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# Concentration of Copper(II) Ion in Water Using a Water-Soluble Chelating Polymer and a Microporous Hollow Fiber

Tahei TOMIDA,* Tatsuya INOUE, Kazuhisa FUJITA, and Seizo MASUDA
Department of Chemical Science and Technology, The University of Tokushima, Tokushima 770

A new method using a water-soluble chelating polymer and a microporous hollow fiber was developed for concentration of copper(II) ion in water. The copper(II) ion recovered into a chelating polymer (polyacrylic acid) solution could be determined directly with ICP or UV-spectrophotometer. Cu(II) in a sample solution was calculated from the rate of concentration. It was demonstrated that this method was useful for concentration of Cu(II) existing in dilute solutions (1-1000 $\mu$g dm$^{-3}$).

A method for concentrating metal ions using a water-soluble chelating polymer and a microporous hollow fiber membrane was developed, and applied to the concentration of copper(II) ion exsiting in dilute solutions. In this method, metal ions permeate into the chelating polymer solution through a microporous hollow fiber membrane, and form metal-chelating polymer complexes. The hollow fiber membrane allows permeation of metal ions, but not water-soluble chelating polymer and metal-polymer complexes. In contrast with membrane solvent extraction, there is no aqueous-organic interface, which causes unfavorable resistance against mass transfer, and so the rate of concentration seems to be higher than that by extraction methods. In addition, this method does not need any devices for filtration, such as that required for membrane filtration of a water-soluble chelating polymer-metal complex.[1)]

In this study, we examined the concentration of copper(II) ion using polyacrylic acid, PAA (number average molecular weight 90000; Aldrich Chemical Co., Inc.) and a microporous hollow fiber membrane. The microporous hollow fiber used was a polyacrylonitrile fiber of 0.8 mm inner diameter, 0.3 mm thickness, and 1.2 m length with a molecular cut-off of 13000 (Asahikasei Kogyou Co.). Experiments were carried out in two modes: (1) a "circulating mode", in which the chelating polymer (PAA) solution circulated inside the hollow fiber immersed in a sample solution at a fixed rate with a peristaltic pump, and (2) a "once-through mode", in which PAA solution passed inside the hollow fiber immersed in a sample solution. The sample solution was stirred with a magnetic stirrer at 600-620 r.p.m. The concentration of Cu(II) recovered into PAA solution was determined directly with ICP (ICPS-5000, Simadzu Co.) or spectrophotometrically with 2,7-Bis(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (Arsenazo III). In this case, the absorbance at 605 nm was proportional to the concentration of Cu(II) if the concentration of Cu(II) was higher than 0.05 mg dm$^{-3}$.

Figure 1 shows the time course of the concentration of Cu(II) recovered by the circulating mode. After a lag time of about twenty minutes, the concentration of Cu(II) recovered in PAA solution increased almost linearly with time, and reached to about 20-fold of the sample solution within three hours. In steady state, the rate of concentration (dC/dt) can be approximately represented by the following equation:

$$dC/dt = (kA/V_P)\ C_S \qquad (1)$$

where k and A are the coefficient of permeation and effective surface area of the hollow fiber, respectively. Therefore, the slope of the each line was dependent only on the concentration of the sample solution ($C_S$) when other experimental conditions such as the flow rate of PAA solution, the stirring speed of the sample solution and the volume of PAA solution ($V_P$) were fixed. Thus, the concentrations of Cu(II) in water can be calculated from the rate of concentration when there is enough amount of the sample solution to keep the concentration constant. In addition, the concentration factor is inversely proportional to $V_P$ if there is a sufficient stoichiometric amount of PAA. The rate of concentration was not affected by a concomitant metal ion, Ni(II) (Table 1).

Figure 2 shows the results by the once-through mode. The relationship between the concentrations of Cu(II) in the outlet polymer solution and the sample solution was almost linear. The outlet concentration of Cu(II) in the polymer solution was ten times as large as that of the sample solution when the solution was fed at a flow rate of 0.08 cm$^3$/min. However, it takes about thirty minutes for the outlet concentration to become steady. When the outlet solution from the hollow fiber was connected to a UV-spectrophotometer after mixing with Arsenazo III solution, the concentration of Cu(II) recovered could be determined by spectrophotometry.

These results demonstrate that the method proposed here is useful for concentration of Cu(II) existing in dilute solutions (1-1000 μg dm$^{-3}$). The enrichment factor or the rate of concentration should be increased by increasing the number of the microporous hollow fiber membrane.

References

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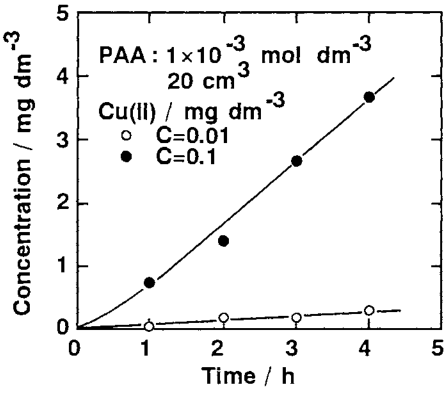

Fig.1. Time course of concentrations of Cu(II) recovered. Feed rate, 2.28 cm$^3$ min$^{-1}$; Fiber length, 1.2 m; Sample solution, 3 dm$^3$.

Table 1. Effect of a concomitant Ni(II) on the recovery rate of Cu(II)

| Cu(II) | Ni(II) | Recovery rate in 3 h |
|---|---|---|
| / mg dm$^{-3}$ | | / mg dm$^{-3}$ s$^{-1}$ |
| 0.1 | 0 | 2.69 × 10$^{-4}$ |
| 0.1 | 1.0 | 2.69 × 10$^{-4}$ |
| 1.0 | 0 | 2.14 × 10$^{-3}$ |
| 1.0 | 1.0 | 2.09 × 10$^{-3}$ |

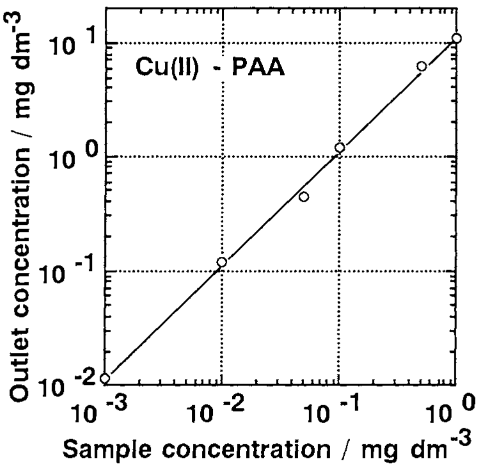

Fig. 2. Relation between concentrations of Cu(II) in outlet polymer solution and sample solution. Feed rate, 0.08 cm$^3$ min$^{-1}$; Fiber length, 2.4 m; Sample, 3 dm$^3$.

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