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Research Article
Removal and Recovery of Heavy Metals from Industrial Wastewater by Precipitation and Foam Separation Using Lime and Casein

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Abstract

Background and Objective: Even today, a strong need exists for the quick and easy removal and recovery of heavy metals from industrial wastewater at low cost. In this study, recovery of heavy metals from artificial wastewater containing Cr, Cu, Cd, Pb and Mo (each concentration, 10 mg L^{-1}) by precipitation and foam separation using lime and milk casein was investigated. In addition, the performance of foam separation was tested using mining tailing water collected from a mining plant. **Materials and Methods:** Lime was used as an alkaline agent for heavy-metal precipitation. Milk casein functioned as both a collector and a frother for foam separation. After the precipitation process, casein was added to the precipitated wastewater and foam separation was carried out. The removal efficiencies of heavy metals were determined by inductively plasma spectrometry. **Results:** Under the optimum alkaline condition at pH 9, where the pH was adjusted by lime addition and a casein dosage of 15 mg L^{-1}, 96% of Cr, Cu, Cd and Pb were removed from the wastewater and recovered in the foam, however, Mo remained in the water. When the pH of the treated water was re-adjusted at 5.3 and the water was reprocessed by foam separation, 76% of Mo was removed from the treated water. To demonstrate the effectiveness of the proposed precipitation and foam separation method under actual conditions, it was applied to mining tailing water collected from an ore-mining facility in Mongolia. The removal efficiencies of heavy metals such as Mn, Fe and Cu included in the mining tailing water were greater than 85%. Furthermore, more than 90% of the suspended solids were also removed from the tailing water. **Conclusion:** The casein enabled the collection and recovery of the precipitation components of heavy metals within a total processing time of 10 min. Precipitation and foam separation using lime and casein is an effective and adaptable method for treating industrial effluents that contain heavy metals.

Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Increasing population and increasing human activity have led to rapid industrial development, which has in turn led to the serious heavy-metal pollution of water resources in developing countries. Heavy metals are directly or indirectly discharged from industrial areas into the environment and profoundly affect human health; metals are specifically linked to the transmission of diseases such as cancer, cholera, diarrhea and typhoid[1-3]. In fact, industrial facilities use 99.2% of groundwater resources and 99.6% of surface water resources, which represent 12.7 and 87.3% of the whole water resources in Mongolia, respectively[4]. If water pollution continues under the present situation, two out of every three persons in the world may be living under water-stressed conditions as defined by the World Health Organization (WHO)[3] and water shortages will be faced by an estimated 2.7 billion people by 2025 according to the United Nations (UN)[5]. Therefore, a treatment process for the highly efficient removal of hazardous heavy metals from industrial effluents is urgently needed. The recovery of the heavy metals as valuable materials is also desirable.

Although numerous methods for the removal of heavy metals from wastewater have been developed, including methods based on precipitation, membrane filtration, ion exchange, electrochemical recovery, biological separation and adsorption, these approaches still face shortcomings such as long processing times, sludge generation in large quantities, high costs and filtrate blockage[6,7]. In recent years, special attention has been devoted to developing low-cost, efficient and environment friendly methods for the removal and recovery of heavy metals from wastewater[7-11].

As considered in previous studies, the flotation method using bubbles is one of the fastest methods of solid-liquid separation. Moreover, foam separation or foam fractionation, which is generally classified as an adsorptive bubble separation method, has received considerable interest because of its simplicity, rapidity, high efficiency, easy scale-up and cost-effective removal of hazardous components from aqueous solutions[12-20]. In previous studies, researchers focused on coagulation and foam separation as a method for the removal and recovery of heavy metals[12-14]. Specifically, researchers developed a technique that combines coagulation

and foam separation (a solid-liquid separation method for the removal of suspended substances from wastewater and surface water) using iron(III) chloride as a coagulant and milk casein as a surface-active agent. Foam separation has strong potential for removing and concentrating pollutants from water into the generated foam. Because the floc formed with iron(III) hydroxide adheres to the surface of bubble functionalized with casein as a collector, researchers inferred that the hydroxides of heavy metals should also adhere to the bubble surface using casein. Casein has known due to its unique characteristics such as surface-active protein, including a high foaming capacity and eco-friendliness and possesses various metal-ion-binding sites in its molecular structure, including amino groups, phosphate groups and carboxylate groups[21-23]. Therefore, casein, when used as a surface-active substance, can bind hazardous components via electrostatic interaction while also acting as a frother; in addition, the linked particles can be reformed into hydrophobic colloidal particles[14,22].

In this study, the removal and recovery of heavy metals from artificial wastewater using dispersed bubbles and milk casein were investigated with pre-precipitation of heavy metals using alkaline chemicals. In addition, to demonstrate the effectiveness of the proposed precipitation and foam separation method under actual conditions, the method was applied to the mining tailing water collected from a mining operation in Mongolia.

MATERIALS AND METHODS

Artificial wastewater polluted by heavy metals: The Cr, Cu, Cd, Pb and Mo were selected as important heavy metals. The Mo, in particular, is a main Mongolian strategic mineral resource. Each stock solution of heavy-metal with a concentration of 10 g L^{-1} was prepared by dissolving the appropriate weight of molybdenum(V) chloride, copper(II) chloride, cadmium(II) chloride, lead(II) chloride or chromium(III) chloride hexahydrate. All of the reagents used to prepare stock solutions were analytical reagent-grade chemicals produced by Wako Pure Chemical Industries, Japan.

Artificial wastewater containing heavy metals Cu, Mo, Cr, Cd and Pb, each with a concentration of 10 mg L^{-1}, was prepared with moderately hard water (Table 1)[24] immediately before the experiment.

Table 1: Composition of artificial fresh water

Water type	Salts required (mg L^{-1})				Water quality		
	$NaHCO_3$	$CaSO_4 \cdot 2H_2O$	$MgSO_4$	KCl	pH	Hardness (mg L^{-1} $CaCO_3$)	Alkalinity (mg L^{-1} $CaCO_3$)
Moderately hard	96	60	60	4	7.4-7.8	80-100	60-70

Sampling of mining tailing water: Samples of mining tailing water were collected from a tailing processing plant in the mine ore processing facility (Erdenet mining) located near the town of Erdenet in the Orkhon province in Mongolia during the summer of 2017. Erdenet mining is one of the largest ore mining companies in Asia, especially for Cu-Mo ore, the company operates a concentration plant with technological unification of processes that include ore crushing, grinding, flotation, filtration drying and shipping of the Co and Mo concentrates[25]. In the general ore processing, a certain amount of water is recycled for technological processes and residual effluent is compressed to the tailings pond. Treated mining tailing water as the mining tailing water is then collected from the tailing processing plant after flocculation and settling processes. Finally, the treated mining tailing water is discharged to the tailings pond.

Precipitation and sedimentation: To simulate the optimum pH for precipitation and foam separation and the effect of the coagulant as well as to compare the effects of alkaline chemicals such as sodium hydroxide (NaOH) and lime ($Ca(OH)_2$), jar tests were performed as a pre-processing method using a conventional jar tester (MJS-8, Miyamoto, Japan) under different conditions. Artificial wastewater (500 mL) was placed in a 500 mL beaker. The pH was adjusted by addition of 1 M hydrochloric acid (HCl) solution or 1 M NaOH or $Ca(OH)_2$ solution. Jar tests were carried out with and without a ferric coagulant (39% iron(III) chloride, Takasugi Seiyaku, Japan) at 150 rpm mixing for 5 min. After the mixtures were allowed to stand for 15 min, the supernatant water was sampled into a new vial using a pipette and the concentrations of heavy metals were determined.

Precipitation and foam separation: The procedures and conditions for foam separation were the same as those used in authors' previous report[25]. After the precipitation process, a proper amount of milk casein (5, 10, 15 mg L^{-1}) was added to the precipitated wastewater as a surface-active substance. The milk casein was dissolved at a concentration of 1000 mg L^{-1} in 0.01 M NaOH solution. The precipitated wastewater was agitated at a mixing speed of 150 rpm by the jar tester for 1 min to enhance interaction between the heavy metals and the casein. The foam was subsequently separated by transferring the prepared artificial wastewater into a cylindrical column (height, 62 cm, diameter, 4 cm) of the batch flotation equipment illustrated in Fig. 1. Dispersed air was supplied from the bottom of the column via a glass-ball filter (Kinoshita Rika, Japan), the glass balls were 1.5 cm in diameter, with pore sizes ranging from 5-10 μm. Foam generated on the water surface was recovered in a trap bottle by an aspirator. The recovered foam is referred to as "foam water." The processing time for foam separation was 2 or 4 min, the flow rate of the air supply was 0.3 L-air min^{-1}. The treated water was sampled from the drain.
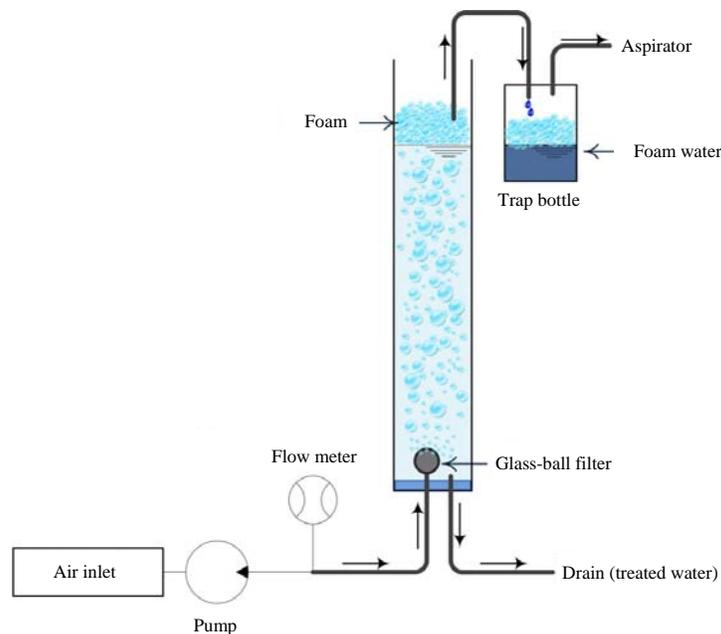

Fig. 1: Foam separation batch equipment system

In the case of foam separation of the mining tailing water, all foam separation procedures were the same as those used for the artificial wastewater except for the addition of heavy metals and coagulant. Each experiment was repeated at least three times and the average values and standard deviations were calculated.

Re-acidification and foam separation for removal of Mo: For the selective recovery of Mo, the pH of the water subjected to precipitation and foam separation under alkaline conditions was adjusted to $5 \leq pH \leq 6$ via the addition of 1 M HCl solution. After acidification, casein was added to the treated water and the resultant mixture was stirred for 1 min. The previously described foam separation process was then repeated.

Analytical methods: The concentrations of all heavy metals in the wastewater and the treated water were determined by inductively coupled plasma spectrometry (ICPS 8100, Shimadzu, Japan). Prior to measurement of the samples, all of the samples were acidified with nitric acid to pH<2 to dissolve any precipitates. For each measurement, calibration curves were constructed for all of the considered elements using a multi element standard solution (multi-element standard solution W-V for ICP, 100 mg L^{-1} Al, B, Cd, Cr, Cu, Fe, Mo, Mn, Na, Ni, Pb and Zn in 1 mol L^{-1} HNO$_3$, Wako Pure Chemical Industries).

The pH, total dissolved solids and electrical conductivity of solutions were measured using a benchtop pH/water quality analyzer (LAQUA, Horiba, Japan). To obtain the removal efficiency of suspended substances, the turbidity of raw water and treated water was measured using a turbidimeter (SEP-PT-706D, Mitsubishi Chemical Analytech, Japan).

RESULTS AND DISCUSSION

Optimum pH for precipitation and estimation for coagulant dosage effect: The pH is one of the essential operating parameters governing the interactions of a surface-active substance and metal ions in the flotation processes because the pH affects the stability and precipitation behavior of heavy-metal ions in the solution. Heavy-metal ions form hydroxide compounds whose composition depends on the pH[26]. Figure 2 shows the removal efficiencies of heavy metals by precipitation with and without the coagulant and with an NaOH or Ca(OH)$_2$ solution used to adjust the pH.

As shown in Fig.2a and b, the removal efficiencies of Cr, Cu, Cd and Pb were approximately 99% over a wide pH range

from 6-11, irrespective of whether NaOH or Ca(OH)$_2$ was used and irrespective of whether the coagulant was used. When the pH was greater than 11, the removal efficiency of Pb decreased because Pb becomes an unstable and negatively charged species such as Pb(OH)$^{3-}$ or Pb(OH)$_4$$^{2-}$, the latter of which is the predominant species under highly alkaline conditions. Calculations using the HYDRA and MEDUSA software[27] indicated that anionic species of Pb^{2+} are stable under alkaline conditions at pH>11. Consequently, precipitation at pH>11 is not feasible for the removal of Pb using NaOH or Ca(OH)$_2$ as a pH modifier. A comparison of the removal efficiencies of heavy metals with and without the coagulant reveals no improvement in the removal efficiencies of Cr, Cu, Cd and Pb upon addition of the coagulant (Fig. 2c, d). The positively charged coagulant could not combine with heavy-metal species that were also positively charged. By contrast, for Mo, the peak corresponding to high removal efficiency was observed at the pH around 5. When Ca(OH)$_2$ solution was used to modify the pH, the removal efficiency of Mo was greater than 80% both with and without the coagulant.

The aforementioned results demonstrate that the optimum precipitation pH for heavy metals other than Mo was in the range from 6-10 and that the pH range for Mo precipitation was around 5, with Ca(OH)$_2$ used as the pH modifier and without the coagulant.

Optimum dosage of casein for precipitation and foam separation: The use of a surface-active substance as both a collector and a frother is the most important factor in the foam separation process. Among surface-active substances, casein exhibits markedly high performance as a collector and a frother. Casein easily adheres to iron(III) hydroxide and aluminum hydroxide flocs and makes the interfaces hydrophobic[12]. Moreover, casein is easy to foam. However, casein cannot function near its isoelectric point between pH 4.6 and 4.9[14]. In addition, the ionic strength of the heavy-metal ions can be increased at pH<5, which can diminish the foam separation efficiency. As such, it can hypothesized that casein would function as a collector and a frother for removing hydroxides of heavy metals under optimum pH conditions of pH >5.

The effect of the casein dosage on the removal of heavy metals from the artificial wastewater by foam separation is shown in Fig. 3. To estimate the optimum dosage, the concentration of the casein from 5 to 10 to 15 mg L^{-1} was increased, the foam separating time was 2 min at pH 5.0 and 9.5, which are the optimum pH levels for precipitating Mo and
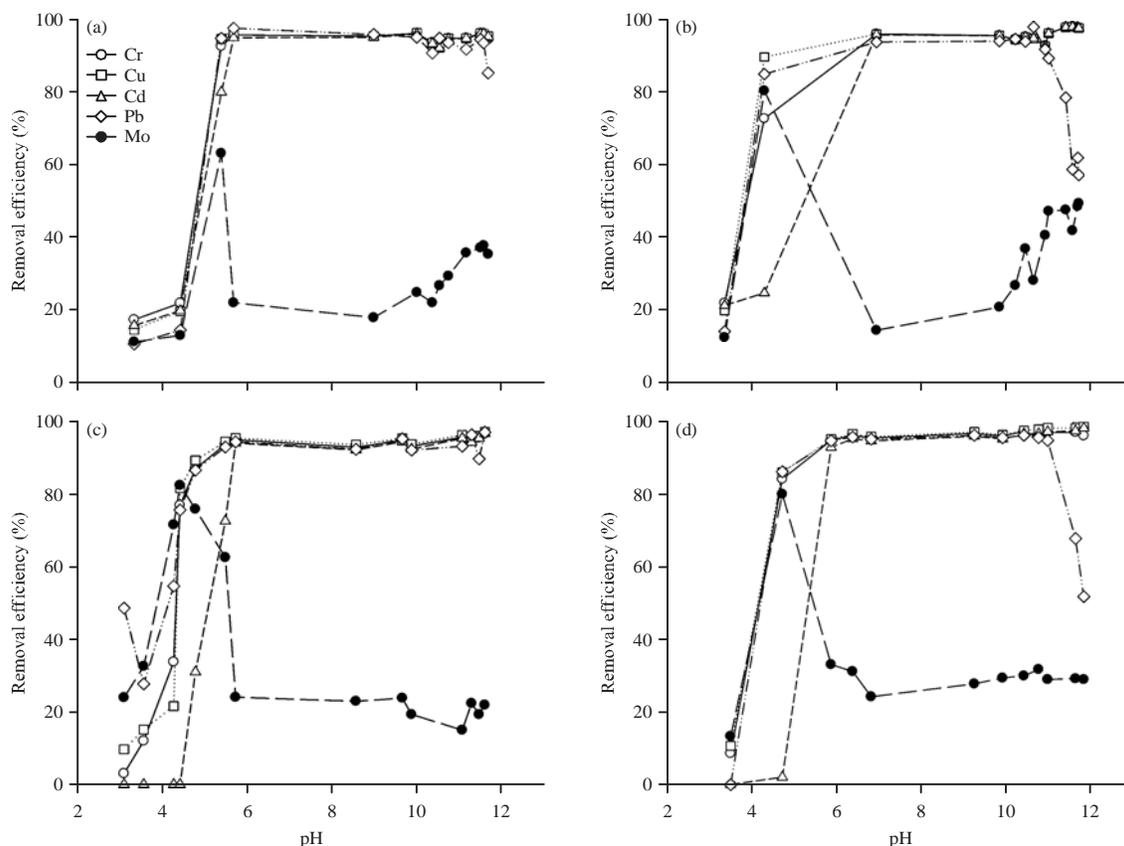
Fig. 2(a-d): Effect of pH modifiers (NaOH and Ca(OH)$_2$) on the removal of heavy metals from artificial wastewater for precipitation with and without coagulation (a) NaOH without coagulation, (b) Ca(OH)$_2$ without coagulation, (c) NaOH with coagulation and (d) Ca(OH)$_2$ with coagulation

The initial concentration of each heavy-metal was 10 mg L^{-1}, the mixing speed was 150 rpm, the mixing time was 5 min and the settling time was 15 min
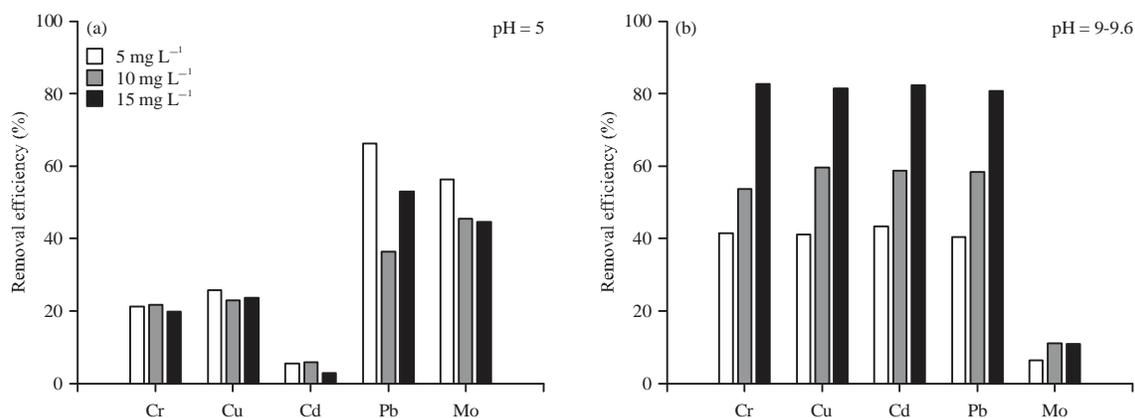

Fig. 3(a-b): Effect of the dosage of the surface-active substance (casein) on the removal of heavy metals from artificial wastewater by foam separation without coagulation at (a) pH = 5 and (b) 9≤pH≤9.6

The initial concentration of each heavy-metal was 10 mg L^{-1}, the mixing time was 5 min and the mixing speed was 150 rpm

the other metals, respectively. The Ca(OH)$_2$ was used to modify the pH. The removal efficiency of Pb and Mo were 50-60% at each casein dosage condition at pH 5.0. By contrast, the removal efficiencies of other metals such as Cr, Cu and Cd were less than 30%. As with the precipitation and sedimentation process, precipitation and foam separation to
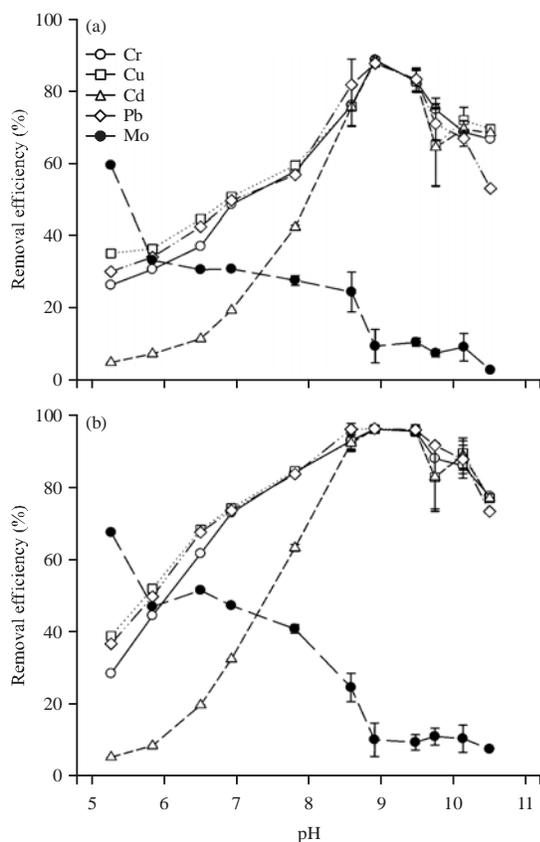
Fig. 4(a-b): Effect of optimum pH and processing time on the removal of heavy metals from artificial wastewater by precipitation and foam separation without coagulation: (a) 2 min and (b) 4 min

The initial concentration of heavy metals was 10 mg L^{-1}, the concentration of surface-active substance was 15 mg L^{-1}, the mixing time was 5 min and the mixing speed was 150 rpm. The error bars indicate the standard deviation obtained from three replicate measurements

remove Cr, Cu and Cd from the wastewater was difficult under acidic conditions. When the pH was adjusted to 9.5, the removal efficiencies of Cr, Cu, Cd and Pb increased remarkably. At the lowest investigated concentration of casein (5 mg L^{-1}), the removal efficiency of heavy metals was less than 50%. In this case, insufficient casein was available to bind the hydroxide colloids of heavy metals and generate foam. When the casein concentration was increased to 15 mg L^{-1}, the removal efficiencies of Cr, Cu, Cd and Pb were greater than 80%. The same experiment was conducted at pH 5.0 for the removal of Mo. Under these conditions, the removal efficiency of Mo was less than 20%. Thus, the pH conditions necessary for efficient precipitation and foam separation clearly differed between Mo and the other heavy metals.

Optimum pH for precipitation and foam separation and the effect of foam processing time: To estimate the effect of pH over a wide range and the effect of foam processing time, the pH was varied in the range from 5.2-10.5 by adding Ca(OH)$_2$ solution and the processing time was set to 2 and 4 min. The dosage of casein was fixed at 15 mg L^{-1}. As shown in Fig. 4a, the removal efficiencies of Cr, Cu, Cd and Pb with a processing time of 2 min gradually increased as the pH was increased from 6-9. The removal efficiencies of Cr, Cu, Cd and Pb reached 88% near pH 9. In the case of Mo, the removal efficiency was approximately 60% at pH 5.2, however, the Mo removal efficiency decreased with increasing pH.

When the foam processing time was extended to 4 min (Fig. 4b), the removal efficiencies of all of the heavy metals increased compared with those achieved at a processing time of 2 min. With a processing time of 4 min, the removal efficiencies of Cr, Cu, Cd and Pb were greater than 96% at pH 9 and the Mo removal efficiency increased to 67% at pH 5.2.

According to the solubility diagrams of the heavy metals[28], positively charged hydroxides dominate at the lower-pH conditions and negatively charged hydroxides dominate at higher-pH conditions. Because the heavy metals effectively removed at pH 9 exist as negatively charged species at pH >10, the negatively charged casein could not effectively bind these components.

Although the heavy metals were sufficiently removed at pH 9, Mo remained in the treated water. The low removal efficiency of Mo is explained on the basis of the species distribution diagram of molybdenum ions in an aqueous environment[27]. The Mo forms negatively charged species such as molybdate ions (MoO$_4^{2-}$) in aqueous environments with pH>6. Furthermore, according to the Pourbaix diagram of the Mo–O–H system in the inter-comparison thermodynamics databases[29], the pH increases with the formation of OH$^-$, which promotes the production of negatively charged species such as MoO$_4^{2-}$ in aqueous solutions. Thus, the negatively charged Mo components cannot interact with the negatively charged casein under alkaline conditions.

Selective removal of Mo by foam separation after acidification: The optimum pH conditions for precipitation and foam separation were distinctly different for Mo and the other heavy metals. Therefore, after removal of the heavy metals under alkaline conditions at pH 9, the treated water containing Mo was acidified by the addition of 1 M HCl and the foam separation process was repeated to selectively remove Mo.

Table 2: Characteristics of mining tailing water

Parameters	pH	Turbidity (TU)	TDS (mg L^{-1})	EC (µS/cm)	Metal concentration (mg L^{-1})									
					Al	Mn	Fe	Ni	Zn	Cr	Cu	Mo	Cd	Pb
Raw water	7.6	23.0	1072	2070	1.14	0.07	5.55	0.19	0.15	0.05	5.90	1.18	0.02	0.35

TU: Turbidity unit as kaolin standard, TDS: Total dissolved solids, EC: Electrical conductivity, Each data was the mean of 3 replicates
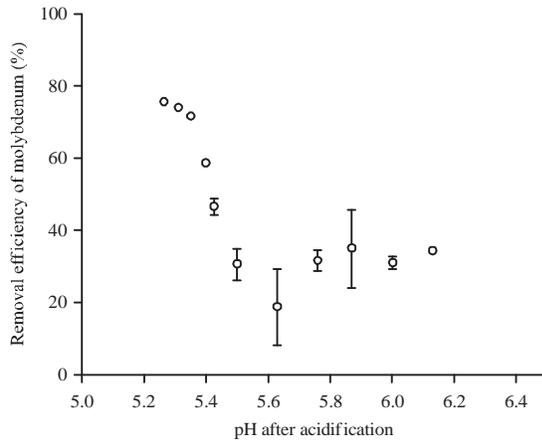

Fig. 5: Selective removal of Mo from artificial wastewater by foam separation after acidification using HCl. The concentration of surface-active substance was 15 mg L^{-1}, the mixing time was 5 min and the mixing speed was 150 rpm

The error bars indicate the standard deviation obtained from 3 replicate measurements
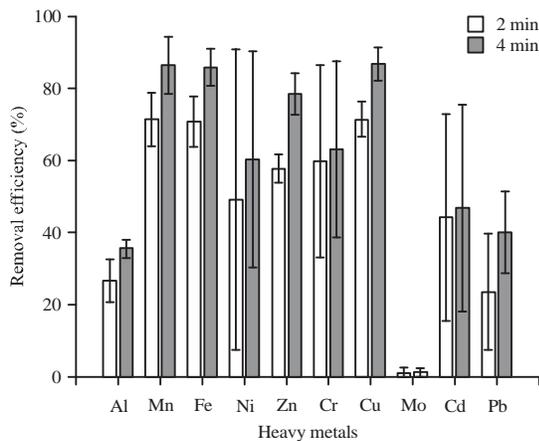

Fig. 6: Removal of heavy metals (Al, Mn, Fe, Ni, Zn, Cr, Cu, Mo, Cd and Pb) from mining tailing water by precipitation and foam separation. The processing time was (a) 2 min and (b) 4 min, the concentration of surface-active substance was 20 mg L^{-1}, the mixing time was 5 min and the mixing speed was 150 rpm

The error bars indicate the standard deviation obtained from three replicate measurements

The efficiency of Mo removal from the treated water under alkaline conditions by foam separation after acidification in the pH range from 5-6 as shown in Fig. 5. The foam generation ceased within 2 min and the cerulean colloids were collected in the foam water. The removal efficiency of Mo increased with decreasing pH and was greater than 76% at 5.2$\leq$pH$\leq$5.3. Mo was also removed as a colloid. With the use of two precipitation and foam separation processing steps-one under alkaline conditions and the other under acidic conditions, Mo and the other heavy metals were removed from the artificial wastewater and recovered in the foam water.

Precipitation and foam separation for the mining tailing water: Water-quality parameters such as pH, turbidity, total dissolved solids, electrical conductivity and initial concentration of metals in the mining tailing water are summarized in Table 2. The Al, Mn, Fe, Ni, Zn, Cr, Cu, Mo, Cd and Pb were detected in the mining tailing water by ICP analysis. The concentrations of Fe and Cu were greater than 5 mg L^{-1} and those of Al and Mo were greater than 1 mg L^{-1}. Because the mining tailing water used for this study had already been treated by flocculation in the treatment plant, the metal concentration was low, similar to that in the mining tailing water used in a previous report[30].

The removal efficiency of heavy metals (Al, Mn, Fe, Ni, Zn, Cr, Cu, Mo, Cd and Pb) from mining tailing water by foam separation is shown in Fig. 6. The foam processing time was set for 2 and 4 min under the following optimum conditions: pH 9; precipitation mixing time, 5 min; agitation speed, 150 rpm; pH modifier, Ca(OH)$_2$ and casein concentration, 20 mg L^{-1}. Removal efficiencies greater than 85% were attained for Mn, Fe and Cu. The removal efficiencies of Al, Ni, Zn, Cr, Cd and Pb ranged from 50-80%. By contrast, the Mo removal rate was extremely low. Notably, for precipitation and foam separation, the suspended solids contained in the mining tailing water were removed together with the heavy metals. The removal efficiency of suspended solids, as determined from turbidity measurements, was greater than 90%. The removal mechanism is the same as the coagulation and foam separation mechanism when a ferric coagulant and

casein are used[12]. Researchers assumed that heavy metals such as Mn, Fe and Cu would function as coagulants. In addition, researchers attempted to remove Mo from the treated tailing water by foam separation after acidification. However, the removal efficiency of Mo was less than 10%. Thus, removal of Mo at a very low concentration (1.2 mg L^{-1}) was difficult. The heavy metals that form positively charged species as hydroxides near pH 9 were removed by precipitation and foam separation. However, the concentration of each metal in the raw water affected their removal efficiency, removing metals present at the low concentrations specified in water quality standards such as those of the WHO is difficult.

CONCLUSION

Under the optimum alkaline condition (pH 9) and with $Ca(OH)_2$ used to adjust the pH and casein added at a dosage of 15 mg L^{-1}, 96% of Cr, Cu, Cd and Pb were removed from the artificial wastewater and recovered in the foam, only Mo remained in the water. The optimum pH condition for precipitation and foam separation was different for Mo than for the other heavy metals. Therefore, after the heavy metals were removed under alkaline conditions at pH 9, the treated water containing Mo was acidified and retreated by foam separation to selectively remove the Mo. When the pH of the treated water was readjusted at 5.3 and reprocessed by foam separation, 76% of the Mo was removed from the treated water. By using two processing steps under alkaline and acidic conditions for the precipitation and foam separation, Mo and the other heavy metals were removed from the artificial wastewater and recovered in the foam water.

To demonstrate the effectiveness of the precipitation and foam separation method under actual conditions, authors applied it to mining tailing water collected from a mining operation in Mongolia. Very high removal efficiencies (greater than 85%) were achieved for Mn, Fe and Cu. Furthermore, the suspended solids contained in the mining tailing water were removed together with the heavy metals. On the basis of turbidity measurements, the removal efficiency of suspended solids was determined to be greater than 90%. The casein enabled the efficient collection and recovery of heavy metals by precipitation. Precipitation and foam separation using $Ca(OH)_2$ and casein is an effective and adaptable method for treating heavy metal containing industrial effluents within a total processing time of 10 min.

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