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Adsorption and Preconcentration of Nickel Ion Using Silica-Dimethylglyoxime Adsorbent

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Separation and preconcentration techniques are of great importance owing to the limited sensitivity and selectivity of modern instrumental methods of trace analysis. Recently, adsorbents obtained by modified of chelating agents on silica gel have gained much attention. Those adsorbents are very useful in the analysis of environmental samples, particularly natural waters. The wide range of preconcentration of metal ions,¹⁻¹⁰ separation of metal ions,^{11,12} solvent clean-up from undesired metal ions and selective extraction of metal ions from different solvent system¹³ have been studied using those adsorbents.

Dimethylglyoxime has been used in gravimetric analysis¹⁴ and in trace analysis for the separation and preconcentration of Nickel(II) ion by extraction and precipitation. This work was devoted to the preparation and examination of the analytical properties of a adsorbent obtained by modifying of dimethylglyoxime on the silica gels. And, we have studied the separation and preconcentration of Ni(II) from the synthetic metal solution using silica-dimethylglyoxime adsorbent.

Experimental

A Shimadzu AA-670 atomic absorption spectrophotometer was used for metal ions determination. An NOVA-310 digital pH-meter was used for pH measurement. Silica gel 60 (70-230 mesh) was a product of Merck Co. The metal ion stock solutions were prepared by dissolving the 1000 ppm AAS standard solutions of Ni(II), Co(II), Zn(II), Fe(II) and Pb(II) obtained from Junsei Chemical Co. The other chemicals were of analytical-reagent grade. The following buffered solutions were prepared: hydrochloric acid-potassium hydrogen phthalate (pH 1-3); acetic acid-sodium acetate (pH 3-6); potassium dihydrogen phosphate-sodium hydroxide (pH 7); and sodium borax-hydrochloric acid (pH 8-9).

Synthesis of adsorbent ; Silica gel was refluxed with 6 M HCl for about 12hr to remove any contaminating metals such as iron. It was then washed with deionized water and dried at 130 °C. The dried silica gel was refluxed with dimethylglyoxime in ethanol (20%) at 70-80 °C for 4hr. The solid thus obtained was filtered and dried under vacuum.

The adsorption of metal ions were performed in the batch and column methods. Excess metal ion (50 mL, 20 µg/mL) was shaken with 0.5 g of adsorbent for 24hr. The pH of solution was adjusted prior to equilibration over a range of 1-8 with buffer solutions. After equilibrium, the solution was filtered through Whatman #2 filter paper. The filtrate was diluted with distilled water and the concentration of metal ions were determined by AAS. In the column method, 10 g of the adsorbent was placed into a column (20 mm in inner diameter) and washed with 100 mL volume of water. The sample was passed through the column at a rate of $0.5 \pm 0.1 \text{ mL min}^{-1}$. The adsorbed metal ions were desorbed with a suitable eluent.

Result and Discussion

pH effects on metal ion adsorption. The chemical stability of the adsorbent was evaluated by measuring the change of adsorption capacity for Ni(II) after a successive contact of silica-dimethylglyoxime adsorbent with an acidic solutions in various concentration range. When this silica-dimethylglyoxime adsorbent was contacted with an acidic solution weaker than 1.0 M HNO₃ or 1.5 M HCl for 24hr, the decomposition was negligibly small and no significant decrease in the adsorption capacity for Ni(II) was observed. From these results, it is believed that this adsorbent has sufficient stability.

The effect of pH on adsorption of Fe(II), Co(II), Zn(II), Ni(II) and Pb(II) in pH 1.0-8.0 was examined by a batch

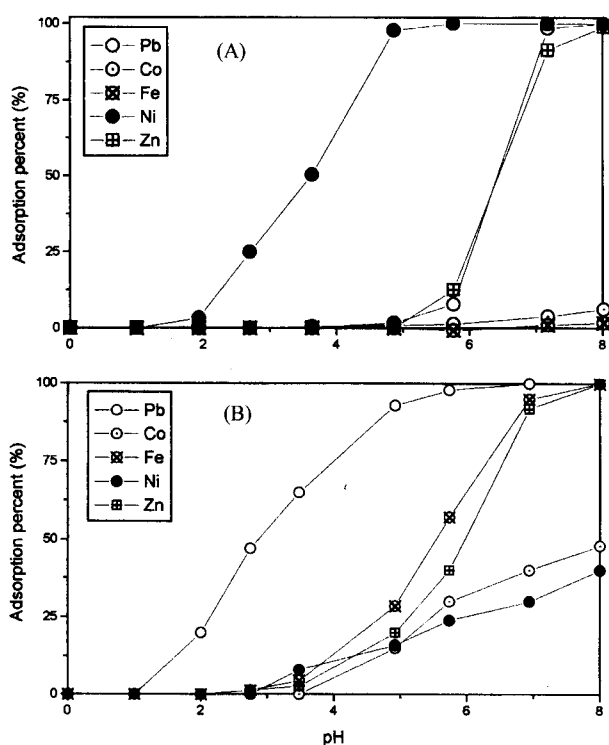


Figure 1. Effect of pH on the adsorption; (A) silica gel-dimethylglyoxime adsorbent and (B) silica gel. Adsorbent weight: 500 mg; Conc. of each metal ion: 1.0 mg/50 mL, Shaking time: 24 hr.

method and the result is presented in Figure 1. The comparison of adsorption of metal ions on silica-dimethylglyoxime adsorbent (Figure 1A) and on silica gel (Figure 1B) shows that a remarkable difference in the retention of metal ions was observed. Figure 1B shows that silica gel has also adsorption capacity of metal ions.

For the quantitative separation of Ni(II) ion from Pb(II) and Zn(II) ions the optimum pH is 5.0. Co(II) and Fe(II) which have a lower tendency to form chelates with silica-dimethylglyoxime adsorbent were not adsorbed at all even at pH 7 as is expected. From the results, it was found that the separation of Ni(II) from the other metal ions was possible by varying only the pH of the solution.

The effect of shaking time on the adsorption of the metal ions in the batch method was studied. After 5 minutes of shaking, 74% of the Ni(II) was adsorbed from the solution and 98% of the Ni(II) was adsorbed in 15 minutes of shaking. Compared with Ni(II), other metal ions needed a longer time to reach adsorption equilibrium.

Desorption of Ni(II). Inorganic acids in the concentration range of 0.01-0.1 M were found to be suitable for desorption of Ni(II) (Figure 2). Hydrochloric acid was selected as a desorption agent.

Adsorption capacity of metal ions. The adsorption capacities (mmol g^{-1}) of the metal ions on silica-dimethylglyoxime adsorbent were determined (Table 1). From the Table 1, this adsorbent can be successfully used for selective adsorption of Ni(II). And, the data indicate that this silica-dimethylglyoxime adsorbent has a great affinity for Ni(II) ion.

The silica-dimethylglyoxime adsorbent was studied for

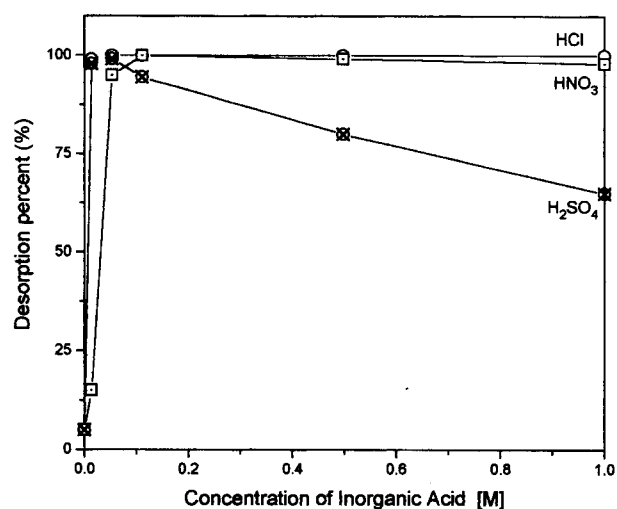


Figure 2. Effect of inorganic acid concentration on the desorption of Ni(II). Adsorbent weight: 500 mg; Conc. of Ni(II) ion: 1.0 mg/50 mL, Shaking time: 24 hr.

Table 1. Adsorption capacity of the adsorbent for different metal ions at pH 5

Metal ion	Capacity (mmol g^{-1})
Ni (II)	3.4
Co (II)	0.086
Pb (II)	0.051
Zn (II)	0.15

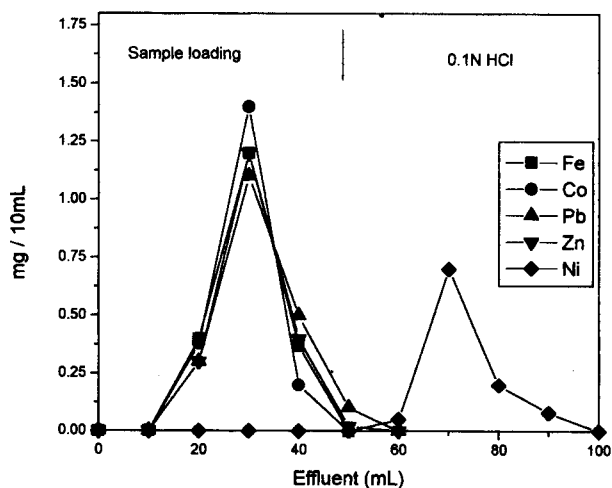


Figure 3. Elution curve of Pb(II), Co(II), Zn(II), Fe(II) and Ni(II). resin: silica-dimethylglyoxime adsorbent, column: $3.14 \text{ cm}^2 \times 5 \text{ cm}$. loading: 2 mg of Pb(II), Co(II), Zn(II), Fe(II) and 1 mg of Ni(II) in 50 mL, pH 5.0. elution: 0.1 M HCl, flow rate: $0.5 \pm 0.1 \text{ mL min}^{-1}$.

the preconcentration of Ni(II) in an artificial water sample. An aqueous Ni(II) sample (1.0 mg/mL) solution of 500 mL was adjusted to pH 5 with acetate buffer. This solution was stirred in of silica-dimethylglyoxime adsorbent of 0.5 g for about 24hr. After stirring the solution was filtered. And, then Ni(II) retained the silica-dimethylglyoxime adsorbent was desorbed with 25 mL of 0.1 M HCl solution and determined by AAS. Ni(II) could be enriched up to 20 times

Table 2. Analytical data of Ni(II) and other metal ions separated in Figure 3

Metal ions, added	Added amount (mg/50 mL)	Recovered amount (mg)	Found* (mg)
Pb(II)	2.0		1.97
Co(II)	2.0	0.994	2.03
Zn(II)	2.0		1.98
Fe(II)	2.0		1.99

*Values agreed with a precision of $\pm 1.5\%$. amount of Ni(II) taken, 1.0 mg/50 mL.

with silica-dimethylglyoxime adsorbent. The results indicate that this adsorbent can act as an effective adsorbent for preconcentration of the Ni(II) ion.

Separation of Ni(II). The separation of trace amounts of Ni(II) from other metal ions was examined by column method. The 50 mL sample solution containing 1 mg Ni(II), each 2 mg of Co(II), Fe(II), Pb(II) and Zn(II) was loaded through the column ($3.14 \text{ cm}^2 \times 5 \text{ cm}$) at a rate 0.5 mL and eluted with 0.1 M HCl eluent. The results is Figure 3, in which Ni(II) is separation from Co(II), Fe(II), Pb(II) and Zn(II). The recoveries of Ni(II) and the added ions were above 98.5% (Table 2).

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Preparation and Electrical Properties of Delafossite-Type Oxides $\text{AgNi}_{1-x}\text{Fe}_x\text{O}_2$ ($0 \leq x \leq 0.5$)

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Delafossite-type oxides $\text{A}^{\text{III}}\text{B}^{\text{III}}\text{O}_2$ (A=Cu, Ag, Pt, Pd; B=Fe, Co, Ni, Cr, Rh...) ^{1,2} have distinctive features due to their two-dimensional structure and the existence of two kinds of transition metals that occupy different crystallographic sites. Trivalent B cations are octahedrally coordinated by oxides and these octahedral units share edges leading to planar $[\text{BO}_2]^-$ slabs, which are stacked along *c* axis. Monovalent A cations are located in the linear sites furnished with $[\text{BO}_2]^-$ slabs, and form hexagonal planar array in *ab* plane. Delafossite-type oxides crystallize in various polytypes according to the stacking way along *c* axis. ² Among them, the type 3R is represented in Figure 1. The electronic transport properties of delafossite-type compounds had been known to depend primarily on the electronic configuration of A-site ions: With d^{10} as Ag^+ or Cu^+ they become semiconductors, otherwise metallic as are PdCrO_2 and PtCoO_2 . This correlation was rationalized by Rogers *et al.*, by using a schematic MO diagram of $[\text{AgO}_2]^{3-}$ cluster. ³ However, semimetallic properties of AgNiO_2 were reported ^{4,5} later. In this case both NiO_2 and hexagonal Ag sublattices were considered for the electronic structure, and charge carriers were

generated through a slight overlap of Ag 4d and $\sigma^*(\text{Ni-O})$ bands (Figure 2). The substitution effects on the electrical transport properties have been studied with a solid solution system $\text{AgNi}_{1-x}\text{Co}_x\text{O}_2$ by one of us ⁶: a metal-insulator transition was found around $x_c=0.3$ and the band overlap disappears for $x \geq 0.4$. However, further works on the substitution effects seemed necessary to get more general understanding about the band overlap of AgNiO_2 . For this purpose, we report here the synthesis of new solid solutions $\text{AgNi}_{1-x}\text{Fe}_x\text{O}_2$ ($0 \leq x \leq 0.5$) and their electrical transport properties.

Experimental

Samples were prepared by cation-exchange reaction, ^{7,8} using precursors of $\text{NaNi}_{1-x}\text{Fe}_x\text{O}_2$, which were obtained by heating the mixtures of Na_2O , NiO and Fe_2O_3 at 600-700 °C under O_2 atmosphere for 14-18 hrs. Each of $\text{NaNi}_{1-x}\text{Fe}_x\text{O}_2$ samples was crystallized in single phase with $\alpha\text{-NaFeO}_2$ structure (R3m) for $0 \leq x \leq 0.5$, but bi-phased with $x > 0.5$ with the appearance of NaFeO_2 , even at higher reaction tem-