *Biochem. Eng. J.* **2018**, *139*, 85–94.
- (193) Khondee, N.; Tathong, S.; Pinyakong, O.; Müller, R.; Soonglerdsongpha, S.; Ruangchainikom, C.; Tongcumpou, C.; Luepromchai, E. Lipopeptide Biosurfactant Production by Chitosan-Immobilized *Bacillus* Sp. GY19 and Their Recovery by Foam Fractionation. *Biochem. Eng. J.* **2015**, *93*, 47–54.
- (194) Juang, Y.-P.; Liang, P.-H. Biological and Pharmacological Effects of Synthetic Saponins. *Molecules* **2020**, *25* (21), 4974.
- (195) Bartnik, M.; Facey, P. C. Glycosides. In *Pharmacognosy*; Badal, S., Delgoda, R., Eds.; Elsevier, 2017; pp 101–161. DOI: 10.1016/B978-0-12-802104-0.00008-1.
- (196) Yan, J.; Wu, Z.; Zhao, Y.; Jiang, C. Separation of Tea Saponin by Two-Stage Foam Fractionation. *Sep. Purif. Technol.* **2011**, *80* (2), 300–305.
- (197) Ding, L.; Wang, Y.; Wu, Z.; Liu, W.; Li, R.; Wang, Y. A Novel Technology Coupling Extraction and Foam Fractionation for Separating the Total Saponins from *Achyranthes Bidentata*. *Prep. Biochem. Biotechnol.* **2016**, *46* (7), 666–672.

(198) Zhang, X. M.; Li, X.-B.; Zhang, S. S.; He, Q. X.; Hou, H. R.; Dang, L.; Guo, J. L.; Chen, Y. F.; Yu, T.; Peng, D. J.; Han, L. W.; Liu, K. C. LC-MS/MS Identification of Novel Saponins from the Viscera of Sea Cucumber *Apostichopus Japonicus*. *Chem. Nat. Compd.* **2018**, *54* (4), 721–725.

(199) Wang, Z.; Zhang, W.; Gan, W.; Nie, S.; Gao, H.; Song, L. Preparation of Dioscin from *Trigonella Foenum-Graecum* by Foam Separation-Preparative High-Performance Liquid Chromatography. *Eur. Food Res. Technol.* **2022**, *248* (2), 477–483.

(200) Lei, L.; Zhang, W.; Gao, Z.; Liu, L.; Yu, X. Preparation of Diosgenin from *Dioscorea Zingiberensis* C. H. Wright by Stepwise Biocatalysis-Foam Separation-Preparative High-Performance Liquid Chromatography (P-HPLC). *Eur. Food Res. Technol.* **2018**, *244* (8), 1447–1452.