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Extraction of uranium from low-concentration solutions using P204 bubbling organic liquid membrane technology

Zuli Mo [1], Jun Long [1], Weiliang Wang [1], Xintong Qian [1], Qingliang Wang [1], Zhimin Guo [1,2], Zhiwu Lei [1], Yibo Hu [1], Ayoub Bayoussef [3], Pengfei Hu [1,2]

[1] School of Resources & Environment and Safety Engineering, University of South China, Hengyang 421001, Hunan, China

[2] Key Laboratory of Coal Processing and Efficient Utilization, (China University of Mining and Technology), Ministry of Education, Xuzhou 221116, Jiangsu, China

[3] Ecole Supérieure de Technologie Fkih Bensalah, Sultan Moulay Slimane University, Beni-Mellal, Morocco

Corresponding author: hpf0830@usc.edu.cn (Pengfei Hu)

Abstract: The uranium leaching process generates a substantial volume of wastewater, in which the uranium is difficult to concentrate and recover due to its extremely low concentration. In this study, the bubbling organic liquid membrane extraction method using Di-(2-ethylhexyl) phosphate (P204) as the extractant was proposed and evaluated for the effective enrichment and recovery of low-concentration uranium. The effects of the organic to aqueous phase ratio (O/A), the initial pH value of the wastewater, the initial uranium concentration and coexisting ions on the uranium recovery were investigated. The results indicated that the uranium recovery increased with the initial solution pH. A relatively high uranium recovery of 94.3% was achieved at pH 6 and an O/A ratio of 1:10. The uranium recovery decreased with increasing initial uranium concentration. Furthermore, elevated concentrations of Al^{3+}, Fe^{3+}, and Mg^{2+} in the aqueous phase were found to adversely affect uranium extraction, likely due to competitive coordination with the extractant or interference with the extraction equilibrium.

Keywords: bubbling organic liquid membrane extraction, Di-(2-ethylhexyl) phosphate, low concentration uranium solution

1. Introduction

Nuclear energy, as an efficient and low-carbon energy source, plays a significant role in the global energy structure. However, the development and utilization of nuclear energy inevitably lead to the generation of low-concentration uranium-containing wastewater (Ehrig et al., 2021; Pant et al., 2019). These uranium-containing wastes may infiltrate into the soil, leading to groundwater contamination, or be transported by rainwater into rivers, resulting in the pollution of aquatic systems (Kaksonen et al., 2020; Zhenqian & Yuqing, 2017). This not only results in a waste of valuable uranium resources, but also poses a threat to human health and exerts detrimental effects on ecological systems (Singh et al., 2017).

To date, numerous methods have been extensively investigated for the effective removal of uranium ions from industrial wastewater, including chemical precipitation, ion exchange, adsorption, membrane filtration, electrochemical treatment, and bioreactor technologies (Luo et al., 2023; Lv et al., 2021; Lyu et al., 2021; Maher et al., 2018; Wufuer et al., 2021; Xin et al., 2023). Nevertheless, the substantial volume of uranium-bearing wastewater, coupled with its low uranium concentration and complex composition, presents significant challenges to the practical implementation of these techniques (Zhu et al., 2023).

Solvent extraction has been proved to be an effective technology for the enrichment and recovery of uranium (Hung et al., 2020). However, conventional solvent extraction processes and equipment are not well suited for treating industrial wastewater with extremely low concentrations of uranium (Chandramouleeswaran, Ramkumar, & Basu, 2016). This is mainly because the low ratio of organic phase to aqueous phase, making it highly challenging to disperse a small amount of organic phase into

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a large amount of aqueous solution to effectively enrich low-concentration uranium. In addition, operational losses caused by the dissolution of organic extractants in the raffinate cannot be avoided. Conventional extraction methods are mainly applicable for metal ion concentrations at the g/L level, leading to relatively lower enrichments, and more appropriate for small-phase-ratio extraction. The extraction of low concentration uranium from extremely large volumes of wastewater requires high enrichment ratios and large-phase-ratios. The entrainment phenomena in large-phase-ratio extraction pose challenges to oil-water separation, impede mass transfer, and reduce overall extraction efficiency. This leads to limited economic benefits from recovering low-concentration uranium (Liu et al., 2017).

In recent years, significant efforts have been devoted to addressing the challenges of extracting uranium from low-concentration solutions. This progress is primarily reflected in the development of innovative high-efficiency extractants, as well as the optimization of extraction processes and equipment, all aimed at improving uranium selectivity, recovery rates, and mass transfer efficiency (Zahakifar et al., 2025; Yu et al., 2024; Raj et al., 2024). For instance, Wei et al. (2024). conducted research on the extraction and stripping of uranium using a membrane dispersion microextractor in high phase ratio. It was found that both the extraction efficiency and stripping efficiency can reach >90 % at high phase ratio within 10 seconds. Membrane dispersion extraction technology has attracted considerable attention due to its advantages of large throughput, small droplet size and high mass transfer rate, as well as fast phase separation (Fourieet al., 2018; Zheng al., 2022). Given these similar advantageous characteristics, another extraction technique, namely bubbling organic liquid membrane extraction, has consequently entered the research scope of our team for uranium extraction. It involves the formation of small oily bubbles by coating the surface of dispersed small bubbles with the organic extractant in a custom-designed bubbling organic liquid film extraction column device. The use of extractant coated on these small oily bubbles enables high water-oil ratio operation and facilitates the extraction of low-concentration uranium from uranium-containing wastewater, thereby improving mass transfer and extraction efficiency. In addition, by appropriately setting the operational parameters, the disruption of these oily bubbles can be precisely controlled, enabling the formation of an organic layer at the top of the column that subsequently flows out through the organic phase outlet. The bubbling organic liquid membrane extraction method is also employed to r minimize extractant entrainment loss and achieve exceptionally low oil content in the raffinate phase (Geng et al., 2020). This method has been successfully applied to the treatment of solutions with very low concentrations of target components. Wang et al. (2022) employed foam-supported organic liquid membrane extraction technology with the use of saponified naphthenic acid as the extractant to treat yttrium-rich heavy rare earth ore leachate, achieving selective and preferential separation of non-yttrium rare earth elements and yttrium. Liu et al. (2017) employed N1923 bubbling organic liquid membrane extraction technology to extract very low concentrations of rare earth elements from acidic leaching solutions. Xianxian et al. (2021) used a bubble-supported organic liquid membrane to enhance the salt interface effect, thus promoting the extraction of low-concentration Er(III) ions. To the best of our knowledge, the application of bubbling organic liquid membrane extraction method to the treatment of low-concentration uranium-containing wastewater has not been reported in the existing literature.

The primary aim of this paper was to conduct fundamental studies on the optimal conditions and kinetics of uranium extraction using a bubbling organic liquid membrane extraction method, and to evaluate the feasibility of this method for the efficient reovery of low-concentration uranium from wastewater. The effects of the organic phase to aqueous phase ratio (O/A) ratio, the initial pH value of the wastewater, and the concentrations of uranium and coexisting ions in the wastewater on the extraction efficiency were systematically examined. This study presents a promising approach for recovering low-concentration uranium from wastewater.

2. Materials and methods

2.1. Materials

The preparation of a low-concentration uranyl sulfate solution involved dissolving a specific amount of U_3O_8 in concentrated sulfuric acid and H_2O_2 solution, adding HNO_3 solution for solubilization, heating to complete dissolution until the liquid became transparent, cooling, and then transferring the solution into a 1000 mL volumetric flask to achieve the desired concentration of the uranyl sulfate stock solution.

Various concentrations of uranium solutions used in the experiment were obtained by diluting the stock solution with distilled water. In the experiments, with the exception of the tests regarding the influence of various concentrations of uranium solution, the concentration of uranium in the aqueous phase employed in all other tests was maintained at 2 mg/L.

The organic extractant P204, with a chemical purity of over 95%, was procured from McLean Reagent Co., Ltd. Concentrated sulfuric acid, sodium hydroxide, aluminum sulfate, iron sulfate, and magnesium sulfate were all chemically pure reagents obtained from Sinopsin Group Chemical Reagent Co., Ltd.

Preparation of uranium solutions with diverse initial pH values. The initial pH value of the aqueous phase was determined using a PHS-3E type instrument (Shanghai, China). Firstly, the pH value of the uranium solution with a concentration of 2 mg/L was measured, and subsequently, sodium hydroxide or sulfuric acid solution was added to adjust the pH to the requisite value.

2.2. Experimental instruments

2.2.1. Bubbling organic liquid membrane extraction

A self-developed bubbling organic liquid membrane extraction column device, as shown in Fig. 1, was used for the extraction tests. The column had a diameter of 2.5 cm and a height of 52 cm. The aeration rate was precisely regulated using a Sunsheng Type 10 air pump (ACO-010, Guangdong, China) and monitored by a Darhor rotor gas flowmeter (DFG-6T, manufactured by Darhor Instrument Inc, USA). The amount of the extractant was controlled by a laboratory injection pump (LSP01-2Y, Hebei, China).

When air was steadily introduced into the organic phase through the air pump, bubbles were formed and rose in the organic phase to the bottom of the sieve plate with a very fine aperture. When these bubbles passed through the sieve plate and entered the water phase, they experienced a pressure change and their size decreased. Simultaneously, an organic liquid film enveloped each bubble, forming "small oily bubbles" that continued to rise in the water phase. The formation process of small oily bubbles is consistent with previous work by other scholars (Liu et al., 2022; Song, et al., 2022). During this rising process, these small oily bubbles contacted and reacted with the uranium ions in the water phase, extracting them from the water phase.

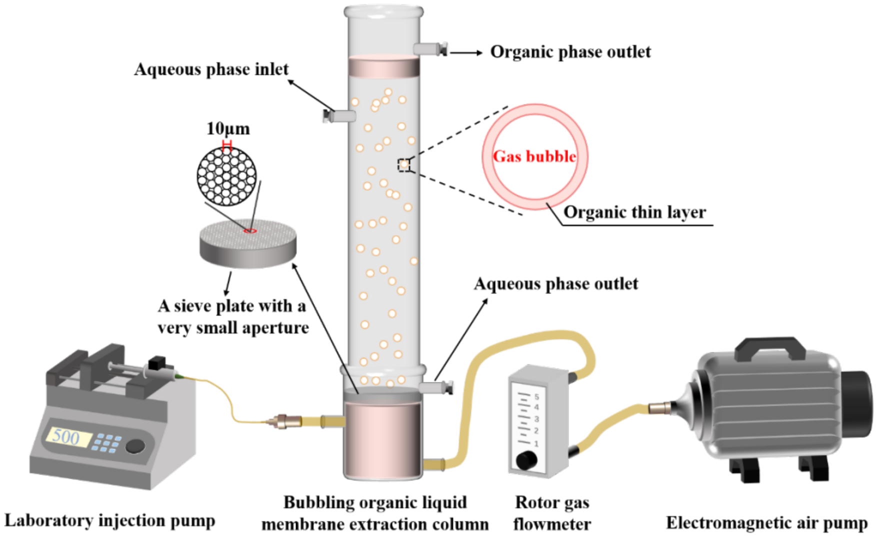

Fig. 1. A self-constructed device employing a bubbling organic liquid membrane extraction column model

2.2.2. Traditional extraction

The experimental setup for the traditional extraction method is depicted in Fig. 2. A magnetic stirrer was employed for the stirring reaction. The organic phase and the aqueous phase were separated by a 125 mL pear-shaped separating funnel. The two-phase components were blended using a magnetic stirrer. After completion of stirring, the mixture was allowed to stand in a separating funnel. The two phases were segregated based on their density disparities and immiscibility.

It should be noted that in both the bubbling organic liquid membrane extraction and the traditional extraction experiments, pure P204 was used without incorporating any diluent. This is to ensure that observed differences in extraction behavior can be directly attributed to the different mass transfer mechanisms of the two techniques, rather than changes in the physical properties of the organic phase caused by the diluent.

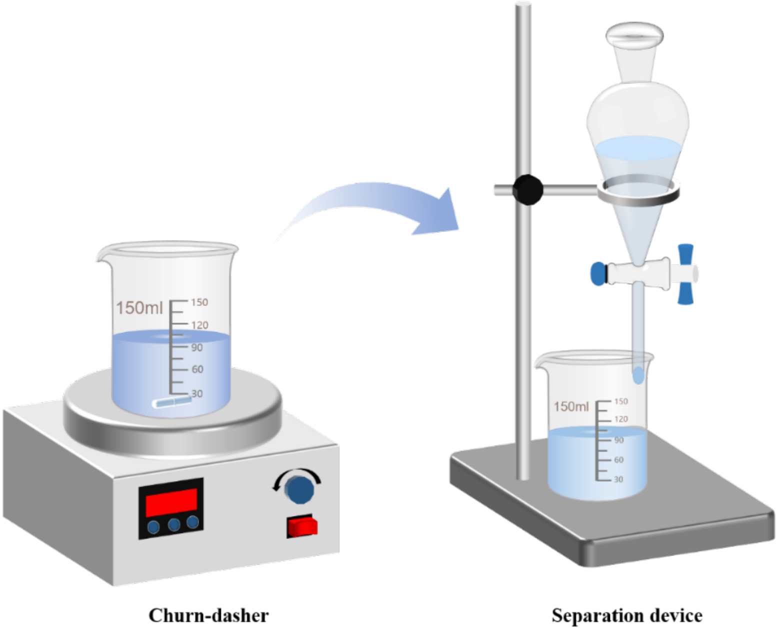

Fig. 2. Diagram of the experimental setup for the traditional extraction method

2.3. Experimental approach

2.3.1. Bubble column extraction

From the upper aqueous phase inlet, 50 milliliters of the prepared uranyl sulfate solution with a concentration of 2 mg/L was introduced into the column. P204 is injected into the organic phase chamber from the lower inlet of the extraction column using a laboratory syringe pump. The total amount of P204 was calculated based on the O/A ratio, with specific values provided in Table 1. Air was introduced into the extraction column from the air inlet at the bottom via an air pump, and the flow rate was adjusted to 0.3 milliliters per minute using a flowmeter to guarantee a stable flow. Timing commences when the oily bubbles coated with P204 enter the aqueous phase region. These oily bubbles gradually rise in this area and eventually coalesce at the top of the column, then break to form an organic phase layer and flow out from the organic phase outlet. At each sampling interval, one milliliter of the treated solution was extracted from the aqueous phase outlet and analyzed using the PerkinElmer NexION 300D inductively coupled plasma mass spectrometer (ICP-MS).

Table 1. The dosage of P204 in bubble extraction under various O/A ratios

O/A ratio	1:50	1:25	1:17	1:13	1:10	1:8	1:6
P204(ml)	1	2	3	4	5	6	8

2.3.2. Traditional extraction

Fifty milliliters of a 2.0 mg/L uranium sulfate solution was poured into a beaker. Varying amounts of P204 were added, and the mixture was positioned on a magnetic stirrer at a stirring rate of 100 revolutions per minute for 11 minutes. The quantity of P204 was determined based on the O/A ratio, with specific values provided in Table 2. After completion of the reaction, the mixture was transferred to a pear-shaped separatory funnel for liquid-liquid phase separation. One milliliter of the solution was sampled from the raffinate and analyzed using the PerkinElmer NexION 300D inductively coupled plasma mass spectrometer (ICP-MS).

Table 2. The dosage of P204 in traditional extraction under various O/A ratios.

O/A ratio	1:50	1:25	1:17	1:13	1:10	1:8	1:6	1:5
P204 (ml)	1	2	3	4	5	6	8	10

2.4. Experimental analysis

2.4.1. Calculation method

The uranium recovery (*R*) and distribution ratio (*D*) were calculated according to Equations (1) and (2), respectively (Jin et al. 2020).

The uranium recovery is defined as the ratio of the amount of the uranium transferred from the aqueous phase to the organic phase to the total initial amount of uranium in the aqueous phase. Due to the small volume of sample, its influence on the calculation of uranium recovery percentage was ignored. Assuming no loss of the liquid phase during the extraction process, the volume is considered to remain constant, the percentage of uranium removal was calculated as:

$$\mathrm{R}=\left(\frac{\mathrm{C_I}\text{-}\mathrm{C_A}}{\mathrm{C_I}}\right)\times100\% \tag{1}$$

where R (%) is the uranium recovery; C_A (mg/L) is the content of uranium element in the aqueous phase; C_I (mg/L) is the original content of uranium element in the aqueous phase before the extraction.

The distribution ratio is the ratio of the uranium concentration in the organic phase to that in the water phase after the extraction process (Rajeswari, Karunakaran et al., 2019):

$$D=\frac{C_O}{C_A} \qquad 2)$$

where D is distribution ratio; C_O (mg/L) is the uranium concentration in the oil phase, which is obtained through mass balance calculation:

$$C_0=\frac{(\mathrm{C_I}-\mathrm{C_A})\times\mathrm{V_a}}{\mathrm{V_o}} \tag{3}$$

where V_a (L) is the volume of the aqueous phase; V_o (L) is the volume of the P204 extractant employed. The calculation neglected any loss of the extractant into the aqueous phase.

2.4.2. Analysis of recovery kinetics

The uranium recovery process utilizing bubbling organic liquid membrane extraction is an open system characterized by the continuous flow of oily bubbles, and its kinetics are predominantly governed by the concentration of uranium ions in the liquid phase. Consequently, the recovery data can be suitably described by a pseudo-first-order kinetic model. The equation is written as follows:

$$\mathrm{R(t)} = \mathrm{R_{max}}(1\text{-}\mathrm{e}^{-kt}) \tag{4}$$

where $R(t)$ is the uranium recovery (%) at time t (min), R_{max} is the maximum uranium recovery (%), and k is the rate constant (min^{-1}). Fitting was performed using Origin software.

2.4.3. In-situ photography analysis of oily bubbles and oil droplets

The oily bubbles in the column and the oil droplets in the stirred extraction beaker were monitored in situ using a microscope camera (G520M Pro, HF Agile Device, China). A 2x magnification lens was used with the camera positioned 15 centimeters from the subject. Following the capture of oily bubbles and oil droplet images, a photograph containing a slide micrometer (with gradations of 0.1 mm) was subsequently taken from the same distance to calibrate the spatial scale.

3. Results and discussion

3.1. Effect of O/A ratio on uranium recovery

To investigate the effect of the O/A ratio on uranium recovery, a series of tests were conducted using a fixed volume of aqueous phase and varying volumes of organic phase, with the aqueous phase pH maintained at 6. The results of these tests are presented in Fig. 3, which shows the uranium recovery as a function of extraction time. As the extraction time increases, uranium recovery exhibits a steady increase and approaches equilibrium after approximately 9 minutes of extraction.

The correlation of pseudo-first-order kinetic model (solid lines) with the experimental data (markers) across all tested O/A ratios is shown in Fig. 3. The kinetic parameters derived from the model are summarized in Table 3. The maximum uranium recovery (R_{max}) increased from 67.50% at the O/A ratio of 1:50 to 94.30% at the O/A ratio of 1:10. However, further increases in the O/A ratio did not result in any additional improvements, indicating that extraction equilibrium had been reached. Therefore, maintaining an O/A ratio of 1:10 not only ensured optimal extraction performance but also minimized organic solvent consumption. The rate constant (k) increased from 0.343 min^{-1} to 0.667 min^{-1} as the O/A ratio increased, suggesting decreased mass transfer resistance at higher extractant concentrations.

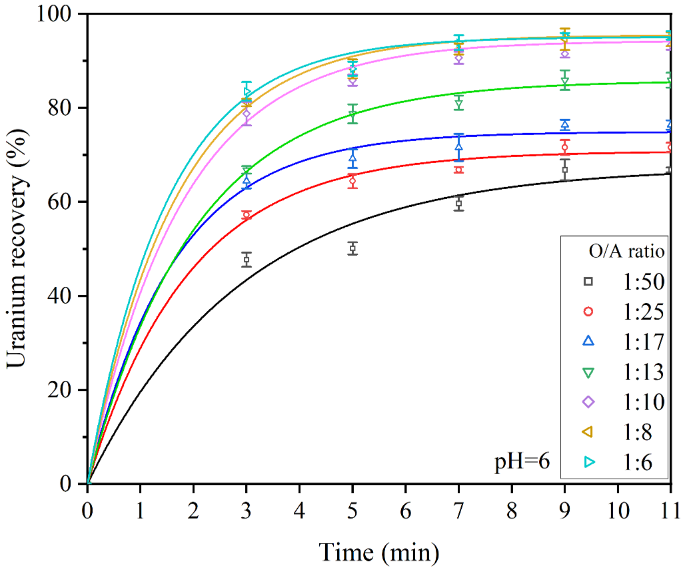

Fig. 3. Uranium recovery profiles at different O/A ratios under pH 6 conditions; the solid lines represent fitting results based on the pseudo-first-order kinetic model; error bars denote one standard deviation from three independent experiments

Table 3. Fitting parameters of pseudo-first-order kinetic model on effect of O/A ratios to uranium recovery

O/A ratio	R_{max} (%)	K (min^{-1})	R^2
1:6	95.09	0.667	0.997
1:8	95.49	0.608	0.998
1:10	94.30	0.565	0.997
1:13	85.79	0.496	0.999
1:17	74.91	0.614	0.995
1:25	70.79	0.525	0.997
1:50	67.50	0.343	0.978

To highlight the advantages of bubbling organic liquid membrane extraction for uranium recovery, a comparative experiment was conducted using conventional stirring-based extraction. Fig. 4 illustrates the effect of bubbling organic liquid membrane extraction and conventional stirring-based extraction on uranium recovery under varying O/A ratio conditions. Evidently, the bubbling organic liquid membrane extraction technology exhibits superior efficiency compared to conventional methods, highlighting its potential for improved uranium recovery. At an O/A ratio of 1:10, bubbling extraction reached equilibrium and achieved a uranium recovery of 93.4%. In contrast, conventional extraction required a larger amount of organic phase and achieved equilibrium at an O/A ratio of 1:6, with a uranium recovery of only 87.4%. The extraction rate of uranium depends on the dispersion rate of oil droplets, which is not only associated with the retention rate of dispersed oil droplets per unit volume in the aqueous phase but also linked to the surface renewal and fresh interfacial area exposed to the aqueous phase (Wang et al., 2020). In traditional extraction processes, the organic extractant is dispersed into small oil droplets that are uniformly distributed within the aqueous phase. The extraction efficiency is determined by the total interfacial area of the oil-water interface per unit time (Jin et al., 2020; Cao et al., 2022). As the volume of the organic phase decreases, achieving uniform dispersion of these oil droplets becomes increasingly challenging, thereby leading to a reduced uranium recovery. While bubbling organic liquid membrane extraction represents a method that disperses and coats bubble surfaces with a minimal volume of organic extractant to form an ultra-thin organic extractant oil film, this approach maximizes contact between the aqueous liquid and the organic extractant by ensuring uniform dispersion of oil-coated bubbles within the water phase during the bubbling process, thereby enabling optimal utilization of organic extractant. This not only significantly reduces the extraction reaction time but also enhances the uranium ion extraction rate. These inferences are corroborated by the micrographic evidence presented in Fig. 5, obtained at pH 6 and an O/A ratio of 1:6. The micrographs clearly show that the oily bubbles in the liquid phase are smaller than the oil droplets. With reference to the scale bar, most oily bubbles have a diameter of less than 0.5 mm and exhibit a uniform size distribution. In contrast, the oil droplets are significantly larger, with many exceeding 1.0 mm in diameter, and display a non-uniform size distribution.

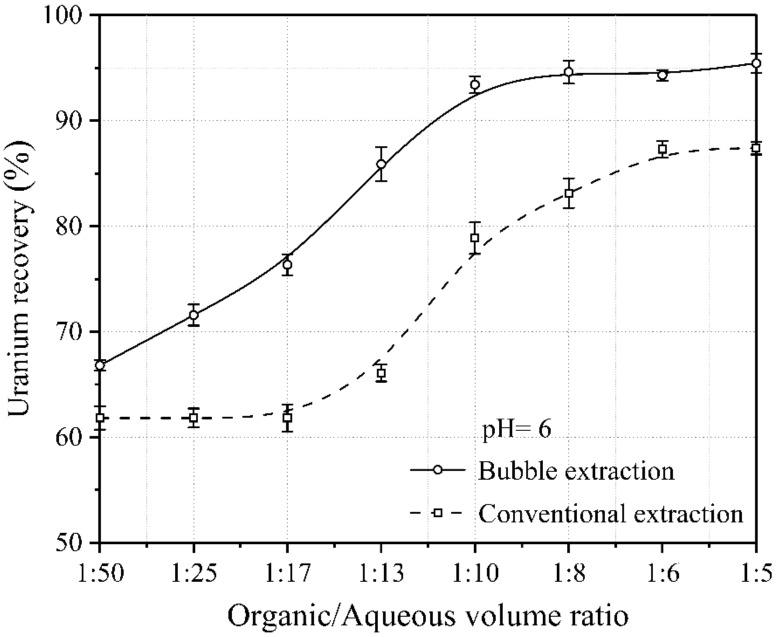

Fig. 4. Comparison of uranium recovery efficiency between bubbling organic liquid membrane extraction and conventional stirring-based extraction at different O/A ratios under pH 6 conditions. Error bars denote one standard deviation from three independent experiments

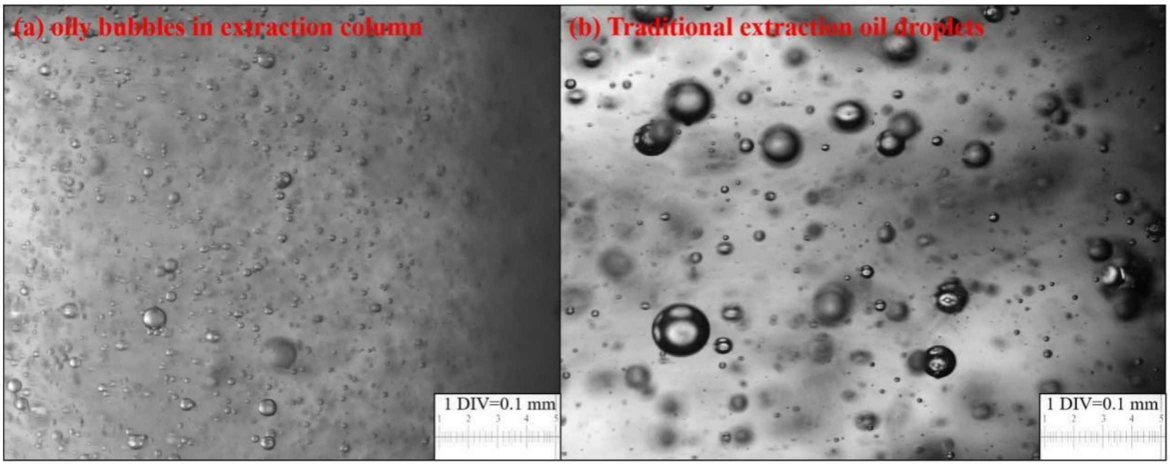

Fig. 5. In-situ photography Images of oily bubbles in the column (a) and oil droplets in the stirred extraction beaker (b) at pH 6 and an O/A ratio of 1:6

Furthermore, as rising from the bottom to the top inside an extraction column involves countercurrent shear with respect to the water phase, it accelerates the surface renewal rate of the oil film while continuously exposing fresh organic interfaces to the aqueous phase. As a result, the mass transfer processes of target ions are strengthened, leading to a further acceleration in uranium ion extraction rates (Liu et al., 2018). The hypothetical mode of oil film renewal is illustrated in Fig. 6.

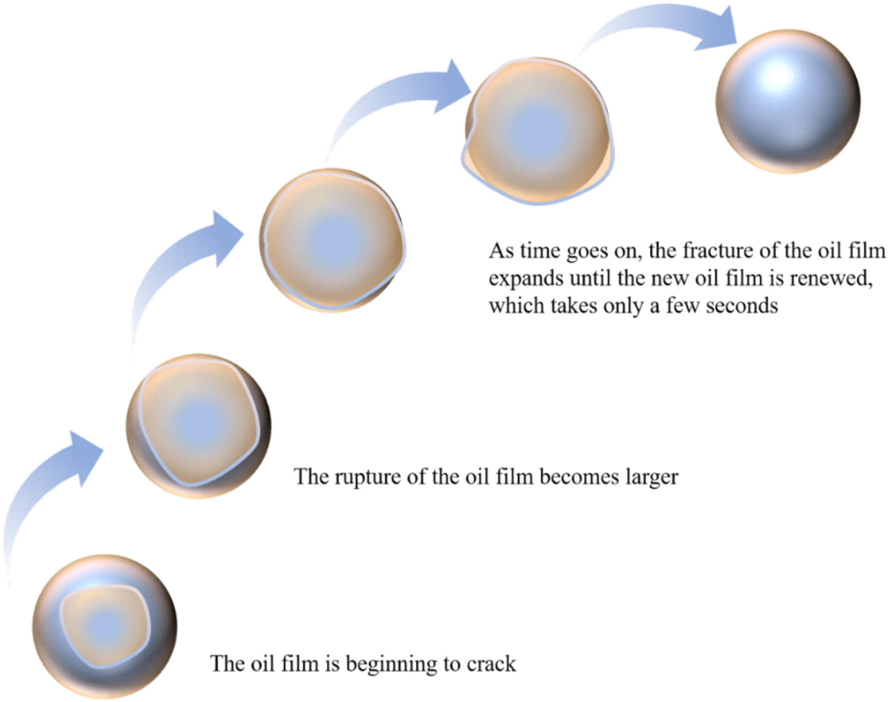

Fig. 6. The renewal process of the surface oil film layer

The bubbling organic liquid membrane extraction technology demonstrates notable economic feasibility, attributed to its inherent mechanistic advantages, including a large specific surface area and high mass transfer efficiency. Bubbling organic liquid membrane extraction technology achieves significantly higher uranium recovery at equilibrium than conventional methods, while requiring a considerably lower dosage of extractant. When the same extractant is employed, the diluent-free operation of the bubbling organic liquid membrane extraction technology enables substantial reductions in operational costs, underscoring its distinct economic benefits and reinforcing its potential for practical and scalable applications.

3.2. Effect of the initial pH value on uranium recovery

The effect of the initial pH value of the aqueous phase on the uranium recovery was investigated at an O/A ratio of 1:10. As depicted in Fig. 7, the extraction equilibrium time under different pH conditions was found to be 9 minutes. The correlation of pseudo-first-order kinetic model (solid lines) with the experimental data (markers) across all tested initial pH values is shown in Fig. 7. The kinetic parameters derived from the model are summarized in Table 4. The rate constant (k) remains relatively stable across the entire test range. The maximum uranium recovery (R_{max}) increased from 78.75% at an initial pH of 3 to 94.30% at an initial pH of 6. As the pH value increases further, the maximum uranium recovery decreases, reaching 83.29% at pH 9. This phenomenon can be attributed to the fact that the extraction efficiency of organic phosphate extractants depends not only on the equilibrium pH, but is also significantly influenced by the initial pH of the aqueous phase.(Cui et al., 2023). According to the extraction equilibrium equation, each UO_2^{2+} ion extraction releases two hydrogen ions into the aqueous phase. As the extraction proceeds, more hydrogen ions are released into the water phase, thereby exerting a substantial influence on the pH of the aqueous phase. When the hydrogen ion concentration in the aqueous phase reaches a certain level, it competes with UO_2^{2+} for extraction from the medium (Liu et al., 2017). Consequently, higher initial pH values of the aqueous phase (i.e., lower hydrogen ion concentrations) favor the forward reactions and enhance uranium extraction. However, as the initial pH of the aqueous phase increases further, the surface tension of the organic phases rises, while the interfacial tension between the oil and water phases decreases simultaneously. These factors deteriorate the stability of the oil films coated on bubble surfaces (Hou et al., 2015). As a result, portions of oil film detach from bubble surfaces and enter the aqueous phase, leading to increased hydrogen ion concentrations that adversely affect forward reaction rate and hinder uranium extraction (Xian et al., 2023). Therefore, to establish a stable bubble capable of supporting the organic liquid film and achieving superior extraction efficiency, an initial aqueous phase with a pH of 6 was selected for subsequent experiments.

The reaction equation of extracting uranium with P204 is as follows (Huang et al., 2015):

$$UO_{2\ (a)}^{2+}+2[H_2A_2]_{(o)}=[UO_2(H_2A_2)]_{(o)}+2[H^+]_{(a)} \tag{5}$$

where: $[H_2A_2]_{(o)}$ is the dimer of p204; $[UO_2(H_2A_2)]_{(o)}$ is the extract; The subscript (o) represents the organic phase and (a) represents the aqueous phase.

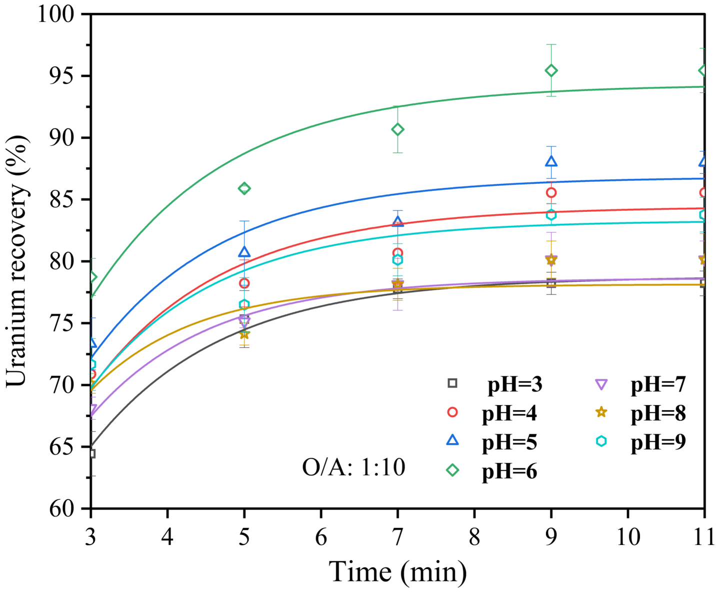

Fig. 7. Uranium recovery profiles at different initial pH values under an O/A ratio of 1:10; the solid lines represent fitting results based on the pseudo-first-order kinetic model; error bars denote one standard deviation from three independent experiments

Table 4. Fitting parameters of pseudo-first-order kinetic model on effect of initial pH values to uranium recovery

pH	R_{max} (%)	K (min^{-1})	R^2
3	78.75	0.583	0.984
4	84.42	0.582	0.997
5	86.81	0.593	0.997
6	94.30	0.565	0.997
7	78.65	0.650	0.975
8	78.14	0.685	0.908
9	83.29	0.601	0.895

3.3. Effect of initial uranium concentration on uranium recovery

The variation in uranium recovery was investigated under different uranium concentrations at an O/A ratio of 1:10 and a solution pH of 6. Additionally, the equilibrium uranium concentration in the raffinate phase was analyzed for each experimental set, and the uranium distribution ratio at varying concentrations was calculated using Equation (2). The data presented in Fig. 8 clearly indicate a significant correlation between initial uranium concentration and uranium recovery. As the initial uranium concentration increases, the uranium recovery decreases. This trend is also observed in the distribution ratio, indicating a strong correlation between uranium recovery and distribution ratio. A higher distribution ratio promotes the allocation of solute to the organic phase and subsequently improves uranium recovery. Indeed, an optimal extraction effect is usually achieved when the distribution ratio exceeds 10 (Villarroel et al., 2022). When the initial uranium concentration was 1.0 mg/L and 2.0 mg/L, the distribution ratios were 23.0 and 20.9, respectively, and the corresponding uranium recovery were 95.8% and 95.4%. However, when the uranium concentration exceeds 2.0 mg/L, the distribution ratio falls below 10, resulting in a significant decrease in the uranium recovery.

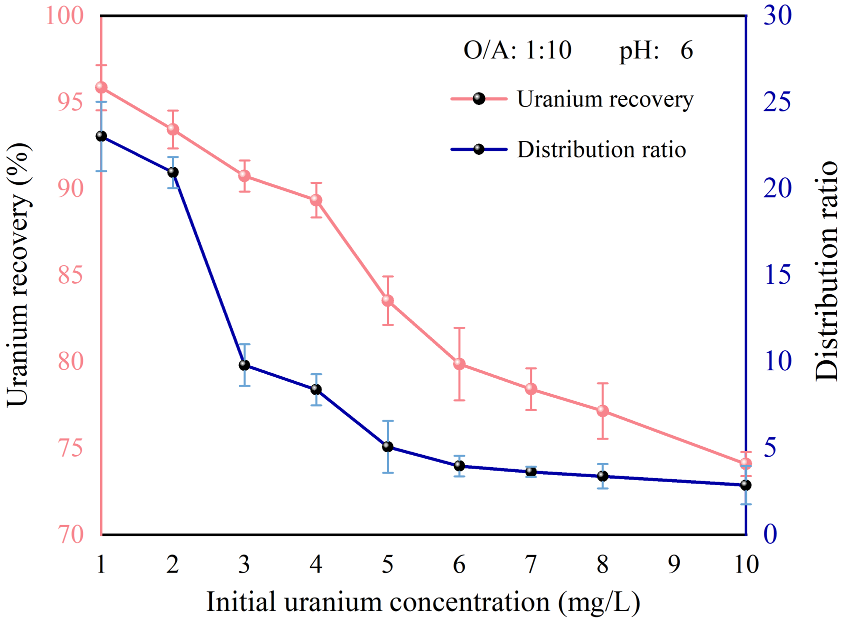

Fig. 8. Variation in uranium recovery and distribution ratio as a function of initial uranium concentration, with the O/A ratio maintained at 1:10 and pH held constant at 6. Error bars denote one standard deviation from three independent experiments

3.4. Effect of coexisting cation concentration on uranium recovery

The chemical reaction between uranium ore and the leaching agent leads to the release of cations, such as Al^{3+}, Fe^{3+}, and Mg^{2+}, into the leaching solution (Madakkaruppan et al., 2019). The presence of these cations has a specific influence on the uranium extraction process of P204. In the experiment, varying concentrations of $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, and $MgSO_4$ were introduced into the prepared uranyl sulfate solution to simulate different cationic interference environments. Under conditions of an O/A ratio of 1:10 and a solution pH of 6, this experiment investigated the variations in uranium recovery in response to different concentrations of cations. As depicted in Fig. 9, the uranium recovery decreased with increasing concentration of interfering ions. In the absence of interfering cations, the uranium recovery reached 95.4%. When the concentrations of Al^{3+}, Fe^{3+}, and Mg^{2+} were 1.0×10^{-3} M, the uranium recovery were 92.9%, 92.1%, and 85.6%, respectively. When the concentrations increased to 5.0×10^{-3} M, the uranium recovery decreased to 85.6%, 78.6%, and 75.8% for Al^{3+}, Fe^{3+}, and Mg^{2+}, respectively. This indicates that with increasing concentration of interfering cations, the extraction of uranium becomes progressively more challenging due to the co-extraction and competition of interfering cations with uranium ions during the extraction process (Ye et al., 2018; Zhang et al., 2021). The binding affinity of the organic phosphate extractant for Fe^{3+} and Mg^{2+} is slightly stronger than that for uranium ions, owing to the smaller ionic radii of Fe^{3+} and Mg^{2+} compared to uranium ions. Consequently, at higher concentrations in solution, these interfering cations exhibit a more pronounced co-extraction behavior, thereby exerting a greater adverse effect on uranium extraction. These metal ions undergo varying degrees of hydrolysis, complexation, flocculation, and precipitation during the extraction process, facilitating their transfer into the organic phase and promoting emulsification of the extractant (Sánchez-García et al., 2019). Therefore, when these interfering cations are present at high concentrations in aqueous solutions, pretreatment should be conducted to reduce their concentration before extraction.

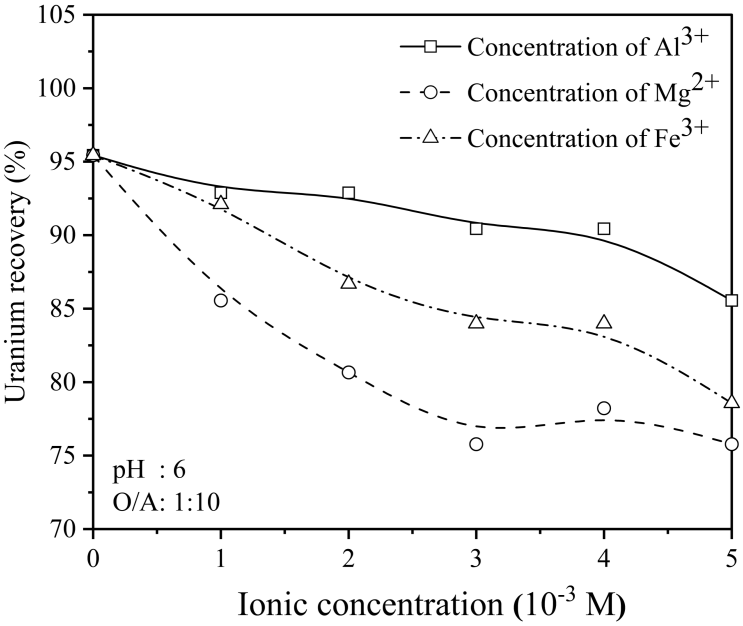

Fig. 9. Effect of coexisting cation concentration on uranium recovery. Experiments were conducted under an O/A ratio of 1:10, a solution pH of 6, and an initial uranium concentration of 2.0 mg/L

4. Conclusions

This study demonstrates the effective enrichment and recovery of low-concentration uranium via the bubbling organic liquid membrane extraction method with P204 as the extractant. It was found that the uranium recovery data obtained from bubbling organic liquid membrane extraction can be well described by a pseudo-first-order kinetic model. This agreement supports the hypothesis that mass transfer of uranium across the liquid membrane interface is the predominant rate-controlling step in the extraction process. The uranium recovery reached 95.4% when the initial pH value was 6 and the O/A ratio was 1:10. However, increasing initial uranium concentration resulted in a decline in P204's extraction efficiency. Furthermore, it was observed that an increase in interfering cation concentrations in the solution led to a reduction in uranium recovery.

Overall, the findings underscore the potential of bubbling organic liquid membrane extraction as an effective method for the recovery of low-concentration uranium. The optimized parameters established in this study offer a foundation for scale-up and application of this method.

Acknowledgment

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References

CAO, Q., QIAN, Y., LI, J., YANG, S., 2022. *Performance and mechanism study on surfactant-stabilized oil microdroplets extraction from oily wastewater.* Separation and Purification Technology. doi:10.1016/j.seppur.2022.122470

CHANDRAMOULEESWARAN, S., RAMKUMAR, J., BASU, M., 2016. *Insight of solvent extraction process: Reassessment of trace level determinations.* Analytica Chimica Acta. doi:10.1016/j.aca.2016.08.018

CUI, L., CAO, J., JIAO, S., PANG, G., WEI, Z., 2023. *Selective Solvent Extraction of Vanadium Over Chromium from Alkaline Leaching Solution of Vanadium Slag by D2EHPA/TBP.* Solvent Extraction and Ion Exchange. doi:10.1080/07366299.2023.2185097

EHRIG, K., KAMENETSKY, V. S., MCPHIE, J., MACMILLAN, E., THOMPSON, J., KAMENETSKY, M., MAAS, R., 2021. *Staged formation of the supergiant Olympic Dam uranium deposit, Australia.* Geology. doi:10.1130/g48930.1

FOURIE, M., VAN DER WESTHUIZEN, D. J., KRIEG, H. M., 2018. *Uranium recovery and purification from simulated waste streams containing high uranium concentrations with dispersion liquid membranes.* Journal of Radioanalytical and Nuclear Chemistry. doi:10.1007/s10967-018-5860-y

GENG, Y., LI, Z., ZHAO, H., CHEN, M., ZHANG, L., 2020. *Removal of entrained organic phase from raffinate in spent fuel reprocessing with graphene-based composites.* Journal of Radioanalytical and Nuclear Chemistry. doi:10.1007/s10967-020-07015-w

HOU, H., JING, Y., WANG, Y., WANG, Y., XU, J., CHEN, J., 2015. *Solvent extraction performance of Ce(III) from chloride acidic solution with EHEHPA using membrane dispersion micro-extractor.* Journal of Rare Earths. doi:10.1016/s1002-0721(14)60534-2

HUANG, K., LIU, J., WU, H., LIU, H., 2015. *A new bubbling extraction tower: Toward liquid–liquid solvent extraction at large aqueous-to-oil phase ratios.* AIChE Journal. doi:10.1002/aic.14904

HUNG, N. T., THUAN, L. B., THANH, T. C., et al., 2020. *Separation of thorium and uranium from xenotime leach solutions by solvent extraction using primary and tertiary amines.* Hydrometallurgy. doi:10.1016/j.hydromet.2020.105506

JIN, N., YUE, J., ZHAO, Y., LÜ, H., WANG, C., 2020. *Experimental study and mass transfer modelling for extractive desulfurization of diesel with ionic liquid in microreactors.* Chemical Engineering Journal. doi:10.1016/j.cej.2020.127419

KAKSONEN, A. H., LAKANIEMI, A.-M., TUOVINEN, O. H., 2020. *Acid and ferric sulfate bioleaching of uranium ores: A review.* Journal of Cleaner Production. doi:10.1016/j.jclepro.2020.121586

LIU, J., HUANG, K., WU, X.-H., LIU, H., 2017. *Enrichment of low concentration rare earths from leach solutions using bubbling organic liquid membrane (N1923).* ACS Sustainable Chemistry & Engineering. doi:10.1021/acssuschemeng.7b01682

LIU, J., HUANG, K., WU, X., LIU, W., SONG, W., LIU, H., 2018. *Extraction of rare earths using bubbling organic liquid membrane with un-saponified P507.* Hydrometallurgy. doi:10.1016/j.hydromet.2017.12.015

LIU, J., JIA, M., SONG, C., XIA, W., HUANG, K., 2022. *Controllable enhancement of mass transfer kinetics related with the thickness of organic thin-layer liquid membrane on gas bubble surface.* Chemical Engineering and Processing. 172, 108775

LUO, K., WANG, Q., XIN, Q., et al., 2023. *Preparation of novel PVA–CNT/ionic liquid/chitosan hydrogel for highly efficient uranium extraction from seawater.* International Journal of Biological Macromolecules. doi:10.1016/j.ijbiomac.2023.128751

LV, Y., TANG, C., LIU, X., et al., 2021. *Optimization of environmental conditions for microbial stabilization of uranium tailings and microbial community response.* Frontiers in Microbiology. doi:10.3389/fmicb.2021.770206

LYU, P., WANG, G., CAO, Y., WANG, B., DENG, N., 2021. *Phosphorus-modified biochar composite for immobilizing uranium in contaminated soil.* Chemosphere. doi:10.1016/j.chemosphere.2021.130116

MADAKKARUPPAN, V., PIUS, A., SREENIVAS, T., SUNILKUMAR, T. S., 2019. *Behaviour of Si, Al, Fe and Mg during oxidative sulfuric acid leaching of low-grade uranium ore.* Journal of Environmental Chemical Engineering. doi:10.1016/j.jece.2019.103139

MAHER, C. J., BOUYER, C., GRIFFITHS, T. L., et al., 2018. *Impact of uranium carbide organics treated by boiling/electrochemical oxidation on uranium and plutonium solvent extraction.* Radiochimica Acta. doi:10.1515/ract-2017-2799

PANT, S., SINGH, S., SAHOO, P. R., et al., 2019. *Mineral chemistry and geothermometry of chlorites related to uranium mineralization in Singhbhum Shear Zone.* Ore Geology Reviews. doi:10.1016/j.oregeorev.2019.102997

RAJ, S., CARRIER, A., YOUDEN, B., et al., 2024. *Electrochemical techniques for uranium extraction from water.* Chemical Engineering Journal. doi:10.1016/j.cej.2024.152341

RAJESWARI, S., KARUNAKARAN, R., KALAIARASU, T., SELVAN, B. R., VENKATESAN, K. A., 2019. *Performance evaluation of a cylindrical air-lift mixer–settler for uranium(VI) extraction from nitric acid.* Journal of Radioanalytical and Nuclear Chemistry. doi:10.1007/s10967-019-06732-1

SÁNCHEZ-GARCÍA, I., BONALES, L. J., GALÁN, H., PERLADO, J. M., COBOS, J., 2019. *Spectroscopic study of AHA hydrolysis in presence of europium: Implications for lanthanide–actinide separation.* New Journal of Chemistry. doi:10.1039/c9nj03360b

SINGH, D. K., HAREENDRAN, K. N., T, S., KAIN, V., DEY, G. K., 2017. *Phosphate precipitation method for recovery of uranium from alkaline leach liquor.* Hydrometallurgy. doi:10.1016/j.hydromet.2017.05.021

SONG, F., WANG, J., SUI, H., LI, X., HE, L., 2022. *Kinetics of CO_2 gas bubbling for separation of residual solvent from waste solids: Effect of bubble size.* Journal of Environmental Chemical Engineering, 10(3), 107981

VILLARROEL, E., OLEA, F., ARAYA-LÓPEZ, C., et al., 2022. *COSMO-RS evaluation for predicting solvents in dispersive liquid-phase microextraction.* Journal of Molecular Liquids. doi:10.1016/j.molliq.2022.118861

WANG, J., CUI, K., ZHOU, H., HUANG, K., 2022. *Environmentally friendly bubble-supported organic liquid membrane for treating yttrium-rich ore leaching solutions.* ACS Sustainable Chemistry & Engineering, 10(51), 17094–17106

WANG, J., LI, X., MA, G., SUI, H., HE, L., LIU, R., 2020. *Removal of residual solvent from unconventional oil ores by gas bubbling.* Separation and Purification Technology. doi:10.1016/j.seppur.2020.117551

WEI, Z., GE, X., WANG, H., YUAN, Z., YAN, T., ZHENG, W., 2024. *Intensified extraction and stripping of uranium using membrane dispersion microextractor.* Results in Engineering. doi:10.1016/j.rineng.2023.101675

WUFUER, R., DUO, J., LI, W., FAN, J., PAN, X., 2021. *Bioremediation of uranium- and nitrate-contaminated groundwater after in-situ leach mining.* Water. doi:10.3390/w13223188

XIAN, X., YE, Z., TANG, L., et al., 2023. *Molecular dynamics simulation of complex surfactants at oil–water interface.* Langmuir. doi:10.1021/acs.langmuir.3c01990

XIANXIAN, Z., KAIHUI, C., KUN, H., 2021. *Enhanced interfacial salt effect on extraction of Er(III) using bubble-supported organic liquid membrane.* Separation and Purification Technology. doi:10.1016/j.seppur.2021.120344

XIN, Q., WANG, Q., LUO, K., et al., 2023. *Mechanism for selective adsorption of uranium from seawater using carboxymethyl-enhanced polysaccharide amidoxime adsorbent.* Carbohydrate Polymers. doi:10.1016/j.carbpol.2023.121576

YE, Q., LI, G., DENG, B., et al., 2018. *Solvent extraction behavior of metal ions and selective separation of* Sc^{3+} *using P204 in phosphoric acid.* Separation and Purification Technology. doi:10.1016/j.seppur.2018.07.033

YU, K., ZHONG, L., GUO, L., GAO, F., FENG, X., LUO, F., 2024. *Extraction of uranium by a pyrazole-based porous organic polymer.* Inorganic Chemistry. doi:10.1021/acs.inorgchem.4c00660

ZAHAKIFAR, F., KHANRAMAKI, F., NEJAD, D., GHAZANFARI, V., YADOLLAHI, A., 2025. *Solvent extraction and stripping using Alamine 336: Case study of uranium.* Scientific Reports. doi:10.1038/s41598-025-96421-9

ZHANG, W., XIE, X., TONG, X., DU, Y., SONG, Q., FENG, D., 2021. *Effect of impurity aluminum on solvent extraction of rare earths (Nd, Pr, La) by P204–P350.* Minerals. doi:10.3390/min11010061

ZHENQIAN, W., YUQING, N., 2017. *Recovery of uranium from low-concentration acid in-situ leaching liquor.* IOP Materials Science and Engineering. doi:10.1088/1757-899X/191/1/012035

ZHENG, W., ZHUO, C., YUAN, Z., DONG, Y., XU, J., ZHENG, W., 2022. *Efficient removal of dissolved TBP from nitric acid using membrane dispersion microextractor.* Chemical Engineering Science. doi:10.1016/j.ces.2022.117846

ZHU, L., ZHANG, C., ZHU, R., et al., 2023. *Functionalized polyimide COFs for uranium-containing wastewater treatment.* Journal of Hazardous Materials. doi:10.1016/j.jhazmat.2023.133320