

Removal of Trace Metals from Aqueous Solution by $\text{Fe}(\text{OH})_3$ Coprecipitation and Flotation Using Poly-Glutamic Acid

Le Thi Xuan Thuy¹, Le Phuoc Cuong^{1*} and Tomoki Yabutani²

¹Faculty of Environment, Danang University of Science and Technology, 54 Nguyen Luong Bang st., Lien Chieu, Danang, Vietnam.

²Department of Life System, Institute of Technology and Science, The University of Tokushima, 2-1 Minamijosanjima, Tokushima, 7708506, Japan.

Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Iron hydroxide ($\text{Fe}(\text{OH})_3$) coprecipitation and an eco-friendly flotation technique by use of gamma poly-glutamic acid (γ -PGA) was developed for removal of heavy metals from water. Effects of PGA concentration and the flotating time on the flotation of $\text{Fe}(\text{OH})_3$ precipitate and removal efficiencies of metal ions was examined. The removal efficiency of heavy metals was estimated from measurements by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The optimal conditions provided >80 % for Au, Bi, Cd, In, Ga, Mn, Os, Pb, Pt, Te, Sb, Sn, Rh, Ru, W and >60 % for Co, Ni, Se, Zn as the removal efficiency.

Keywords: Coprecipitation; flotation; poly-glutamic acid; trace metals; recovery.

1. INTRODUCTION

The problem of heavy metals pollution in soil and water is a huge concern in public health. To avoid contaminations, a number of technological processes have been developed, such

*Corresponding author: Email: le_p_cuong@mail.ru;

as phytoremediation, electroremediation, adsorption, precipitation, and solidification of contaminated areas. One of the commonly used methods to remove contaminants is a coprecipitation technique [1,2]. Many hydroxides have been used as coprecipitants. Hydroxides are formed by Al [3], Ga [4] rare earth elements (REEs) and so on [5,6]. Since Fe has low toxicity and high abundance in the earth's crust and its hydroxides ($\text{Fe}(\text{OH})_3$) has a quite low solubility, it shows good potential as coprecipitating reagent. Coprecipitation technique has some advantages such as quick, large-amount sample treatment and simultaneous collection of many kinds of metals. However, collection of precipitants with filtration or decantation are commonly time consuming process.

We are interested in flotation technique. Comparing with the filtration technique, flotation method can separate the pollutants from the solution easily and quickly. In particular, it has advantageous for separation and concentration of trace substances in the sample solution. Generally, surfactants as flotating reagent are added into aqueous samples with precipitates or adsorbents. We can suggest that the flotating reagents has to be low and eco-friendly reagents. Thus, utilization of biodegradable biopolymer flocculants as poly-glutamic acid (PGA) has been investigated. PGA is a non-animal origin biodegradable poly-amino acid, which is known as a sticky paste formed on the surface of fermented soybeans, "Natto". Since PGA is a low-cost, non-toxic, water-retentive material, it has a large potential as a material in various fields, such as cosmetics, food, plastics and a flocculant for water treatment. In a previous paper, Yokoi et al. reported that γ -PGA may be applicable to solid-liquid separation and purification of wastewater containing inorganic compounds such as $\text{Fe}(\text{OH})_3$ [7], $\text{Mg}(\text{OH})_2$ [8,9].

In this work, simultaneous removal of metals from aqueous solution containing Au, Bi, Co, Cd, In, Ga, Mn, Ni, Os, Pb, Pt, Te, Sb, Se, Sn, Rh, Ru, Zn, W using combining the coprecipitate by $\text{Fe}(\text{OH})_3$ colloids and flotation by poly-glutamic acid (PGA) was investigated.

2. EXPERIMENTALS

2.1 Reagents and Solutions

The standard solutions for the calibration curves used in the ICP-AES and ICP-MS measurements, and evaluation of the adsorption of trace metal ions were prepared in 4 separate groups by mixing the single element standard stock solutions ($1000 \mu\text{g}\cdot\text{g}^{-1}$) for atomic absorption spectrometry, purchased from Wako Pure Chemicals (Osaka, Japan) and Kanto chemicals (Tokyo, Japan). The compositions of the elements in each standard solution were chosen, taking into consideration the stabilities of the elements dissolved in $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ solution (or $0.1 \text{ mol L}^{-1} \text{ HCl}$) and the concentration ranges of the analytic elements. A stock solution of Iron (40 mg g^{-1}) was prepared by dissolving 7.952 g of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (Wako Pure Chemicals, Japan) in 50 ml of $0.1 \text{ mol L}^{-1} \text{ HCl}$ solution. Nitric acid, hydrochloric acid and sodium hydroxide were all analytical grade (Kanto Chemical). All chemicals were used without further purification. Poly-glutamic acid was kindly supplied by Nippon Poly Group. PTFE membrane filters (pore size, $0.20, 0.45 \mu\text{m}$) were also purchased from Nihon Millipore Kogyo (Tokyo, Japan). Purified water was prepared by a Milli-Q purification system (Nihon Millipore Kogyo, Tokyo, Japan).

2.2 Preconcentration Work

Evaluation of trace metals adsorption onto $\text{Fe}(\text{OH})_3$ colloids was performed as follows. 0.5 g of Iron(II) ion solution (40 mg g^{-1}) into 19.5 g of aqueous solution containing Au, Bi, Co, Cd,

Cu, In, Ir, Mn, Ni, Pb, Pd, Pt, Te, Sb, Rh, Ru, Zn (0.1 mg g^{-1} each). Then, 3 g of 3 mol L^{-1} NaOH solution was added and stirred at 200 rpm for 30 (or 60, 180) minutes. 1 g of the supernatant solution was removed, filtered by PTFE membrane filters (pore size, $0.20 \mu\text{m}$) and diluted by 0.1 mol L^{-1} HNO_3 solution. The analytes in the final solution were determined by ICP-AES and ICP-MS. In this study, we utilized synthetic solution contaminated with polluted heavy metals.

2.3 Flotation Separation

Flotation process was prepared following Fig. 1. After the sorption stage, put the previous resulting colloidal solution into flotation column (total height of 30 cm and an inside diameter 4 cm). Air was fed into the column through a bubbler tube, located near the bottom of the column, for bubble generation. Stirrer placed at the bottom of the column, for agitating the solution. PGA was added as sorbents of $\text{Fe}(\text{OH})_3$ colloids and as flocculating agents. The precipitate is floated with bubbles and collected in the sampling bottle by using suction pump. The precipitate is dissolved in 1 ml of 60% Nitric acid and 9 ml of water and analyzed by ICP-MS for trace metal ions and ICP-AES for iron ion.

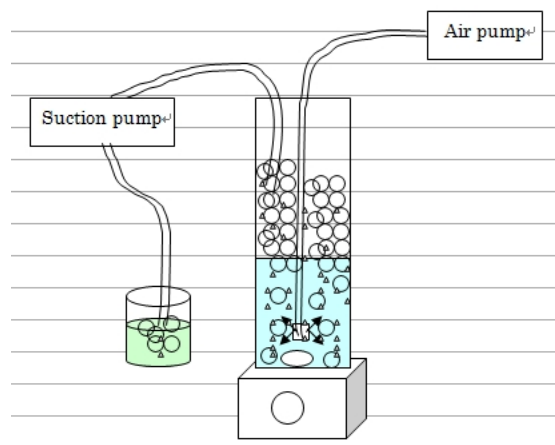


Fig. 1. Scheme of flotation process

Furthermore, the residual solution in the column was collected and analyzed for the concentration of metal ions. The removal efficiency of trace metal was estimated at the end of each experiment by measuring the concentration of residual trace metal ion in residual solution in the column. Effects of several parameters on the separation efficiency of trace metal ions were studied and evaluated using the removal rate ($R\%$) and enrichment ratio ($E\%$) as shown below, where C_i and C_e are the initial and equilibrium concentration of metal ion [$\mu\text{g g}^{-1}$] in the solution, respectively. C_f is the final concentration of metal ion [$\mu\text{g g}^{-1}$] in the collapsed foam.

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$E(\%) = \frac{C_f}{C_i} \times 100 \quad (2)$$

2.4 Instruments

An inductive coupled plasma atomic emission spectrometry (ICP-AES); model SPS 1500 VS (Seiko Instruments) was used for the determination of major and minor elements in the samples. An inductive coupled plasma mass spectrometer (ICP-MS); model ICPM-8500 (Shimadzu) was utilized for the determination of trace and ultra trace elements. For the ICP-MS measurements, internal standard correction was carried out in order to correct matrix effects due to major elements as well as instrumental drift. In addition, we used a pH METER (HM-25G) for the pH measurement.

3. RESULTS AND DISCUSSION

3.1 Removal of Trace Metals by Fe(OH)₃ Coprecipitation

Experimental conditions for coprecipitation, such as reagents (Fe, NaOH) and their quantities, aging time were based on previous work [6]. In this study, the concentration of Fe 1 mg g⁻¹ and 10ml NaOH 3 mol l⁻¹ were used.

The result had shown in Table 1. The recovery of almost all of elements by Fe(OH)₃ coprecipitation method were more than 80%. Most elements showed good repeatability for the recovery, as for the relative standard deviation (RSD) within 5% (not shown). It was thought that almost all of elements were adsorbed quickly by iron hydroxide within 30 minutes.

Table 1. Dependences of the recovery for trace metals on the amount of 3 mol l⁻¹ NaOH in the ferric hydroxide coprecipitation

Element	m/z (a.m.u.)	Recovery		
		30 min	60 min	180 min
Mn	55	99.2	95.5	96.7
Co	59	99.8	99.3	99.4
Ni	62	97.4	95.6	75.7
Cu	64	85.9	66	82.7
Zn	66	88.9	87.1	95.6
Ru	101	100	100	100
Rh	103	99.4	98.4	98.1
Cd	111	99.3	97	97.3
In	115	99.3	99.4	99.4
Sb	121	70	79.1	86.7
Te	125	100	100	100
Pt	195	100	100	100
Au	197	100	100	100
Pb	208	99.6	99.5	99.5
Bi	209	99.8	99.7	99.9

Mean of 3-times replicate measurements

3.2 Flotation Separation

3.2.1 Effect of γ -PGA

We used jar testing to decide the most suitable PGA concentration. Added 0.05, 0.125, 0.25, 0.5 and 2.5g PGA in 50 g water to make the PGA solution with 0.1% wt, 0.25% wt, 0.5% wt, 1% wt, 5% wt respectively and used air-pump to observe the state of the made and the collapsed bubbles. Fig.2 was a picture of what a jar testing apparatus might look like. When the concentration of PGA increased, the quantity of the bubble increased. If the concentration of PGA was higher, the bubble were hardly collapsed after stop air-pump. Therefore, the concentration of PGA was chosen for the further research was more than 0.5 %.

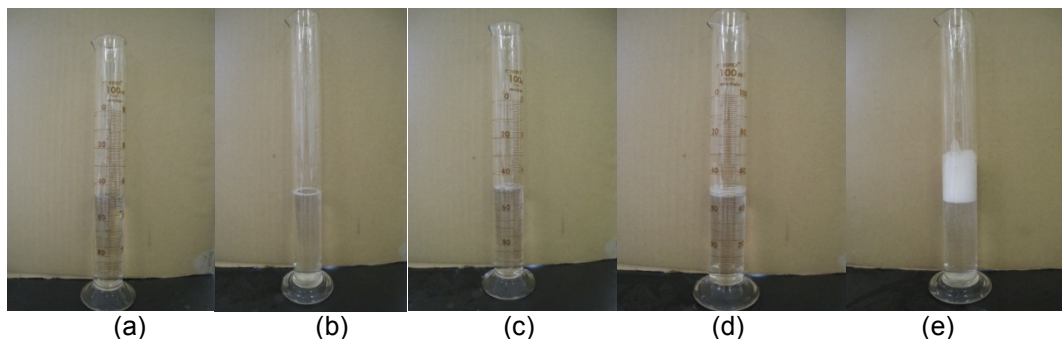


Fig. 2. Effect of PGA amount (a) 0%, (b) 0.1%, (c) 0.25%, (d) 0.5% and (e) 1% in the formation of foam

When the density of PGA increased, the quantity of the air bubbles were increased and the quantity of the carriers ($\text{Fe}(\text{OH})_3$ colloids) which stick to the air bubble were increased. The result from Fig. 3 was thought that when the removal of carriers were increased, the removal of analytes were increased too.

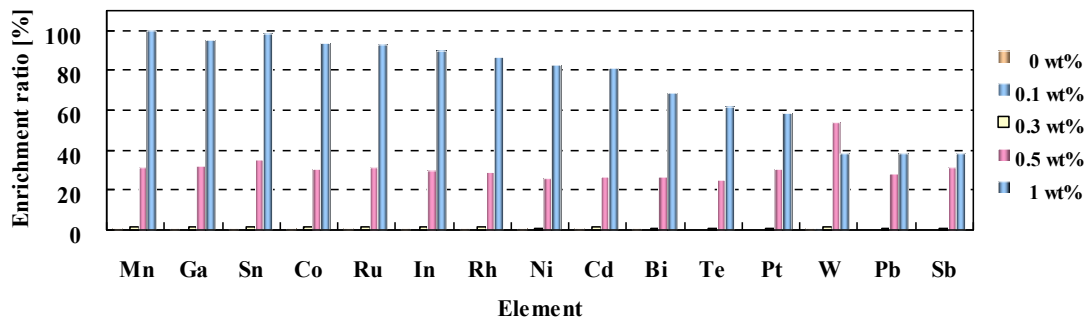


Fig. 3. Effect of the concentration of PGA on the removal of analytes

3.2.2 Effect of pH

When we added NaOH to the solution, the pH was suddenly changed more than 12, so it's difficult to measure the pH of the solution. In addition, it is difficult to coordinate pH with HNO_3 solution because the $\text{Fe}(\text{OH})_3$ particles is easy to dissolve in an acid solvent again.

Therefore almost all of experiments let start with high pH. Furthermore, iron hydroxide is very insoluble and stable in a broad pH range and for this reason it is a suitable coprecipitant. In this study, the pH of the solution came to fall to neutral when an experiment was finished (time when deposition let to surface completely). The reason is thought about as follows. In distilled water, PGA were dissolved and existed in R-COO⁻ and H⁺ form. Carboxyl groups (R-COO⁻) were combined with carriers (Fe(OH)₃ colloids) and metal ions by cross-linking or ionic bond to form a floc and emerge to surface, while the (H⁺) were remained in the solution. As a result, the first alkaline solution was neutralized until near 7. Thus, the initial solution without adjusting pH may be considered. In addition, it was thought that too difficult to conduct the influence of the pH of the solution.

3.2.3 Effect of flotation time

The effect of flotation time was studied. Fig. 4 shows that almost all of analytes were removed after 2 days. At this time, the solution became nearly transparent. Fig. 5 shows that almost all of iron was removed after 2 days so this leads to many metal were got out of the solution.

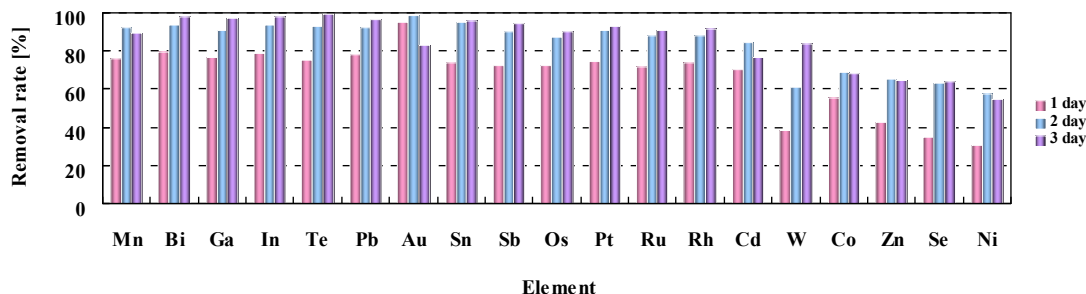


Fig. 4. Effect of flotation time on the separation efficiency of analytes $[Fe]_0 = 1 \text{ mg g}^{-1}$, $[M]_0 = 0.1 \text{ mg g}^{-1}$, $[NaOH] = 0.3 \text{ M}$, $[PGA] = 0.5 \text{ wt\%}$

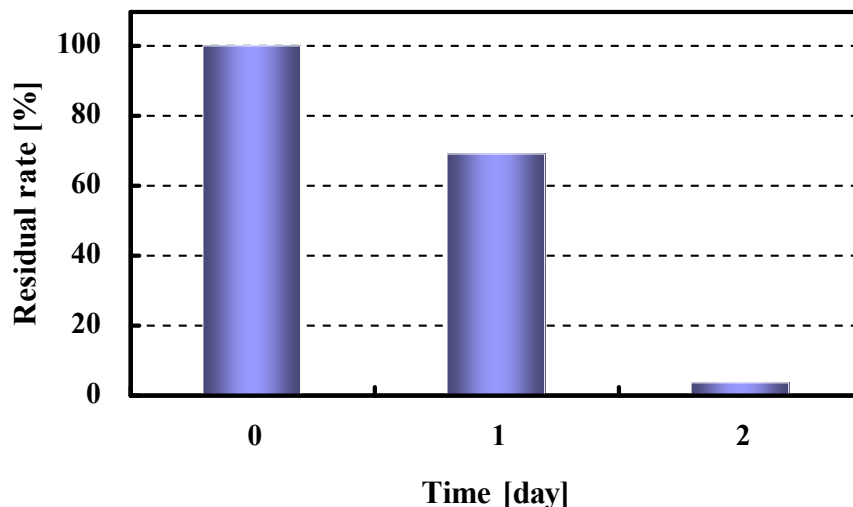


Fig. 5. Effect of flotation time on the removal of Fe ion

4. CONCLUSION

Until now there have been no report using combining the coprecipitate by $\text{Fe}(\text{OH})_3$ colloids and flotation by poly-glutamic acid (PGA) to collect heavy metals. In this study, we succeeded in combination of them to removal several metals from aqueous solution containing Au, Bi, Co, Cd, In, Ga, Mn, Ni, Os, Pb, Pt, Te, Sb, Se, Sn, Rh, Ru, Zn, W. However, more investigations are needed on different types of carriers which lighter than iron hydroxide such as activated carbon. In the future, we will study the characteristics of various types of carriers in waste water treatment technology.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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