Novel Fluorinated Tensioactive Extractant Combined with Flotation for Decontamination of Extractant Residual during Solvent Extraction

Xue Wu[1], Zhidong Chang[1,*], Yao Liu[1] and Chol Ryong Choe[1, 2]

[1]Department of Chemistry and Chemical Engineering, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, PR China
[2]School of application chemistry, Kim Chaek University of Technology, Pyongyang 999093, DPR of Korea

*Email: zdchang@ustb.edu.cn

Abstract. Solvent-extraction is widely used in chemical industry. Due to the amphiphilic character, a large amount of extractant remains in water phase, which causes not only loss of reagent, but also secondary contamination in water phase. Novel fluorinated extractants with ultra-low solubility in water were regarded as effective choice to reduce extractant loss in aqueous phase. However, trace amount of extractant still remained in water. Based on the high tensioactive aptitude of fluorinated solvent, flotation was applied to separate fluorinated extractant remaining in raffinate. According to the data of surface tension measurement, the surface tension of solution was obviously decreased with the addition of fluorinated extractant tris(2,2,3,3,4,4,5,5-octafluoropentyl) phosphate (FTAP). After flotation, the FTAP dissolved in water can be removed as much as 70%, which proved the feasibility of this key idea. The effects of operation time, gas velocity, pH and salinity of bulk solution on flotation performance were discussed. The optimum operating parameters were determined as gas velocity of 12ml/min, operating time of 15min, pH of 8.7, and NaCl volume concentration of 1.5%, respectively. Moreover, adsorption process of FTAP on bubble surface was simulated by ANSYS VOF model using SIMPLE algorithm. The dynamic mechanism of flotation was also theoretically investigated, which can be considered as supplement to the experimental results.

1. Introduction

Solvent extraction is extensively used in hydrometallurgy, waste-water treatment and biopharmacy, etc. However, extractant loss is an alarming problem after solvent extraction, which causes wastage of commercial solvent extractants as well as serious environmental contamination[1]. Many research suggested that the loss of organic extractants primarily depended on the solubility of the extractant in aqueous phase[2]. The novel fluorinated extractants with ultra-high hydrophobicity, such as tris(2,2,3,3,4,4,5,5-octafluoropentyl) phosphate, were proposed to be an effective method to reduce extractant loss in aqueous phase[3-4]. Nevertheless, trace amount of fluorinated extractants still remained in water. Hence, it is meaningful to seek for methods to further decontamination.

There are several industrial methods to remove organic solvents from water, such as physical heat treatment like distillation, chemical treatment like membrane adsorption and extraction, which are energy-intensive and contaminative. As a combination of chemical and physical method, floatation is on the basis of the fact that the contaminant in the wastewater itself are surface active and adsorbed on the gas-liquid two-phase interface by the bubbles floating in waste water. It has gradually become a new method of wastewater treatment because of low energy consumption and pollution. Compared with traditional physical and chemical treatments, floatation is particularly suitable for the low concentration substances and has been widely used as separation technology for the purification of oily wastewater[5-7]. Except for ultra-high hydrophobicity, high tensioactive is another prominent aptitude of fluorinated compounds[8]. Hence, flotation is assumed to be an appropriate method to separate and enrich the residual of fluorinated extractant.

In the present research, tris(2,2,3,3,4,4,5,5-octafluoropentyl) phosphate (FTAP) was chose as model fluorinated extractant. Novel fluorinated tensioactive extractant combined with flotation was proved to be a promising and eco-friendly strategy to tackle the problem of extractant residual during solvent extraction as shown in figure 1. Due to the complexity of the gas-liquid two-phase fluid and the interface phenomenon, floatation simulation was also conducted.

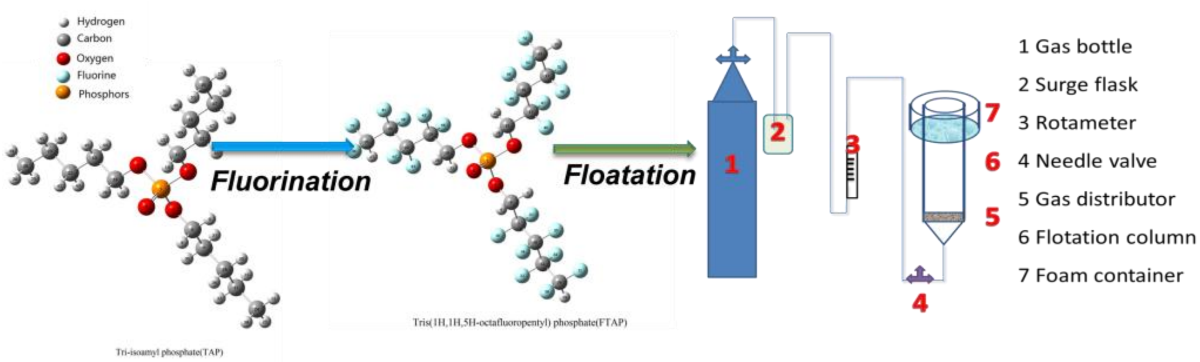

Figure 1. Schematic of research approach and flotation device.

2. Research methods

2.1. Measurement of surface tension

Surface tension of water solution containing different proportion of FTAP was determined by QBZY-1 automatic surface tensiometer.

2.2. Floatation process

FTAP dispersing in water phase was separated by floatation using CO_2. The amount of FTAP in solution was tested by fluorescence spectrophotometry (λ Ex=290 nm, Em=400nm). The separation efficiency E is defined as:

$$E\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 stands for the initial FTAP concentration in the aqueous phase and C_t stands for FTAP concentration in the aqueous phase at certain time. The effects of operation time, gas velocity, pH and salinity of bulk solution on flotation performance were discussed.

2.3. Theoretical simulation

Adsorption process of FTAP on bubble surface was simulated by ANSYS VOF model using SIMPLE algorithm. The simulation was set in the 0.003 m × 0.005 m region. The quadrilateral grid length was 0.001 mm. The time step was 0.1 ns. The top boundary was set as the pressure outlet, and the other boundary was no slip wall. The finite volume method was used to discretize the partial differential equations, and the coupling relationship between pressure and velocity was solved by SIMPLE algorithm.

3. Results

3.1. Surface tension of FTAP solution at different volume ratio

The prerequisite of flotation is high tensioactive target materials. Therefore, the ability of FTAP to decline surface tension of water phase was firstly investigated. Surface tension curve of FTAP solution at different volume ratio was shown in figure 2. As shown in figure 2, it can be seen that with the increase of the content of FTAP, the surface tension of the FTAP solution decreases. When gas-liquid interface, i.e. bubbles, appears in the water, FTAP molecules dispersing in solution would tend to gather around bubbles, which benefits separation process.

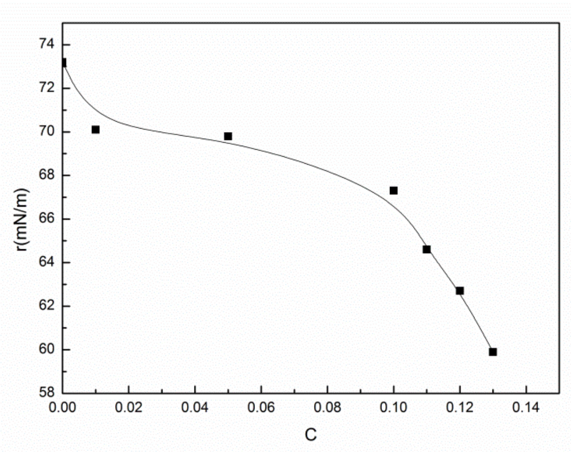

Figure 2. Surface tension curves of FTAP solution at different volume ratio.

3.2. Separation of FTAP in water by floatation

The residual of FTAP in water phase was separated by floatation using CO_2. The effects of operation time, gas velocity, pH and salinity of bulk solution on flotation performance were shown in figure 3, 4, 5, and 6, respectively. As shown in figure 3, with the increase of flotation time, the separation efficiency increases rapidly and gradually becomes flat after 10 mins, which implies that adsorption was close to equilibrium. From figure 4, it is obvious that separation efficiency is enhanced with increase of gas velocity, and maximizes at 12ml/min, indicating that increase of gas-liquid interface was beneficial for separation and enrichment of FTAP in water. Whereafter, separation efficiency decreases when gas velocity further increases. This could be the result that violent mix at the top of air flotation tower broke bubbles. Figure 5 shows the effect of pH on the separation efficiency at different gas velocities. By adjusting pH during experiments, the separation efficiency reaches the maximum when the pH is 8.7, indicating that slight alkalinity was conducive to maintaining stability of CO_2 bubble membrane. Figure 6 shows that the separation efficiency increases with the increase of NaCl concentration in a certain concentration range. When the NaCl concentration is about 1.5%, the separation efficiency reaches the maximum value. This indicates that the salinity of bulk solution had great effect on the formation of bubbles. Low concentrations of salt can prevent the rapid mixing of bubbles and increase the specific surface area of bubbles.

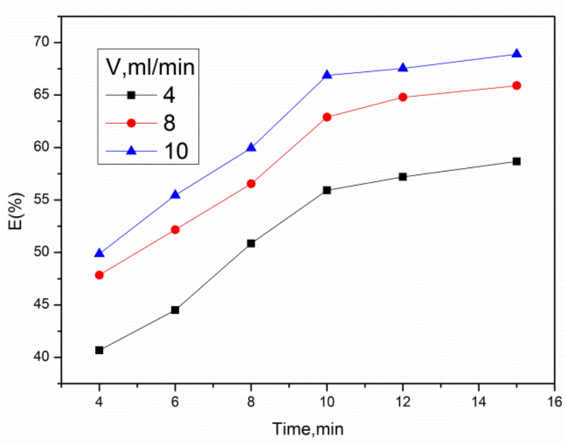

Figure 3. The effects of operation time on separation efficiency of FTAP.

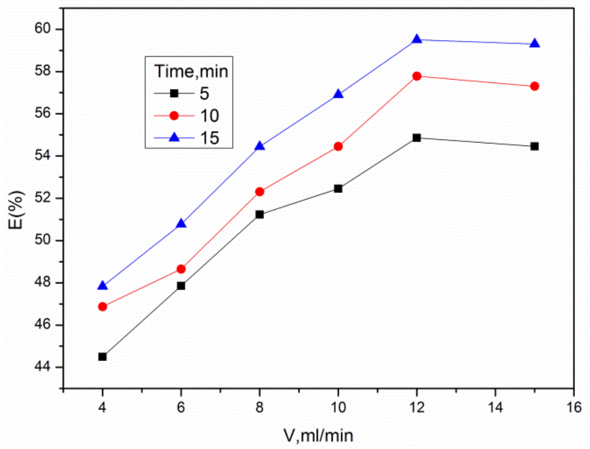

Figure 4. The effects of gas velocity on separation efficiency of FTAP.

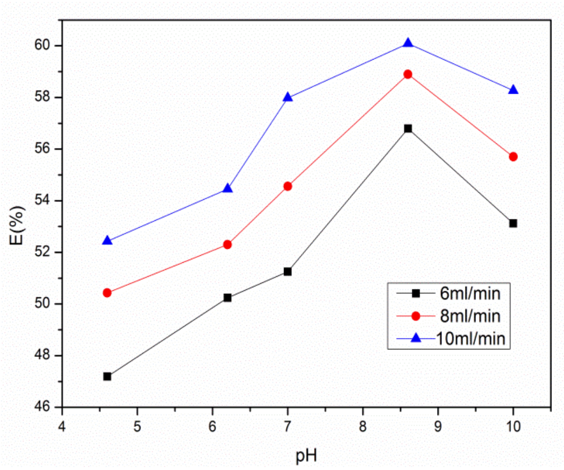

Figure 5. The effect of pH of bulk solution on separation efficiency of FTAP..

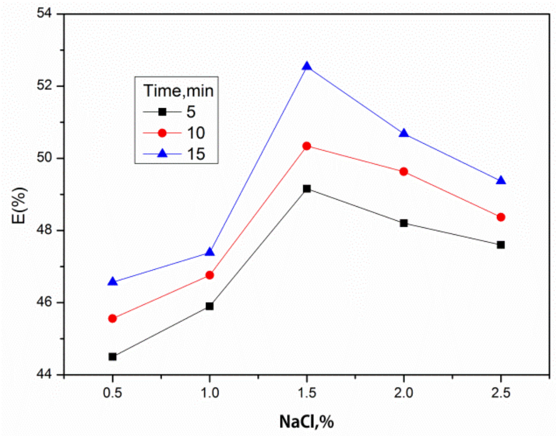

Figure 6. The effect of salinity of bulk solution on separation efficiency of FTAP..

3.2. Simulation of adsorption process during flotation

Based on ANSYS VOF method, flow volume change in flow field grid was chased to capture interface of two-phase flow[9-10]. The calculation method is small, accurate and easy to implement. The initial parameters of simulation of flotation bubble absorption were listed in table 1.

Table 1. Initial parameters of simulation of flotation bubble absorption

Parameter	Value
Initial diameter of bubble / mm	1
Density of CO_2 / (kg m^{-3})	1.784
Density of FTAP / (kg m^{-3})	1770
Density of water / (kg m^{-3})	998.2
Viscosity of CO_2 / (Pa.s)	1.4932×10^{-5}

Viscosity of FTAP / (Pa.s)	5.89×10^{-4}
Viscosity of water / (Pa.s)	1.003×10^{-3}
Surface tension of water / CO_2 / (N m^{-1})	0.0732[a]
Surface tension of FTAP / CO_2 / (N m^{-1})	0.0181[a]
volume fraction of FTAP in system	1×10^{-4}

[a] Refer to the correlation coefficient of air

Figure 7 (a) shows the initial form of a fixed position bubble in model system. The volume fraction contours of FTAP and volume fraction curves of FTAP in centreline at 80 ns, 90 ns, 100 ns, 200 ns, 300 ns were presented in figure (b), (c), (d), (e), and (f), respectively. During the simulation process, FTAP molecules in water can spontaneously congregate around the bubble. The content of FTAP adsorbing on the surface of bubble increases with time and then decreases, which is in accordance with the experimental results. The bottom of the bubble adsorbs more FTAP than other position. It is because during the air flotation process, organic materials aggregate in the bottom of bubble on account of gravity. Hence, organic materials would slide from the bubble surface over a certain degree of time. The bubbles loading with FTAP should be scraped out opportunely in order to increase the separation effect. The simulation of the adsorption process can provide better understand to air flotation process and help to optimize the operating conditions.

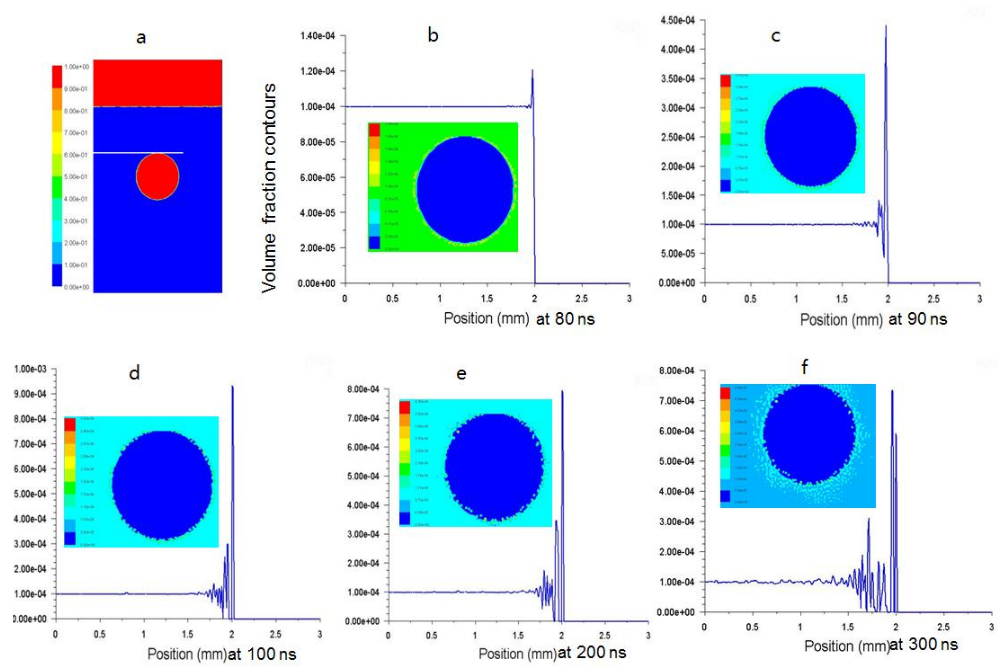

Figure 7. (a) Initial form of a fixed position bubble. The volume fraction contour of FTAP and volume fraction curve of FTAP in centreline at (b) 80 ns, (c) 90 ns, (d) 100 ns, (e)200 ns, (f)300 ns.

4. Conclusion

In summary, novel fluorinated extractant possess very low solubility in water and satisfactory extraction capability. Flotation was applied to further purify water phase on the basis of the high surface tension of fluorinated extractants. Operation time, gas velocity, pH and salinity of bulk solution were important factors affecting the separation efficiency. The residual of tris(2,2,3,3,4,4,5,5-octafluoropentyl) phosphate in water phase was separated by floatation using CO_2. The optimum operating parameters were determined as gas velocity of 12ml/min, operating time of 15min, pH of 8.7, and NaCl volume content of 1.5%, respectively. Simulated adsorption process of FTAP on bubble surface by ANSYS VOF model using SIMPLE algorithm was in accordance with the experimental results. Novel fluorinated tensioactive extractant combined with flotation was proved to be a promising strategy to tackle the problem of extractant residual during solvent extraction

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 21276022).

References

[1] Liu C Cao J Shen W Ren Y Mu W and Ding X 2016 Liquid–liquid equilibria of quaternary system phosphoric acid/sulfuric acid/water/tri-n-butyl phosphate and the formation of extraction complex at 303.2 K *Fluid Phase Equilib* **408** 190-195.

[2] Semenov A Abramov A Sobol Y B Galieva Z N Galantsev A and Gerya V 2016 Preparation of Nd2O3 through the extraction separation of rare-earth concentrate recovered from phosphogypsum *Inorg. Mater* **52 (2)** 233-237

[3] Wu X Chang Z Blamo B J Yuan J Uslu H Li W and Ryong C C 2017 Strategy for extractant residual reduction: Experimental and computational investigation of fluorinated phosphate *Fluid Phase Equilib* **449** 167-174

[4] Luo YChang Z Wu X Uslu H Li W Hua C Liu S Sun C and Im S 2015 Efficiency of fluorinated alcohol for extraction of organic acid from its dilute aqueous solution: A model study *J. Fluor. Chem* **178** 260-265

[5] Sun X Chang Z Shen S Hu X and Liu H 2006 Effects of emulsion properties on recovering butyl acetate from wastewater of penicillin plant by solvent sublation *Colloids Surf. Physicochem. Eng. Aspects* **286 (1)** 8-16

[6] Rubio J Souza M and Smith R 2002 Overview of flotation as a wastewater treatment technique *Miner. Eng* **15 (3)** 139-155

[7] Zhu J Wu F Pan X Guo J and Wen D 2011 Removal of antimony from antimony mine flotation wastewater by electrocoagulation with aluminum electrodes *JEnvS* **23 (7)** 1066-1071

[8] Mohamed M and Mohamed A 2009 Synthesis and some properties of fluorinated cationic surfactants *Journal of surfactants and detergents* **12 (4)** 345-349

[9] Chakraborty D Guha M and Banerjee P 2009 CFD simulation on influence of superficial gas velocity, column size, sparger arrangement, and taper angle on hydrodynamics of the column flotation cell *Chem. Eng. Commun* **196 (9)** 1102-1116

[10] Cai X Chen J Liu M Ji Y and An S 2017 Numerical studies on dynamic characteristics of oil-water separation in loop flotation column using a population balance model *Sep. Purif. Technol.* **176** 134-144