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Removal of trace $FeCl_3$ from aqueous solution by foam fractionation

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ABSTRACT

A foam fractionation technology of $FeCl_3$ from the simulated aqueous solution was studied by using dodecylbenzenesulphonic acid and (1-hexadecyl)trimethyl ammonium hydroxide as the surfactants, in order to develop a new desalination method, which has the virtues of simple equipments and technology, non-pollution and low cost. The effects of operating parameters such as pH and height of the bulk liquid, superficial gas velocity, surfactant dosage and separation sequence of Fe^{3+} and Cl^- on the enrichment ratio and removal rate of $FeCl_3$ were investigated. The experimental results show that, under the optimum conditions, the removals of $FeCl_3$ approached to 60.5%, enrichment ratio reached 1.7. Compared with the other surfactants, this technology will not introduce new acid radical ions and metal ions in the aqueous solutions and provides a basis for a new method of removing salt by foam fractionation.

Keywords: dodecylbenzenesulphonic; (1-hexadecyl)trimethyl ammonium hydroxide; foam fractionation; desalination

1. Introduction

Desalination is an important unit operation in the chemical and biochemical engineering separation process. At present, the desalination of industrialisation is processed by using ion exchange and all kinds of membrane separation methods, but these methods need higher costs, complex equipments and technologies. However, foam fractionation technology attracts a great deal of attention [1–3], because it is a simple, inexpensive, environment-friendly, and easy for scale-up method for the effective separation of surface-active compounds, proteins [4–6], microorganisms [7], suspended solids [8], aromatic substances [9], and pigments [10] from diluted aqueous solutions. In recent years, zinc, chromium, copper, cadmium, etc. metal ions [11,12] and BF_4^- [13], etc. acid radical ions can be effectively removed by foam fractionation, but at the same time, it will introduce new metal ions such as Na^+ [14] and acid radical ions such as Cl^- [15].

Therefore, there are no any reports on removing salts from aqueous solution by foam fractionation. The so-called desalination is defined as removing all kinds of metal cations and acid radical anions which compose the salts. Therefore, by using hydrogenous anion surfactants and hydroxy cation surfactants, the problem of desalination from the diluted aqueous solution will be resolved. Metal cations exchange with the H^+ of hydrogenous anion surfactants and combine with the hydrophilic parts of the surfactants. Acid radical anions of salts exchange with OH^- of hydroxy cation surfactants and combine with the hydrophilic parts of the surfactants. So when these surfactants are removed by foam fractionation, the metal cations and acidic radical anions of salts are also removed, and the residual H^+ and OH^- in the bulk liquid of the foam fractionation column are combined into H_2O.

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We have studied the removal of Cu^{2+} [16], SO_4^{2-} [17] by using foam fraction respectively.

But simultaneous removal of metal cations and acid radical anions has not been reported. Thus, in this paper, a foam fractionation of $FeCl_3$ from the simulated aqueous solution was studied by using dodecylbenzenesulphonic acid and (1-hexadecyl)trimethyl ammonium hydroxide as surfactants. Thereby a new method is put forward for removing salts by foam fractionation.

2. Materials and methods

2.1. Materials

$FeCl_3.6H_2O$ was obtained from Wen ta xi gui Chemical Regent Company (Tianjin, China). Ethanol was from Fuyu Fine Chemical Limited Company (Tianjin, China). Dodecylbenzenesulphonic acid and (1-hexadecyl)trimethyl ammonium hydroxide were purchased from Letai Chemical Limited Corporation (Tianjin, China).

The 752 UV-spectrophotometer was from Exactitude Apparatus Company (Shanghai, China), Hitachi U-3010 was from Shimadzu Corporation (Japan), fluorescence-spectrophotometer F-4500 was from Shi mad zu Corporation (Japan) and the pH meter, PHS-3CResearch type was from Exactitude Apparatus Company Shanghai (Shanghai, China). LZB rotameter and AC0-318 air compressor were from Five Circle Meter Factory (Tianjin, China).

2.2. Principle and quantification

The anion surfactant-dodecylbenzenesulphonic acid ($C_{18}H_{29}SO_3H$) can be ionized into $C_{18}H_{29}SO_3^-$ and H^+ in the aqueous solution; (1-hexadecyl)trimethyl ammonium hydroxide ($[(CH_3)_3NC_{16}H_{33}OH]$) also can be ionized into $(CH_3)_3NC_{16}H_{33}^+$ and OH^-, and thereby, in the aqueous solution of $FeCl_3$, ions exchange reaction can be written as:

$$3C_{18}H_{29}SO_3H + Fe^{3+} \rightarrow (C_{18}H_{29}SO_3)_3Fe + 3H^+ \qquad (1)$$

$$2(CH_3)_3NC_{16}H_{33}OH + Cl^- \rightarrow [(CH_3)_3NC_{16}H_{33}]_2Cl + 2OH^- \qquad (2)$$

$$H^+ + OH^- \rightarrow H_2O \qquad (3)$$

Fe^{3+} exchanges with H^+, combines with $C_{18}H_{29}SO_3H^-$ and forms $(C_{18}H_{29}SO_3)_3Fe$, which is absorbed to the interface of the gas–liquid and concentrated in the foam phase; Cl^- exchanges with OH^-, combines with $(CH_3)_3NC_{16}H_{33}^+$ and forms $(CH_3)_3NC_{16}H_{33}^+Cl$, which is also absorbed to the interface of the gas–liquid and concentrated in the foam phase. At the same time, H^+ and OH^- are combined into H_2O. Thus, this process will not introduce new metal ions and acid radical ions in the aqueous solution.

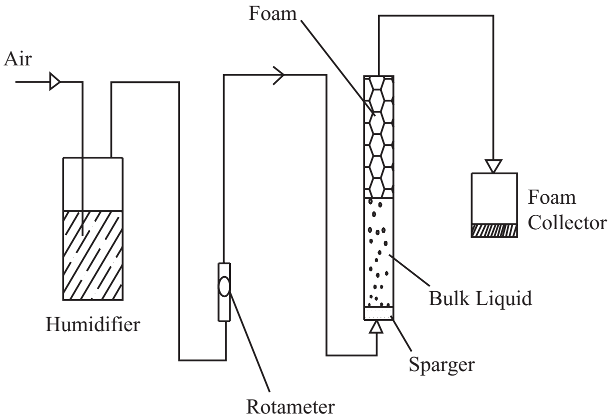

Fig. 1. Schematic diagram of the foam fractionation system.

The technology is quantified as follows:

$$\text{Enrichment ratio } (\beta) = \frac{\text{concentration of sample in the enrichment liquid}}{\text{concentration of sample in the initial solution}}$$

$$\text{Removal rate } (R, \%) = \frac{\text{mass of sample in the enrichment liquid}}{\text{mass of sample in the initial solution}} \times 100\%$$

2.3. Apparatus

For the process, a foam fractionation system was designed and setup as shown in Fig. 1. The column consisted of a cylindrical resin tube (inside diameter 0.04 m, and total length 1.2 m) with one outlet at the top, and one inlet at the bottom. A quantitative feed solution of desired concentrations was prepared by dissolving $FeCl_3$, surfactants in distilled water. The solution was placed in the column, and the compressed air was passed through a stainless steel orifice-plate distributor (porosity, 70 μm) at a definite superficial velocity (the ratio of cross-section of the column to the air flow rate). Water loss in the effluent air stream was minimized by humidifying the air which was passed through a humidifier and then went into the column. The complexes of surfactants with metal cations or acidic radical anions were combined with the air bubbles rising from the distributor at the bottom of the column, the foam was allowed to overflow the top of the column into a container and collapsed, until no suitable amount of foam was generated in the foam fractionation, then its residual solute concentration and the foamate volume were measured to give the removal rate (R) and enrichment ratio (β).

3. Results and discussion

3.1. The techniques of removing $FeCl_3$ by foam fractionation

In the experiment, the metal ions (Fe^{3+}) and acid radical ions (Cl^-) are removed by using dodecylbenzenesulphonic acid and (1-hexadecyl)trimethyl ammonium hydroxide as surfactants. Through the single factor experiments, some technological parameters were confirmed such as pH, superficial gas velocity and so on. On the basis of these single factor experiments, and by changing the sequences of removal of the $FeCl_3$ (namely, the order of removing cations and anions), we obtained the optimum technology. The technology that iron ions (III) were removed before chloride ions was defined as technology one, and reversely, the technology that chloride ions were removed before iron ions (III) was defined as technology two. Technology one was first studied.

3.1.1. Effect of dodecylbenzenesulphonic concentrations

Different amount of dodecylbenzene-sulphonic was added into $FeCl_3$ aqueous solution with 1,000 ml, 0.05 g/L to let its concentration into 0.16, 0.18, 0.20, 0.24, 0.28 g/L, respectively. Superficial velocity was 19.1 m/h, pH was 5.0 and liquid height was 0.80 m. When there are no suitable amount of foam was generated in the foam fractionation, (1-hexadecyl)trimethyl ammonium hydroxide was added into the bulk liquid for further separation of the chloride ions. At the end of the experiments, the volume of the foamate and residual liquid were measured, at the same time, the concentrations of the Fe^{3+} and Cl^- in the foamate and the residue were calculated by using the calibration curve: C (g/L) = 9.26×10^{-3} A (absorbance),with $R^2 = 0.9981$; C (g/L) = 2.86×10^{-2} A, with $R^2 = 0.9984$, respectively. The experiments results are shown in Fig. 2 (-■- and-●- represent removal-◆- and -▲- represent enrichment ratio).

Fig. 2 shows that the removal rate of Fe^{3+} firstly increases and then decreases with increasing of the dodecylbenzenesulphonic concentration from 0.16 to 0.28 g/L at a superficial velocity of 19.1 m/h, but its enrichment ratio firstly decreases and then increases. When the concentration of the surfactant was too low, the foam phase was unstable and cannot form continuous foam phase, as a result, the enrichment ratio was high, and the removal rate was low. At dodecylbenzenesulphonic concentration 0.20 g/L, 98.6% of the iron ions (III) were removed, but the enrichment ratio was only 2.1. When the addition amount of the surfactant was more than its critical micelle concentration, it will form micelle and compete for effective gas–liquid interface. As a result, the removal rate of iron ions (III) was decreased [18]. It can be seen from Fig. 2 that the removal rate of iron ions (III) was higher than that of chloride ions and when the concentration of the surfactant was 0.20 g/L, the removal rates of the iron ions (III) and chloride ions are 98.6% and 62.9%, respectively. The increase of the concentration of surfactant results in a downward trend of the enrichment ratio of the chloride ions.

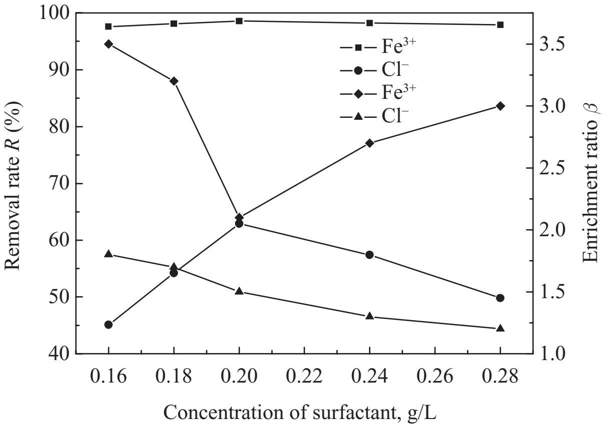

Fig. 2. Influence of surfactant concentration on β and R.

3.1.2. Effect of superficial gas velocity

The initial concentration of $FeCl_3$ solution was 0.05 g/L with the volume of 1,000 ml, the concentration of dodecylbenzenesulphonic solution was 0.24 g/L, the pH of bulk liquid was 5.0, and the liquid height was 0.80 m. The effect of superficial gas velocity on removal rate is shown in Fig. 3.

Superficial gas velocity is an important parameter in the foam fractionation system. As it can be seen from Fig. 3 that the removal rate of Fe^{3+} firstly increases and then decreases, but the enrichment ratio presents downward trend. The removal rate and enrichment ratio are affected by the hydromechanical characteristics of the column. At lower superficial gas velocity, the air bubbles stay on the bulk liquid for a long time, the mass transfer of the gas–liquid interface was full and the liquid holdup of the foam was small, so the enrichment ratios of iron ions (III) and chloride ions reach 2.5 and 1.6, respectively. With the increasing of the superficial gas velocity, the time of the air bubbles stay on the bulk liquid was shortened, the mass transfer of the gas–

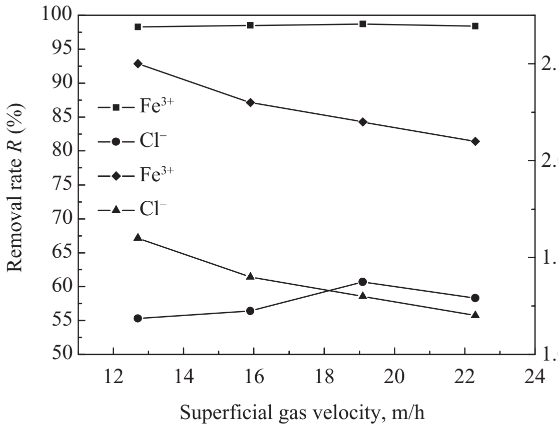

Fig. 3. Influence of superficial gas velocity on β and R.

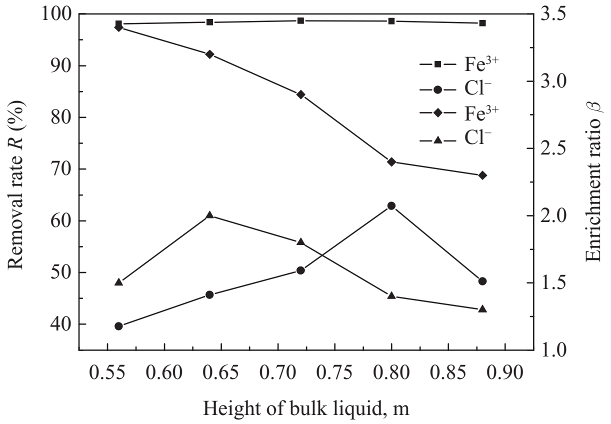

Fig. 5. Effect of height of bulk liquid on β and R.

liquid interface can not be processed fully and the rising rate of the foam phase was speeded up, all of these factors will result in increase of the liquid holdup and decrease of the enrichment ratio.

3.1.3. *Effect of pH*

The effect of the foam fractionation of $FeCl_3$ was also dependent on the pH of the initial solution. The bulk liquid was adjusted pH to 3.5, 4.0, 4.5, 5.0, 5.5 (using HAc or NaOH), respectively. At superficial velocity 15.9 m/h, liquid height 0.80 m and concentration of the surfactant 0.24 g/L, the foam fractionation was conducted.

Fig. 4 presents that the removal rate and enrichment ratio increased to a maximum (98.9% and 1.9, respectively) with the increasing of the pH from 3.5 to 4.5, then decreased from pH 4.5 to 5.5. With low pH values, the little foam was produced from bulk liquid and entrained more liquid holdup, so it can be seen from Fig. 4 that the effect of removing iron ions (III) was very low. This was caused by the excess hydrogen ion concentration. According to the electrostatic adsorption principle, hydrogen ion also combined with surfactant and was adsorbed to the surface of the bubble to compete the limited gas–liquid interface, thus the removal rate of the iron ions (III) was decreased. With the increasing of the pH, the liquid holdup of the foam was decreased gradually, and the enrichment ratio of iron ions (III) was increased. When the pH was more than 4.5, the foam was produced slowly, the removal rate decreased again. According to the above-mentioned, we can conclude that: the pH not only influences the binding mode between the metal ions and the surfactant, but also influences the liquid holdup of foam and the removal rate of the metal ions [19,20], Sarkar et al. [21] and Xie Jihong et al. [20] also proved that pH play an important role in the foam fractionation.

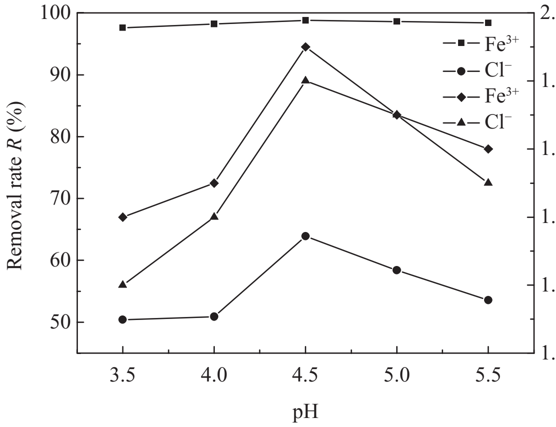

Fig. 4. Influence of pH on β and R.

3.1.4. *Effect of height of bulk liquid*

The initial concentration of $FeCl_3$ solution was 0.05 g/L with the volume of 1,000 ml. The height of bulk liquid was changed to 0.56, 0.64, 0.72, 0.80, and 0.88 m, respectively. At superficial velocity 15.9 m/h, pH 4.5 and concentration of the surfactant 0.24 g/L, the foam fractionation was conducted.

When the height of bulk liquid was low, the foam stays on the column for a long time and the liquid among the bubbles have enough time to reflux, so higher enrichment ratio can be obtained; conversely, the greater height of the bulk liquid results in the smaller height of foam phase, then the foam phase can not fully discharge the liquid, thus the liquid holdup of the foam phase was increased. It can be seen from Fig. 5 that the removal rate of Fe^{3+} reaches 98.7% at height of bulk liquid was 0.72 m.

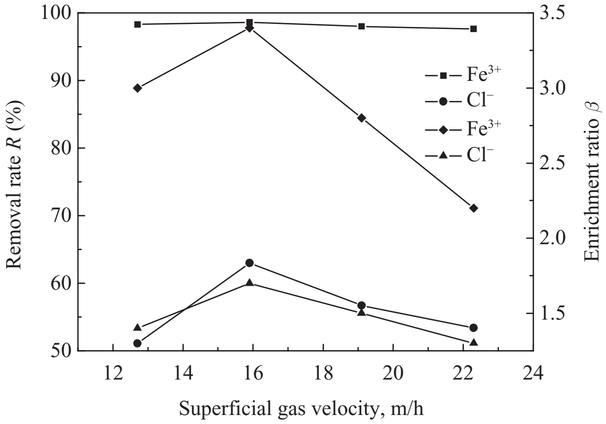

Fig. 6. Influence of superficial gas velocity on β and R.

According to the above-mentioned, the suitable single factor conditions of removing iron ions (III) can be obtained: pH 4.5, superficial gas velocity 15.9 m/h, height of bulk liquid 0.72 m and concentration of the dodecylbenzenesulphonic 0.24 g/L. Then, fixing the conditions of separating iron ions (III), foam fractionation of the chloride ions were conducted by varying the superficial gas velocity and the concentration of the (1-hexadecyl)trimethyl ammonium hydroxide. The results can be seen from Figs. 6 and 7.

Fig. 6 represents the influence of superficial gas velocity on the removal rate of chloride ions. When the superficial gas velocity increased from 12.7 to 22.3 m/h, the removal of chloride ions firstly increase and then decrease. The superficial gas velocity increased continuously can increase the gas–liquid interface of bubbles, at the same time more chloride ions exchange effectively with hydroxide ions and are adsorbed to the gas–liquid interface, thus it was helpful for the foam fractionation [22,23]. But the higher superficial gas velocity, on the one hand, shortens the residence time of the air bubbles; on the other hand, increases the gas holdup, and result in the enrichment ratio to be decreased. The lower superficial gas velocity prolong the time of the air bubbles stay on column, thus when the foam get to the top of the column, the liquid holdup was little, this agree with the reported by Liu et al. [24] and Uraizee and Narsimhan [25].

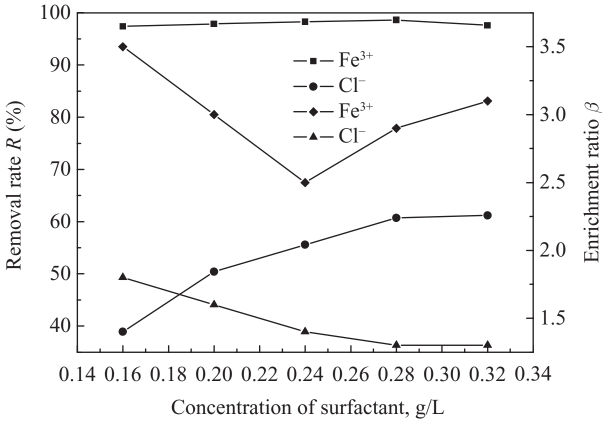

Fig. 7. Influence of surfactant concentration on β and R.

As it can be seen from Fig. 7 that the removal rate of chloride ions increased with the increasing of the concentration of (1-hexadecyl)trimethyl ammonium hydroxide from 0.16 to 0.32 g/L. Because the concentration of the surfactant wont exceed its critical micelle concentration, it will not form the micelle, at the same time, the surface tension of the bulk liquid decreased from 59.4 to 51.3 N/m^2. The foamability and surface adsorption capacity of the bulk liquid increased with the increasing of the concentration of the surfactant, and then the chloride ions have more chances to combine with the surfactant. At low concentration of the surfactant, the surface tension of the bulk liquid was high; the foamability of the bulk liquid decrease and the foam phase was unstable. What's more, when the concentration of the (1-hexadecyl)trimethyl ammonium hydroxide was low, the coalescence was serious among the bubbles, the liquid holdup in the foam phase was very low, thus the enrichment was high.

3.2. The comparison of two different technologies

Because the single factor experiment of technology two was similar to technology one, it will not be made a concrete analysis, and its suitable single factor condition of removing chloride ions can be obtained: pH 4.5, superficial gas velocity 19.1 m/h, height of bulk liquid 0.72 m and surfactants concentration 0.28 g/L. The suitable single factor conditions of the two different technologies were compared and the results are shown in Table 1. As it can be seen from Table 1 that: the removal rate of iron ions (III) in technology one was close to that of chloride ions in technology two. In technology one, the removal of iron ions reaches 98.6%, and that of chloride ions 63.0%; in technology two, the corresponding values are 98.4% and 60.5%. However, the enrichment ratio of iron ions (III) and chloride ions in technology two are higher than that of technology one. So technology two was the more reasonable operation technology.

4. Conclusions

(1) Dodecylbenzenesulphonic acid and (1-hexadecyl) trimethyl ammonium hydroxide have shown excellent foaming quality, and when the metal ions or

Table 1
Comparison of results of two technologies

Parameters	Technology one	Technology two
Operating parameters		
Height of the bulk liquid (m)	0.72	0.72
pH of the initial bulk liquid	4.5	4.5
Concentration of dodecylbenzensulphonic acid for removal of Fe^{3+} (g/l)	0.24	0.24
Superficial gas velocity for removal of Fe^{3+} (m/h)	15.9	15.9
Concentration of (1-hexadecyl) trimethyl ammonium hydroxide for removal of Cl^- (g/l)	0.28	0.28
Superficial gas velocity for removal of Cl^- (m/h)	15.9	19.1
Results		
RFe^{3+} (%)	98.6	98.4
RCl^- (%)	63.0	60.5
βFe^{3+}	2.1	2.8
βCl^-	1.3	1.7

acid radical ions were removed in the simulated aqueous solution by using them as the surfactants, the system wont be introduced new metal ions or acid radical ions.

(2) By comparing the two different technologies, technology two was the more reasonable operation technology. The single factor conditions of removing Cl^- are pH 4.5, Superficial gas velocity 19.1 m/h, height of bulk liquid 0.72 m and concentration of (1-hexadecyl)trimethyl ammonium hydroxide 0.28 g/L; and that of the Fe^{3+} are superficial gas velocity 15.9 m/h, concentration of dodecylbenzensulphonic acid 0.24 g/L, then the removal rate and enrichment ratio are 60.5% and 1.7, respectively.

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References

[1] T. Kinoshita, Y. Ishigaki, K. Yamaguchi, et al., Novel operational method of continuous foam separation of gold-injection of metal and/or surfactant solutions into rising foam bed. Sep. Purif. Technol. 52(2) (2006) 357–362.

[2] D. Linke, H. Zorn, B. Gerken, et al., Laccase isolation by foam fractionation – New prospects of an old process. Enzyme Microb. Technol., 40(2) (2007) 273–277.

[3] R.C. Darton, S. Supino and K.J. Sweeting, Development of a multistaged foam fractionation column. Chem. Eng. Process., 43(3) (2004) 477–482.

[4] F. Uraizee and G. Narsimhan, Foam fractionation of proteins and enzymes: Applications. Enzyme Microb. Technol., 12(3) (1990) 232–233.

[5] C.E. Lockwood, P.M. Bummer and M. Jay, Purification of proteins using foam fractionation. Pharmaceut. Res., 14(11) (1997) 1511–1515.

[6] A.K. Brown, A. Kaul and J. Varley, Continuous foaming for protein recovery: Part II. Selective recovery of proteins from binary mixtures. Biotechnol. Bioeng., 62(3) (1999) 291–300.

[7] K.H. Bahr and K. Schuegerl, Recovery of yeast from cultivation medium by continuous flotation and its dependence on cultivation conditions. Chem. Eng. Sci., 47(1) (1992) 11–20.

[8] N.C. Weeks, M.B. Timmons and S. Chen, Feasibility of using foam fractionation for the removal of dissolved and suspended solids from fish culture water. Aquacul. Eng., 11(4) (1992) 251–265.

[9] M. Backleh, G. Leupold and H. Parlar, Rapid quantitative enrichment of carnosic acid from rosemary (Rosmarinus officinalis L.) by isoelectric focused adsorptive bubble chromatography. J. Agricul. Food Chem., 51(5) (2003) 1297–1301.

[10] M. Backleh, P. Ekici, G. Leupold and H. Parlar, Quantitative elimination of Flavokavines A and B from Kava Kava (Piper methysticum G. Forst) by isoelectric focused adsorptive bubble separation. Naturwissenschaften, 90(8) (2003) 366–369.

[11] Xiaolian Hu, Yunquan Yang and Wenying Liu, The study on adsorptive foam separation recovery of zinc in low concentration solution. Natural Sci. J. XiangTan University, 25(2) (2003) 49–52.

[12] Zhiyuan Guan, Fuxin Ding and Naiju Yuan, Application of loop flotation separation approach intreatment of wastewater containing Cu(II). J. Tsinghua Univ. (Sci. & Tech.), 39(1) (1999) 114–117.

[13] Juan Wang and Jiaying Chu, Adsorptive separation of fluoborate anion in a foam column. J. Chem. Ind. Eng. (China), 45(3) (1994) 380–384.

[14] Jiazhen He, Study on the separation of Cu(II) and Zn(II) in aqueous solution by adsorptive bubble fractionation. J. Xiangtan Normal Univ. (Natural Science Edition), 28(4) (2006) 31–34.

[15] Xinrong Wen, Study on flotation separation of lead(II) by potassium iodide–cetyltrimethyl ammonium chloride-water system in the presence of sodium nitrate. J. Metall. Anal., 23(2) (2003) 8–10.

[16] Qian Li, ZhaoLiang Wu and YanLi Zhao, Removal of trace Cu2+ from aqueous solution by foam fractionation. Chin. J. Process Eng., 7(4) (2007) 679–683.

[17] WeiGuang Song, ZhaoLiang Wu and Ke Lu, Removal of trace sulfuric acid radical in aqueous solution with foam fractionation. Chin. J. Process Eng., 8(3) (2008) 489–493.

[18] Xihe Xiao, Wenhao Shen and Xiangfei Zhang, Study on foam separation I. Treatment of waste water containing Zn2+ by batch-fermentation. Chem. World, S1 (2002) 138–140 (in Chinese) (肖希和，沈文豪，张翔飞．泡沫分离技术的研究I．间歇法处理含锌废水．化学世界, 2002, S1: 138–140).

[19] Bo Yang, Yonghua Wang, Ruhua Yao, et al., Foam fractionation of proteins. Food Ferment. Ind., 27(2) (2001) 76–79 (in Chinese) (杨博，王永华，姚汝华等．蛋白质的泡沫分离．食品与发酵工业, 2001, 27(2): 76–79).

[20] Jihong Xie, Xiaoming Cheng and Xiu Deng, Study on separation of soybean protein by foam fractionation technique I. Operation conditions. J. East China Univ. Sci. Technol. (Natural Science edition), 23(3) (1997) 270–274 (in Chinese) (谢继宏, 程晓鸣, 邓修. 精馏大豆蛋白质的泡沫分离研究：Ⅰ. 操作工艺条件. 华东理工大学学报, 自然科学版, 1997, 23(3): 270–274.

[21] P. Sarkar, P. Bhattacharya, R.N. Mukherjea, et al., Isolation and purification of protease from human placenta by foam fractionation. Biotechnol. Bioeng, 29(8) (1987) 934–940.

[22] J.E. Kiefer and D.J. Wilson, Time-dependent foam flotation stripping column operation. Sep. Sci. Technol., 16(2) (1981) 147–171.

[23] Bing Yu and Yajun Shi. Foam fractionation technology V dynamics of gas-liquid two phase in foam fractionation column.

J. East China Univ. Sci. Technol., 16(1) (1990) 13−20 (in Chinese) (於兵，施亚钧. 泡沫分离技术的研究—V. 泡沫分离塔内气—液两相的流体力学. 华东理工大学学报, 1990, 16(1): 13–20.

[24] Zhihong Liu, Zheng Liu, Fuxin Ding, et al., Concentration and separation of proteins by foam fractionation (I) study on the apparatus and the separation process. J. Tsinghua Univ. (Sci. &Tech.), 37(12) (1997) 50–54.

[25] F. Uraizee and G. Narsimhan, Foam fractionation of proteins and enzymes: II. Performance and modeling. Enzyme Microb. Technol., 12(4) (1990) 315–316.