CELLULOSE CHEMISTRY AND TECHNOLOGY

STUDY ON THE ADSORPTION AND SELECTIVE SEPARATION OF INDIUM FROM ZINC WITH CHELATING CELLULOSE

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For selective preconcentration and separation of indium, functionalized cellulose with iminodiacetic acid (Chelest Fiber IRY-HW) was examined. The chelating cellulose as well as its indium complex was characterized by elemental analysis and IR-spectroscopy. The surface concentration of the functionalized ligand was determined to be 2.0 mmol g^{-1}. The Langmuir adsorption capacity of the adsorbent for indium was found to be 1.5 mmol g^{-1}. The applicability of IRY-HW for the selective separation of indium from metallic zinc and zinc sulfate compound was investigated. The maximum adsorption of indium was observed in the pH range 1.6-8.0 and the retained indium was eluted with 20 mL of 1mol/L HNO_3. The effect of interferences on the sorption of indium ion was also studied. A preconcentration factor of 100 can be achieved by passing 2000 mL of sample through a column and using 20 mL of elution volume. The method can be successfully applied to the determination of indium in metallic zinc and zinc sulfate samples.

Keywords:indium,zinc, chelating cellulose, solid-phase extraction

INTRODUCTION

Indium is obtained mainly from residues generated during zinc ore processing. It is also extracted from iron, lead and copper ores. Compounds of indium are used in the semiconductor industry for germanium transistors, thermistors, rectifiers and photocells. Indium-tin oxide thin films are used for liquid crystal displays. Due to the strategic importance of indium, the study of methods of separation and enrichment of this element is of great value. Solvent extraction, co-precipitation or solid-phase extraction have been proposed for the enrichment and separation of trace indium from several materials such asores, metallic zinc and environmental samples.

Many kinds of adsorbents, including amino silica gel[1] modified with gallic acid, nanometer-size titanium dioxide,[2] Amberlite XAD resin[3-5] loaded with chelating reagent, chitosan,[6] ion exchange resin,[7,8] polyurethane foam[9] and others,[10-14] have been used in the solid-phase extraction of indium from different samples. However, the solid-phase extraction for separation and enrichment of trace indium with an adsorbent using regenerated cellulose as base material is still rare. Cellulose is a natural polymer and an environmentally friendly bio-based material. It is present in large quantities in nature and is available at low cost. Cellulose is used often as a support material for adsorbents of trace metals in aqueous samples due to its stability, hydrophilicity and insolubility in water and organic solvents. It is possible to produce a material with a higher adsorption capacity by chemical modification of the cellulose surface with an appropriate organic ligand. So far, a variety of cellulose based adsorbents have been used for separation and concentration of trace heavy metals in aqueous solutions. In our previous studies, cellulose-based sorbents containing iminodiacetic acid,[15-17] EDTA,[18,19] thioglycollic acid[20] and N-methyl glycin[21] have been reported for trace metal preconcentration. Chelest Fiber IRY (abbreviated as IRY) is a product synthesized by reaction of iminodiacetic acid with crosslinked regenerated cellulose. It can form stable chelate compounds with many metal ions, such as Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} etc. Our works indicated that the IRY, which is commercially available from Chelest Corporation, has excellent characteristics enabling the separation and concentration of trace metals. Recently, new Chelest Fiber IRY-HW (abbreviated as IRY-HW) has been developed by Chelest Corporation as an improved form of IRY. The chemical structure of IRY-HW is the same as that of IRY, but the ratio of iminodiacetic acid in IRY-HW is higher than that in IRY. The purposes of the present work are to investigate the adsorption properties of IRY-HW for indium, and the selective separation of trace indium from a large amount of zinc using the IRY-HW. The various parameters for quantitative recoveries of indium have been studied. The present solid phase extraction method was applied to determine indium in metallic zinc and zinc sulfate samples.

EXPERIMENTAL

Apparatus

A Hitachi model A-2000 atomic absorption spectrometer (AAS) with a deuterium background correction was used to determine metal concentration using an air/acetylene flame. The AAS determinations were performed under the recommended conditions for each metal. The IR spectra were recorded over the range 4000-400 cm^{-1} with a FT/IR-4200 spectrophotometer (JASCO, Japan), using KBr disks. A pH meter D-51 Model (HORIBA, Japan) with a glass electrode was employed for measuring the pH values of the solutions. A micro-tube pump EYELA MP-1000 (Tokyo RIKAKIKAI CO. LTD.) equipped with a silicon tube (2.5 mm i.d.) was used for column experiments. Elemental analyses of adsorbents were performed on a LECO model TRuSpecCHN elemental analyser.

Reagents

All chemicals were of analytical reagent grade, and all solutions were prepared with deionized water obtained from Elix®Essential 3 UV (Millipore).

The working standard solutions of indium were prepared by appropriate stepwise dilution of the stock standard solution of 1000 mg/L (Wako Pure Chem., Japan).Ammonium acetate buffers (1mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 3-6.5. The pH below 3.0 was maintained by dil. HNO_3, whilst pH above 6.5 was maintained by dil. NH_3 solution. The adsorbent Chelest Fiber IRY-HW was obtained from Chelest Inc., Japan.

Preparation of the column

A polypropylene column(15 mm x 78 mm) packed with 1.0g of IRY-HW was used as the operation column. Both ends of the adsorbent in the column were suppressed with a polyethylene disk filter to prevent loss of the IRY-HW during sample loading. The height of the column section containing the adsorbent was 20 mm. The column was conditioned with 15 mL of pH 3.5 buffer solution used for the sample prior to percolation.

Column experiment

A 50 mL of sample solution containing 0.30mg of indium was buffered with 10 mL of ammonium acetate solution of pH 3.5. The buffered sample solution was passed through the column at a flow rate of 10 ml/min by a micro-tube pump. After washing the column with deionized water, the indium retained on the sorbent was eluted with a 20 mL of 1 mol/L HNO_3 at a flow rate of 3.0 mL/min. The eluted indium was collected in a 50-mL calibrated flask and the concentration was determined by flame atomic absorption spectrometry.

Batch experiment

The pH of a model solution containing 0.30 mg of indium in 50 mL was adjusted to 3.5 by adding 10 mL of buffer solution. Then 0.20 g of IRY-HW was added to the solution and the mixture was stirred for 90 min with a magnetic stirrer. After filtration with a 0.45μm micro filter, indium in the filtrate was determined. The amount of indium adsorbed on the adsorbent was determined from the difference between the initial and equilibrium concentrations. The pH of the solution was measured after the equilibration. The batch method was used to study the parameters including pH, adsorbent dosage, and sorption kinetics. The sorption capacity and cation influences were also examined by the batch method.

RESULTS AND DISCUSSION

Characterization of adsorbent

Figure 1 shows the FTIR spectra of IRY-HW and IRY-HW-In. In the spectra of IRY-HW and IRY-HW-In, the strong asymmetric absorption bands around 3400 cm^{-1} are related to hydroxyl groups, and the bands around 2900 cm^{-1} are attributable to the C-H stretching from $–CH_2$ groups. The peaks at 1727 cm^{-1} in IRY-HW and 1721 cm^{-1} in IRY-HW-In are assigned to C=O stretching. Symmetric and asymmetric stretching of $OCO^-$is observed at 1390 and 1621 cm^{-1}, respectively.

These results indicate that hydrogen atoms in the –COOH groups are substituted by indium.

The content of C, H and N in IRY-HW and IRY are shown in Table 1. The elemental analysis result of IRY-HW suggests that the quantity of iminodiacetic acid contained in the sorbent was about 2.0 mmol/g, and this value corresponds to two times that of IRY.

Effect of pH

In the solid-phase extraction studies, the pH of the aqueous solution is an important factor for quantitative recovery of the analytes. The influence of pH on the retention of indium and zinc on IRY-HW was investigated in a pH range 2-10 with model solutions containing 0.30 mg of indium and 0.10 mg of zinc keeping the other parameters constant. Indium was quantitatively extracted at a pH above 3.0, while the curve of zinc was shifted to less acid solutions, as shown in Figure 2. To avoid hydrolysis at higher pH values, a pH of about 3.5 was chosen as the optimum pH value for the extraction of indium. The separation of indium from the zinc with this adsorbent is possible by controlling the pH value. In the extraction of trace indium from a large amount of zinc, the pH of the solution was adjusted to about 2.0.

Effect of stirring time on indium extraction by IRY-HW

The effect of stirring time on the extraction of indium was studied in the range of 5-90 min. The result indicates that the extraction equilibrium was attained after 5 min of stirring for 0.30 mg indium and 0.20 g IRY-HW in 200 mL sample volume. The equilibration period of 90 min was selected for all further batch experiments.

Effect of adsorbent amount

The amount of adsorbent is also an important parameter for obtaining quantitative recovery. The quantitative adsorption of 0.30mg indium from 56 mL aqueous solution under the optimal experimental conditions was obtained with more than 0.05 g of adsorbent. Subsequent batch operations were carried out with 0.30 g of the adsorbent.

Effect of foreign ions

The effect of various cations on the adsorption of indium onto the adsorbent was studied using a 64 mL sample solution containing 0.30 mg indium by the batch experiment.

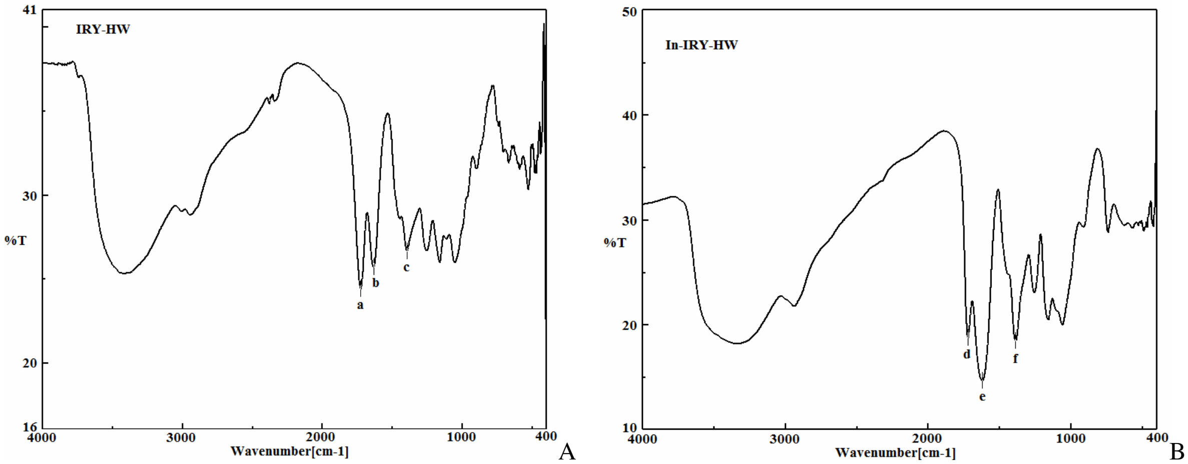

Figure 1: (A) IR spectrum of IRY-HW; a: 1726.94 cm^{-1} (νCO); b: 1633.41 cm^{-1} (νasCO_2^-); c: 1396.21 cm^{-1} (νsCO_2^-); (B)IR spectrum of In-IRY-HW; d: 1721.16 cm^{-1} (νn CO); e: 1621.84 cm^{-1} (νasCO_2^-); f: 1390.42 cm^{-1} (νsCO_2^-)

Table 1
Elemental analysis of IRY-HW and regenerated cellulose fiber

IRY-HW	C (%)	H (%)	N (%)	Loss on drying (%)
Without drying	30.1	7.86	1.78	-
Dried at 60 °C	48.2	6.43	2.83	38.9
Dried at 105 °C	51.1	6.27	3.01	42.3
Regenerated cellulose (dried at 60 °C)	40.5	6.64	<0.1	-

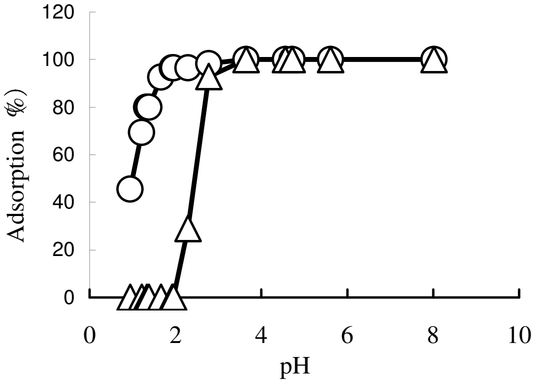

Figure 2: Effect of pH on the extraction of indium and zinc; ○: In(0.30 mg); △: Zn (0.10 mg); stirring time: 90 min; adsorbent: 0.20 g, sample volume: 60 mL

The foreign ions were individually added to a solution containing a fixed amount of indium.

The adsorption rates of 0.30 mg indium on 0.20g of IRY-HW were more than 96%, indicating that the foreign ions shown in Table 2 do not affect the indium adsorption under the applied experimental conditions.

Table 2
Effect of foreign ions (indium:0.30 mg, sample volume:65 mL, stirring time: 90 min, pH=2~3)

Metal ions	Added, mg	Amount of IRY-HW, g	Adsorption of In, %
Na	3.0	0.10	100
		0.20	100
Mg	3.0	0.10	100
		0.20	100
Al	3.0	0.10	93.9
		0.20	99.4
Ca	3.0	0.10	100
		0.20	100
Fe(III)	3.0	0.10	81.0
		0.20	98.7
Co(II)	3.0	0.10	97.5
		0.20	100
Ni	3.0	0.10	99.6
		0.20	99.6
Cu	3.0	0.10	26.7
		0.20	96.6
Zn	3.0	0.10	99.8
		0.20	99.6
Cd	3.0	0.10	100
		0.20	100
Pb	3.0	0.10	99.6
		0.20	100

Flow rate of sample

The effect of flow rate on the adsorption of indium was studied by the column method. The flow rate was varied in the range of 3.0-20 mL/min. The retention of indium was found to be quantitative at all points in the range. Subsequent column operations were carried out at a flow rate of 10 mL/min. On the other hand, the adsorbed indium was eluted from the column with 20 mL of 1mol/L HNO_3 at a flow rate of 3.0 mL/min.

Enrichment factor

The influence of sample volume on the recovery of indium was also examined by increasing the volume of metal ion solution while keeping the amount of indium constant at 0.30 mg in the column mode procedure. The recovery of indium with 1.0 g of adsorbent was not affected by increasing the sample volume up to at least 2000 mL. The retained indium was eluted with 20 mL of 1mo/LHNO_3 with a flow rate of 3.0 mL min^{-1}. The maximum preconcentration factor was 100 for indium final volume of 20 mL.

Adsorption isotherm

The adsorption isotherm is important to describe how solutes interact with the adsorbent. The relationship between the amount of indium adsorbed per unit mass of adsorbent and its final concentration remaining in solution at equilibrium time is presented in Figure 3. The experimental data for the equilibrium adsorption of indium onto IRY-HW were fitted to the Langmuir isotherm based on following the equation:

$$\text{Cads}= \frac{\text{N}\cdot\text{K}\cdot\text{Ce}}{1+\text{K}\cdot\text{Ce}}$$

which can be rearranged to obtain a linearized form:

$$\text{Ce} = \frac{\text{N}\cdot\text{Ce}}{\text{Cads}} - \frac{1}{\text{K}}$$

whereCe is the equilibrium concentration of metal ion (mg/L); Cads is the amount of metal ion adsorbed per unit weight of adsorbent at equilibrium concentration (mg/g); N is the maximum monolayer adsorption capacity (mg/g). A linearized plot of Ce versus Ce/Cads is obtained from the Langmuir equation as shown in Figure 4. The sorption parameters N and K are evaluated from the slope and intercept. The maximum adsorption capacity of indium on IRY-HW was found to be 1.5 mmol/g.

Analytical application

The method was applied for the determination of indium in metallic zinc and zinc sulfate samples.

A 15.00 g piece of metallic zinc (99.99%) was digested with 50 mL of concentrated nitric acid, then the solution was evaporated until near dryness on a steam-bath, cooled and diluted with deionized water to 200 mL in a calibrated flask. 10-mL aliquots were diluted to 50 mL with deionized water and adjusted to pH 2.0 and passed through the column.

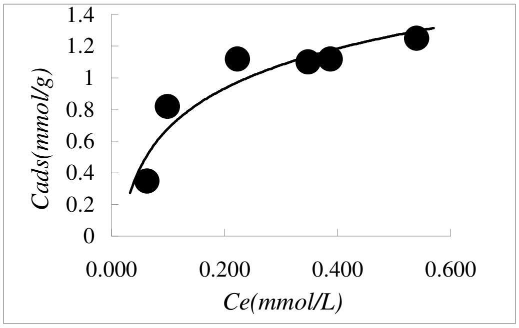

Figure 3: Adsorption isotherm plots for indium; IRY-HW: 0.011 g; stirring time: 90 min; temp.: 22±2 °C; Ce: equilibrium concentration of indium (mmol/L); Cads: amount of indium adsorbed per unit weight of adsorbent (mmol/g), sample volume: 65 mL, pH=4.5±0.5

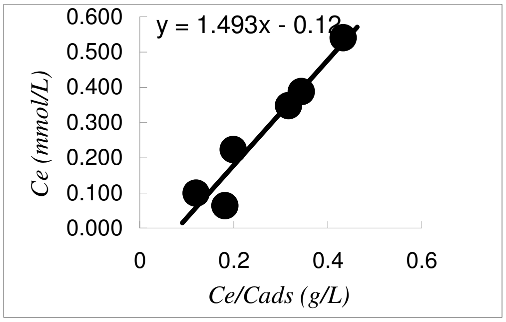

Figure 4: Langmuir plots for indium (the conditions were the same as those described in Figure 3)

Table 3
Recovery of indium in metallic zinc and zinc sulfate samples
(sample volume:65 mL, final volume:50 mL, n=3)

Sample	Sample taken (g)	In added (mg)	In found (mg)	Recovery (%)
Metallic zinc (99.99%)	1.50	0.0	0.0	
	1.50	0.15	0.14±0.00	93.3
$ZnSO_4 \cdot 7H_2O$	5.00	0.0	0.0	
	5.00	0.30	0.28±0.01	93.3
	10.00	0.0	0.0	
	10.00	0.30	0.26±0.002	86.7

Different amounts of $ZnSO_4$ samples (5.0 g and 10.0 g) were weighed and then they were dissolved in 50 mL of deionized water. After adjusting the pH to 2.0, these solutions were used for indium analysis.

The accuracy of the method was verified by the spiked sample solution with a known amount of indium. The results given in Table 3 show that the percentage recovery of indium on standard addition is more than 86% with a standard deviation of 0.0 ~ 3.6%.

CONCLUSION

In the present work, chelating cellulose sorbent (IRY-HW) functionalized with iminodiacetic acid was applied to the separation and determination of indium in zinc samples. Indium can be preconcentrated quantitatively over a wide pH range. The maximum sorption capacity of the adsorbent for indium was found to be 1.5 mmol/g.

The fast adsorption and desorption kinetics of the IRY-HW allowed the quantitative recovery of indium from a sample solution ata high flow rate in the column method.Trace indium was extracted quantitatively at pH of cca. 2.0 without the effect of zinc ion.

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