Continuous Liquid–Liquid Extraction of Uranium from Uranium-containing Wastewater Using an Organic Phase-refining-type Emulsion Flow Extractor

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A previously reported emulsion flow (EF) extraction system does not equip the refining device for any used organic phase. Therefore, the processing of large quantities of wastewater by using the EF extractor alone could lead to the accumulation of extracted components into the organic phase, and a lowering of the extraction performance. In the present study, we developed an organic phase-refining-type EF system, which is equipped with a column for refining a used organic phase to prevent accumulation, and successfully applied it for treating uranium-containing wastewater.

Keywords Continuous extraction, emulsion flow extractor, uranium, uranium-containing wastewater, organic phase-refining

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Introduction

Liquid-liquid extraction is an effective method for several processes related to the nuclear fuel cycle, which involves the process of milling uranium from uranium mines,1–4 the reprocessing of spent fuel,1,4,5 or the partitioning for high-level liquid waste.6–12 Such extraction has recently also received attention in industrial fields as a method for the recovery and recycling of minor metals from industrial waste.13–16 As an alternative to the existing continuous liquid-liquid extraction apparatus to recover valuable substances or to remove hazardous materials from wastewaters, such as mixer-settler, centrifugal extractor, or spray extraction column, we have developed a new continuous liquid-liquid extraction method using an emulsion flow (EF) extractor.17–21 We confirmed the ability of the EF extraction method to remove uranium from uranium-containing wastewater,22 and to recover nickel from electroless nickel plating wastewater.23

However, because the EF extractor does not have a device for refining the used organic phase, the treatment of a large quantity of water samples using the EF method alone would cause the accumulation of extracted components into the organic phase, and thus lowering its extraction performance. Refining the organic phase is one possible countermeasure to avoid accumulation of the components. In the present study, we developed an organic phase-refining-type EF system, equipped with a column for refining the used organic phase to facilitate the continuous refinement of any used organic phase as the extraction proceeds. The effectiveness of developed system has been demonstrated through experiments of removing uranium from uranium-containing wastewater by comparing the extraction performances achieved by refining the organic phase to that without refining the organic phase.

Experimental

Outline of organic phase-refining-type EF extractor

Figure 1 shows a schematic of the structure of the desktop organic phase-refining-type EF extractor used in the present study. This apparatus is primarily composed of two EF columns, namely an extraction column and a refining column, which had the same structure and size in the present study. The details concerning the column were reported previously.18,20

In the extraction column, an emulsified mixture of feed solution and organic solution forms at the middle of the apparatus mainly by spraying fine droplets of the organic solution into the feed solution through a lower nozzle head. The feed solution is introduced into the apparatus through an upper nozzle head. In the emulsified phases, the target components in the feed solution are extracted into the organic solution. When the emulsified phase reaches the upper or lower part of the EF apparatus, it disappears, and separates into the organic or aqueous phase. The aqueous phase separated in the lower part is drained outside for continuous treatment. By contrast, when the refining column is not used, the organic phase separated in the upper part of the apparatus is withdrawn to outside and recycled into the extraction column through the lower nozzle head. The EF extractor, itself, does not have a device for refining the used organic phase. Consequently, because the organic phase is circulated within the system without refinement, it accumulates the target component during the circulation, which could lead to diminish the extraction performance without the refining column.

To solve this problem, we have developed a new EF system, which comprises not only an extraction column, but also an...
organic phase-refining column (Fig. 1). In the refining column, the organic phase, sent from the upper phase separation part of the extraction column, is sprayed into the refining aqueous solution through the lower nozzle head in the refining column. The refining aqueous solution is introduced into the organic solution through the upper head, and the emulsified mixture of used organic phase and refining aqueous solution forms in the extraction part of the column. In the emulsion, some components in the organic phase are stripped into the refining aqueous solution, refining the organic phase. When the emulsified phase reaches the upper or lower part of the refining column, it disappears, and separates into the organic or aqueous phase. The refining aqueous solution was circulated within the refining column as accumulating the target component. The refined organic phase in the refining column is withdrawn to outside and reintroduced into the extraction column. In this manner, the organic phase is continuously refined as it is being circulated. The size (total volume) of each column is about 0.48 L. The lower nozzle head for spraying the organic phase was a commercial sintered-glass plate with a maximum pore size of 0.02 – 0.03 mm, while the upper nozzle head was a polypropylene hollow cylinder with 30 holes of 0.2 mm in diameter. Prior to system operation, the extraction column was filled with the feed solution and the organic solution, while the refining column was filled with the refining aqueous solution and the organic solution. The total volume of the organic solution in the two columns and the connecting tubes was 0.5 L. In the case of the non-refining experiment, deionized water was used instead of the refining aqueous solution.

Liquid-liquid extraction experiments

Uranium-containing wastewater was prepared as a model solution simulated based on actual decontamination wastewaters (DW) generated from decontamination of the used centrifuges at the Ningyo-toge environmental engineering center of the Japan Atomic Energy Agency. The simulated DW prepared in the present study was characterized by a rather low concentration of uranium \( (2.16 \times 10^{-7} \text{ M}) \) compared with the other constituents such as iron \( (4.12 \times 10^{-3} \text{ M}) \), cobalt \( (5.61 \times 10^{-4} \text{ M}) \) and nickel \( (9.41 \times 10^{-4} \text{ M}) \) ions, and by a relatively low pH \( (\sim 0.55) \) owing to the dilute sulfuric acid solution used for decontamination. All liquid-liquid extraction experiments were conducted at room temperature \((23 - 25^\circ \text{C})\). The extractabilities of the components were determined from batch experiments according to a procedure described in a previous report.\(^{22}\) The organic solution used in the batch experiments was a Shellsol D70 (Shell Chemicals) solution containing 0.02 - 0.2 M tri-n-octylamine (TnOA, Tokyo Chemical Industry Co., Ltd.)\(^{24}\) and 4 vol% 2-ethylhexanol (2-EH, Wako Pure Chemical Industries, Ltd.), which was added to avoid the formation of a third phase. The organic solution was preliminarily equilibrated with a sulfate solution at around pH 0.55. Continuous liquid-liquid extraction experiments were carried out on the DW by using an organic phase-refining-type EF extractor. The organic solution in the EF experiment was a Shellsol D70 solution containing 0.02 M TnOA and 4 vol% 2-EH. The refining aqueous solution was a 1 M HNO\(_3\) solution. The feed volume of the DW was 5 L, which was 10-times larger than that of the organic solution. A control experiment was carried out under a non-refining condition. Raffinates from the extraction column were sampled every 0.1 or 0.2 L and the uranium concentrations in the raffinates were determined. The chemical compositions of aqueous phases were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS; NexION 300X, Perkin Elmer).
TnOA molecules are required for the extraction of one uranium molecule in the TnOA concentration range of 0.02 - 0.1 M. Therefore, the extraction reaction of uranium from the DW was described by the following equation:

\[
\text{UO}_2^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{TnOA(organic)} \leftrightarrow \text{UO}_2(\text{TnOA})_2\text{SO}_4 \text{(organic)}. \quad (1)
\]

In the batch experiment using 0.02 M TnOA, the concentration of uranium extracted into the organic phase was \(1.92 \times 10^{-7}\) M, as estimated from the uranium distribution ratio (\(\sim 8.1\)) and the initial concentration of the DW (\(2.16 \times 10^{-7}\) M). In addition, the other elements were not detected in the aqueous solutions after back extraction of the organic phase by means of ICP-MS analysis, the detection limits of which were \(1.75 \times 10^{-6}\) M for iron, \(1.69 \times 10^{-7}\) M for cobalt and \(1.66 \times 10^{-7}\) M for nickel in the present study. Therefore, it is considered that the TnOA concentration of 0.02 M should be sufficient for uranium extraction in the EF experiments, even after considering that the feed volume of the DW (5 L) in the EF experiments is 10-times larger than the organic phase volume.

Figure 3 shows the changes in the removal rates (\(R\%\)) of uranium estimated using the equation: 

\[
R = \frac{C_{\text{init}} - C_{\text{aq}}}{C_{\text{init}}} \times 100,
\]

where \(C_{\text{init}}\) is the initial uranium concentration of the fresh DW, and \(C_{\text{aq}}\) is the uranium concentration in the raffinate, as a function of the DW feed volume. In the initial stages of feeding, the removal rates are rather low owing to drainage of the pre-filled DW, but they abruptly increase and eventually reach maximum values of \(85 - 90\%\) at \(0.5\) L of the feed volume. After \(0.5\) L of the feed volume, the removal rates under the non-refining condition decrease gradually to \(\sim 36\%\) at 5.0 L. This means that the residual uranium concentration in the raffinate (\(C_{\text{raff}}\)) gradually increased after 0.5 L of the feed volume. Under the non-refining condition, uranium accumulated in the organic phase, that is, the uranium concentration in the organic phase (\(C_{\text{org}}\)) gradually increased during the EF experiment. On the other hand, the uranium concentration ratio of the organic/aqueous phase (\(C_{\text{org}}/C_{\text{aq}}\)) can remain almost constant, judging from a large excess of the TnOA concentration over uranium extraction, as mentioned above. This is also supported by the result that the \(C_{\text{org}}/C_{\text{aq}}\) ratio at 5.0 L of the feed volume was \(\sim 9.2\), and still close to distribution ratio of \(\sim 8.1\) from the batch experiment. Therefore, the gradual increase of the \(C_{\text{org}}\) and the almost constant \(C_{\text{org}}/C_{\text{aq}}\) ratio can result in a gradual increase of \(C_{\text{aq}}\) with the progress of the extraction reaction.

In contrast, the removal rates under the refining condition remained almost constant at \(\sim 89\%\) after 0.5 L of the feed volume. The analysis of the organic phase after the end of the experiment showed that the uranium in the organic phase in the refining column decreased significantly compared to that in the organic phase in the extraction column. Consequently, because the refining was quite effective in terms of preventing the accumulation of uranium in the organic phase, the extraction performance improved under the refining condition. From these results, it was concluded that the proposed organic phase-refining-type EF system is superior to the previous system using EF the extraction column alone for the treatment of large volumes of wastewater.

**Conclusions**

As a continuous liquid-liquid extraction apparatus for treating large quantities of wastewater, we have developed an organic phase-refining-type EF extractor, which was equipped with an organic-phase refining column alongside the extraction column. In this apparatus, the organic phase is circulated between the extraction column and the refining column. During the circulation of the organic phase, the target components in the feed solution are extracted into the organic phase in the extraction column and stripped into the refining aqueous solution in the refining column. The effectiveness of the developed EF extractor was demonstrated through experiments of removing uranium from uranium-containing wastewater. This EF extractor is quite effective in treating large quantities of wastewater, which are otherwise liable to cause the accumulation of extracted components in the organic phase.
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References