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Gel-phase Extraction for the Removal of Heavy-metal Ions

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A novel diffusion process of gel-phase extraction for the removal of heavy-metal ions is proposed in this paper. A typical heavy-metal ion, copper ion, is selectively transported into the gel-phase by its complexation with EDTA or precipitation as hydroxide in the phase. Heavy-metal ions are separated and fixed in the gel-phase as a passive collector without any exterior energy.

The contamination of water is a worldwide problem,[1] and efficient and inexpensive methods for the removal of toxic substances are required especially for developing countries. Effective methods are also necessary for the clean up of polluted soil[2] not only for developing countries but also for developed countries, because the treatment of polluted soil comes at a huge cost at present.

Heavy-metal ions are typically toxic and they are treated by precipitation.[3] There are many treatment processes other than precipitation, but they are more wasteful in cost and energy consumption.

The merit of precipitation is the solidification of the dissolved ions, because the volume of solid is much smaller than that of the wastewater. Solidification is an efficient process and occurs in nature. For example, carbon dioxide is fixed as calcium carbonate over a long period on earth.[4] Liesegang ring is also a solidification phenomenon,[5] where many kinds of ions are diffused into gel and solidified as periodic rings. It needs a long time for formation, but the exterior energy consumption in the diffusion is zero.

Precipitation is a simple method, but it is inefficient especially for low-concentration wastewater, because the water is polluted by the precipitating reagent and the collection of precipitate after the treatment is difficult. We propose a novel gel-phase extraction for the removal of toxic heavy-metal ions. In this process, heavy-metal ions are permeated across an ion-exchange membrane and fixed in a gel phase containing a precipitating reagent or chelating reagent, which is a co-ion of the ion-exchange membrane. The gel phase is a passive collector, and exterior energy is unnecessary. For treatment, the collector is immersed in wastewater or in humidified polluted soil and is drawn up after some period, the gel is separated from the collector, and heavy-metal ions are easily recovered from the gel. The diffusion of the ionic reagent in the gel phase to the wastewater is prevented by the ion-exchange membrane. It is unnecessary to separate the precipitated sediment and precipitating reagent from the solution after treatment.

A transport experiment was carried out with a flow apparatus as described in our previous paper[6] but the cell was composed of two compartments, a source-phase solution compartment and a gel-phase compartment, where only the source-phase solution is circulated. These compartments were divided by a cation-exchange membrane, Selemion CMV (Asahi Glass Co., Ltd.), whose effective membrane area was 20 cm^2. The membrane was pretreated by soaking in acid or base solution alternately, and then in NaCl solution, and was rinsed with pure water to be a sodium-ion membrane. The two compartments were perforated silicone-rubber sheets with a thickness of 10 mm for gel phase and 3 mm for source phase, and the compartments were separated by the sodium-ion membrane. In the source-phase compartment, three sheets of 1.0-mm-thick net spacers for each were placed to press the membrane to the gel. In the gel phase compartment, 20-mL hot sol of 1 wt % agar containing a chelating or precipitating reagent was poured and cooled gelation. These compartments were clamped with acrylic resin frames from the outside.

A 200-mL-source-phase solution was circulated from the reservoirs to the cell with a tubing pump at a rate of 30 mL min^{-1}, and the solution was collected for analysis at definite time intervals. The concentrations of metal ions in the gel phase and membrane phase were also measured after extraction. The gel phase was taken out from the cell, warmed until liquified, and poured into 0.1 M HCl to dissolve the ions in a homogeneous solution. The membrane was immersed into 30 mL of 1 M HCl solution for the ions in the membrane to be desorbed. The concentration of metal ions was measured with an atomic absorption spectrophotometer (Shimadzu Co., AA-6700F).

The extraction carried out at first with the gel phase without precipitating reagents and chelating reagents. The source phase in this experiment was a mixed solution of 10 mM copper chloride and 10 mM potassium chloride. The obvious concentration change in the source phase was observed for the initial 10 h, but the experiment was continued for 7 days. The distribution of metal ion after the experiment was as follows; 82.0% in source phase, 16.9% in membrane, 1.1% in gel phase for copper ion; 92.4% in source phase, 4.0% in membrane, 3.6% in gel phase for potassium ion. Metal ions were transported to the membrane phase and the gel phase, but the concentration of transported ions in the gel phase was low when the gel phase did not contain precipitating or chelating reagents.

Figure 1 shows the concentration change of the source-phase solution during extraction with the gel phase containing the typical chelating reagent EDTA. In the experiment, EDTA-3Na was used to adjust the pH of the gel to be approximately neutral. Copper ion selectively complexes with EDTA in the gel phase and the source-phase concentration changes to 1.8% of the initial concentration. Potassium ion was also transported to the gel phase by ion exchange with the sodium ion in the gel phase but the source-phase-concentration change was stopped at 47% of the initial value achieving equilibrium between the phases. Therefore, heavy-metal ions can be removed by diffusion without any driving force other than the counter diffusion of the ions in the gel phase.

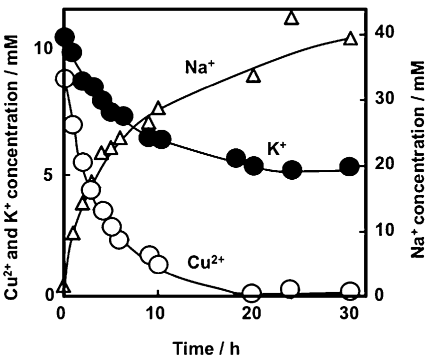

Figure 1. Removal of copper ion to gel phase containing EDTA: source phase, 10 mM $CuCl_2$ and 10 mM KCl; gel phase, agar gel containing 0.2 M EDTA-3Na.

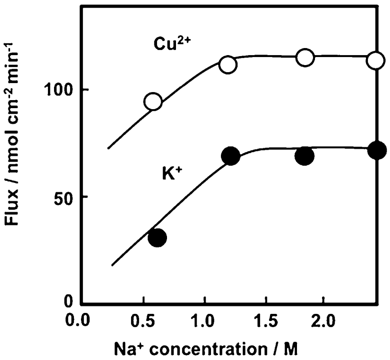

Figure 2. Effect of salt concentration in gel phase on the flux of metal ions: source phase, 10 mM $CuCl_2$ and 10 mM KCl; gel phase, agar gel containing 0.2 M EDTA-3Na and NaCl; x axis, total concentration of sodium ion in gel phase.

The transport rate was affected by some experimental conditions, and it increased with the concentration of sodium chloride added in the gel phase, although it became constant in a high-sodium-ion concentration of over 1 M as shown in Figure 2. The increase of the flux is caused by the increase of the ion-exchange rate, which is effective for the reduction of the treating time. The increase of EDTA-3Na concentration causes not only the reduction of the treatment time for the increase of sodium-ion concentration but also increased capacity for the increasing upper limit of the complex in the gel phase. The transport rate was also affected by the circulating rate of the source-phase solution and the fluxes of ions increased linearly with the circulating rate. The extrapolated value for the circulating rate of zero was about 20% of the normal experimental conditions of this paper, 30 mL min^{-1}, which means that about five-times treatment time will be required without stirring the wastewater.

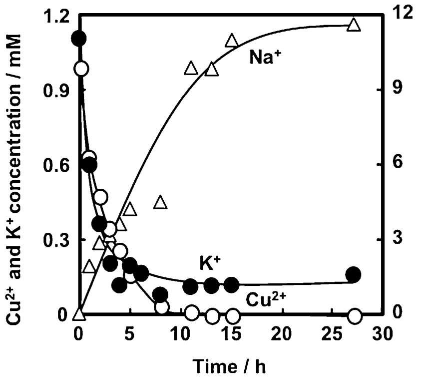

Figure 3. Removal of copper ion to gel phase containing sodium carbonate: source phase, 1 mM $CuCl_2$ and 1 mM KCl; gel phase, agar gel containing 10 mM Na_2CO_3 and 1 M $NaNO_3$.

Precipitating reagents, such as sodium hydroxide or sodium carbonate, were also attempted in this system. Sodium hydroxide is a strong base, which alters the agar, and therefore, sodium carbonate was used as the precipitating reagent. The copper ion in the source-phase solution was also effectively removed, but most of the copper was precipitated not in the gel phase but in the membrane. Copper ion diffuses in the membrane and precipitates as copper hydroxide or copper carbonate at the gel-phase interface of the membrane, and the precipitate clogs the membrane. The addition of salt increased the transport rate as shown in Figure 2, and sodium salt was added in the gel phase. The results are shown in Figure 3, the copper ion is efficiently removed in the source phase, and there was no precipitation in the membrane. The copper in the source phase was decreased to 0.1% of the initial concentration, 78.9% of copper was transported to the gel phase, and the rest was in the membrane. Precipitation in the membrane was prevented by the added sodium salt, and effective sedimentation occurs in the gel phase. The critical concentrations of dissolved copper(II) ion are calculated with the solubility product[7] of copper hydroxide or copper carbonate to be $10^{-14.0}$ or $10^{-7.9}$ M, respectively, for 10 mM aqueous Na_2CO_3 solution. Therefore, the copper ion transported in the gel phase may be fixed as copper hydroxide.

The results shown in this paper are useful for the removal of a typical heavy-metal ion, copper ion, and this novel and simple method can be used for the treatment of wastewater or soil containing any toxic ions with an appropriate selection of precipitating or chelating reagents.

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