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Adsorption of Trace Metal Ions in Aqueous Solution onto Polyaniline / Poly(vinylalcohol) Composite Colloid

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A colloidal powder consisting of polyaniline(PANI), poly(vinylalcohol)(PVA) and silica gel powder was prepared and used to the collection of trace metal ions in aqueous solution. The colloidal powder acts as a chelating resin because of the nitrogen atoms in polyaniline. Thus, the metal ions were incorporated into colloidal powder in the form of polyaniline-metal complex. The adsorption property of the metal ions is affected by the complexation stability and the formation of the composite colloidal matrix. The colloidal powder was applied to the pretreatment of determination using graphite furnace atomic adsorption spectrometry (GFAAS) for the concentration and the separation of the heavy metal cations such as Cu(II), Pb(II), In(III), Cd(II), Co(II) and Ni(II). The present method is simple and rapidly appliciable for the microdetermination of heavy metal ions at ppb levels. Analytical applications for the preconcentration and separation using PANI/PVA composite colloidal powder and the determination of the Cu(II) and Al(III) in sea water and halide salt were carried out.

Key Words: Polyaniline, Composite colloid, Poly(vinylalcohol), Collection, Metal ions

1. INTRODUCTION

Polyaniline (PANI) is made up with structural repeating units formed by two amine molecules, reduced (amine) state and oxidized (imine) state. The degree of oxidation varies smoothly between fully reduced form (leucoemeraldine) and completely reduced form (pernigraniline).[1-3] The structure of polyaniline is transformed by the chemical and electrochemical oxidation and reduction.[4,5] The nitrogen atoms in the oxidation and reductive PANI units are easily protonated in strongly acidic solution and complexed with heavy metal cations. Then, metal ions in the solution are incorporated into colloidal matrix by complexation. On account of the replacement of a chelating metal ions from other cations, such as proton, in the immersed solution at equilibrium. Namely, polyaniline acts as a chelating resin. Thus, polyaniline is expected to used as a trace metal ion separator in aqueous solution.

In the polymerization of aniline with the appropriate polymer surfactant, such as poly(vinylalcohol) (PVA), the PANI/PVA composite colloidal particle can be prepared.[6-9] Colloidal particle of PANI indicates higher hydrophilicity and a surface area due to the relatively uniform pillar morphology with an average diameter of 150-220 nm.[10] In previous paper,[11,12] trace metal ions adsorbed onto PANI/PVA colloidal powder as the anionic complex with anionic ligands. It is considered the difference of ion exchange property is attributable to the sieve effect between the formation of colloidal matrix and exchangeable ions. Thus, the ion exchange property of PANI/PVA colloidal powder can be varied by the modulation of the polymerize conditions.

In this work, the adsorption of trace metal ions onto PANI/PVA colloidal powder directly without anionic ligands. It should be useful for the simple and rapidly ion exchange separator for the pretreatment of the determination using GFAAS.

2. EXPERIMENTAL

2.1 Apparatus

The concentration of metal ions in a sample solution was determined by Hitachi Model 180-30 atomic-absorption spectrometer equipped with Hitachi Model GA-2B graphite-furnace atomizer. A tube type graphite furnace was used in argon atmosphere. Samples were injected by Hitachi autosampler. The analytical signals were recorded and processed with a Hitachi Model D-2500 chromato integrator. The hollow-cathode lamp of cupper, cadmium and lead were purchased from Hitachi Co. Ltd. A deuterium-arc background correction was used throughout.

2.2 Reagents and Chemicals

Poly(vinylalcohol) was purchased from Wako Pure Chemicals (DP=300), and silica gel powder purchased from Waco Chemicals (300 mesh). All the other chemicals used were reagent grade. All of the solutions containing various metal ions were prepared by dissolving nitrate salts in deionized-distilled water.

2.3 Preparation of the PVA/PANI colloidal powder

The colloidal powder was prepared that PANI/PVA composite colloidal particle was synthesized onto the surface of silica gel powder. Colloidal particle incorporated with Cl^- was synthesized by the chemical method. The chemical polymerization of PANI was carried out in a aqueous solution (100 cm^3) containing 0.2 mol dm^{-3} HCl, 0.3 mol dm^{-3} aniline, 3.52 g PVA and 15 cm^3 silica gel powder. After that, oxidizing agent, 0.1 mol dm^{-3} ammonium peroxodisulfate was added with stirring. The stirring was continued for 12 hour at room temperature. The composite colloids fixed on silica gel powder was separated by decantation and washed with 1.0×10^{-3} mol dm^{-3} HCl solution until the washings were no longer colored. This powder was kept in 1.0×10^{-3} mol dm^{-3} HCl solution.

2.4 Adsorption and desorption procedure of trace metal ions onto colloidal powder

Two milliliters of PANI/PVA composite colloidal powder was introduced into a 100ml flask and several washings were made with 1.0×10^{-3} mol dm^{-3} HCl solution. After that, sample solution containing of the various concentration of cupper nitrate and acetic acid buffer was added. In order to reach the equilibrium between colloid and the solution, the flask was shaken sufficiently at room temperature. After that, the colloidal powder was immersed into 0.5 mol dm^{-3} HNO_3 solution and and shaken for 30 min for elutriation.

In column method, one milliliters of PANI/PVA colloidal powder was introduced into glass column and 1.0×10^{-3} mol dm^{-3} HCl solution was passed through the column. Sample solution containing acetic acid buffer was through into the column. The flow rate of sample solution is decided sufficiently slow for the quantitative adsorption of metal ions. After that, 0.5 mol l^{-1} HNO_3 eluting solution was passed through the column for elution.

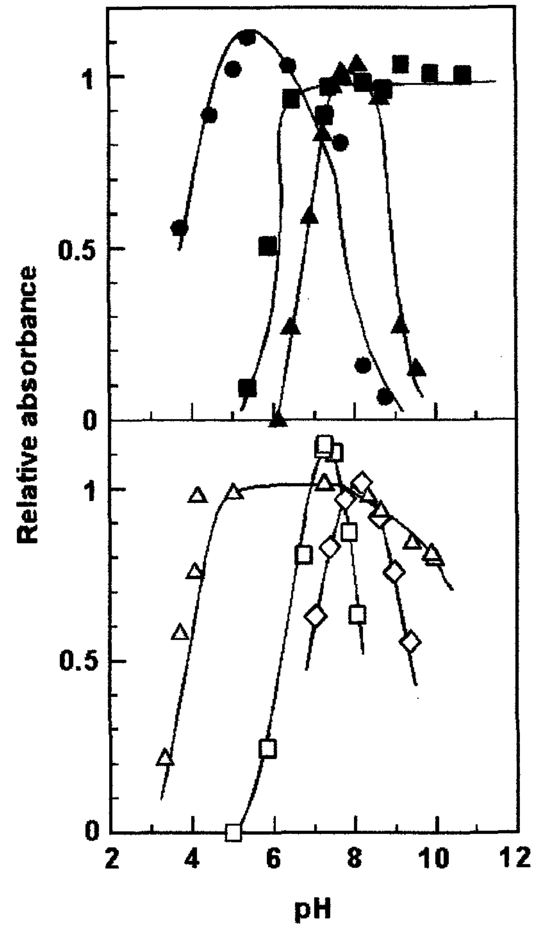

Fig.1 Effects of pH on the collection of Cu^{2+}(▲), Pb^{2+}(■), In^{3+}(●), Cd^{2+}(□), Co^{2+}(◇) and Ni^{2+}(△) in the 15ml sample solution using 2ml PANI/PVA colloidal powder.

2.5 Determination of metal ions using graphite furnace atomic adsorption spectrometry

The concentrations of cupper ions in adsorbed and eluate solution were measured using GFAAS. A 10 μl aliquot of sample solution injected by autosampler. The durations and temperature were 15 sec. at 120℃ for drying, 30 sec. at 528℃ for ashing and 5 sec. at 2800℃ for atomization. The absorbance signals during the atomization step were recorded at 324.75 nm (1.3 nm band pass). The graphite furnace was fired at the attainable maximum temperature (about 3000℃) for 3 sec. after measuring each samples in order to cleaning any residue from surface of the furnace. In other metals, the instrumental conditions were optimized.

3. RESULTS AND DISCUSSION

3.1 Effect of pH on the adsorption of metal ions

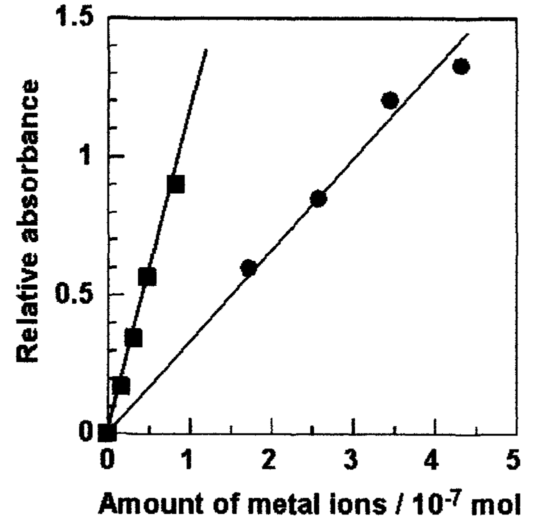

Fig.2 Calibration curve of In^{3+}(●) and Pb^{2+}(■) in the case of batch method using 2ml PANI/PVA colloidal powder.

Sample volume; 15ml, Eluent volume; 10ml, Standard; 2.61×10^{-7}, 3.2×10^{-8} M, respectively.

The amounts of adsorption of metal ions onto PANI/PVA colloidal powder were influenced by the pH in the immersed solution. Two milliliters of PANI/PVA colloidal powder was immersed into sample solution containing $1.0x10^{-6}$ mol l^{-1} Cu^{2+} at various pHs. The colloidal powder was taken out and immersed into eluate solution for elutriation. The similar experiments on various metal ions were carried out. These results are shown in Fig.1. The maximum recovery of Cu^{2+} was obtained on wide pH range from pH 4.5 to 8.0. Similarly, in the Pb^{2+} solution, the high recovery was obtained at wide pH range. It is consider that the complexation of PANI-Cu and PANI-Pb was influenced by the concentration of hydrogen ions, however the complex was stable wide pH range in sample solutions. In the sample solution containing In^{3+}, Cd^{2+}, Co^{2+} and Ni^{2+}, the maximum recovery were obtained at pH 3.0, 7.5, 8.3 and 8.0, respectively. The PANI-metal ion complex is decomposed in an acidic solution and hydrolyzed or alternated to hydrooxide metal complex in a basic solution. Hence, in a solution adjusted at suitable pHs, the metal ions can be adsorbed onto PANI colloidal powder selectively.

The relative absorbance of eluent is plotted as a functions of the amounts of metal ions in sample solution in Fig. 2. The sample solutions containing of In and Pb were adjusted at pH 5.4 and 6.6-7.5, respectively. The absorbance increases almost linearly and agrees with the linearly calibration curve. Thus, PANI/PVA colloidal powder can be applied to an absorbing agent for the pre-concentration of metal ions in an aqueous solution.

3.2 Influence of adsorption conditions on the adsorption of metal ions

The PANI/PVA colloidal powder was applied to pre-concentration of dilute Cu^{2+} solutions. The colloidal powder was immersed into a various volume of sample solution containing 1.5×10^{-6} mol of Cu^{2+}. After that, the absorbed Cu^{2+} was eluted by 0.5 mol dm^{-3} HNO_3 solution (5ml). In this volume, a concentration ratio was changed from 5 to 200. The similar experiments were carried out by column method. These results are shown in Table 1. When the volume of a sample solution were less than 500ml, the pre-concentration of Cu^{2+} by the use of PANI/PVA colloidal powder were carried out quantitatively. And in the 1000ml solution, the recovery of Cu is decreased. However, in column method, the recovery is not decreased until 2000ml, when the concentration ratio is 400 times. Thus, PANI/PVA colloidal powder can concentrate of a trace metal ion in aqueous solution and use for a preconcentration of analyte.

The determination of trace metal ions in an aqueous solution is inhibited by various ions, such as metal ions and halide ions. The recoveries of Cu and In ions in the presence of various co-existing ions were measured. In these results (Table 2), the recoveries of Cu and In ions are not influenced by the metal ions 250 times as concentrate as the analytes. Thus, the inhibition of co-existing metal ions on the GFAAS analysis is reduced by the pretreatment using PANI/PVA colloidal powder. Similarly, the inhabitation of alkali metal

Table 1 Effect of sample volume on the recovery of Cu(II).

Volume/ml	Conc. Ratio	Relative recovery	
		Batch[a)]	Column[b)]
25	5	1.00[c)]	1.00[c)]
250	50	0.96	0.93
500	100	0.99	1.06
1000	200	0.71	0.98
2000	400	–	1.03

a) PANI/PVA colloid; 2ml, Cu; 1.5×10^{-8} mol
b) PANI/PVA colloid; 1ml, Cu; 1.0×10^{-8} mol
c)Standard

Table 2 Effect of co-existing ions on the recovery of 5.0×10^{-8} mol Cu^{2+} and 8.7×10^{-8} mol In^{3+}

Cation	Conc. ratio	Relative recovery	
		Cu	In
Pb^{2+}	100	0.99	1.00
	250	1.00	1.00
Fe^{2+}	100	0.99	0.98
	250	1.02	1.00
Ni^{2+}	100	1.03	1.02
	250	1.05	1.01
K^+	1000	0.99	0.98
	3000	1.00	0.96
Na^+	1000	0.98	1.02
	3000	1.02	1.00
Br^-	1000	1.03	0.99
	3000	1.05	1.04

PANI/PVA colloid; 1ml, volume; 25ml
Eluent; 0.5M HNO_3, 5ml

ions, alkaline-earth metal ions and haloid ions is also reduced until 3000times as concentrate as the analyte. Thus, the determination of trace metal ions in aqueous solution using GFAAS can be improved by the pretreatment using PANI/PVA colloidal powder in the reduce of inhibition by various co-existing ions.

3.3 Analytical application

Analytical separation procedures for trace metal ions can be strongly interfered with by matrix constitutions, e.g. sodium chloride. For this reason, the reliability of the tested preconcentration procedure was examined in the presence of the concentrated sodium chloride matrix, such as halite and sea water. The analytical results of different samples, e.g. sea water (Maruo port, Ube) and Halite (Mexico and Australia) are shown in Table 3. In this result, the experimental data of sea water for the investigated metal ions are in reasonable agreement with comparable reference value. And it was found that the concentration of the determined metal ions in halide salts were obtained with sufficiently small experimental error. Thus, the present pretreatment method can be applied to the sample solution containing salt water matrix.

Table 3 Determination of metal ions in sodium chloride matrix by calibration curve method.

Sample	Metal	Taken /ml	Found /ng	In sample /ng l^{-1}
Sea water	Cu	500	145	290±20
(Maruo port, Ube)	Al	125	129	1030±30
Halite salt	Cu	30	163	5.42±0.01
(Mexico)	Al	2.0	190	95.2±0.53
Halite salt	Cu	30	161	5.36±0.01
(Australia)	Al	2.0	499	249±0.53

PANI/PVA colloid; 1ml, Eluent; 0.5M HNO_3, 5ml

4. REFERENCES

[1] W. S. Huang, B. D. Humphrey and A. G. MacDiarmid, *J. Chem. Soc., Faraday Trans. 1*, **82**, 2385 (1986)

[2] A. G. MacDiarmid, J. C. Chiang, A. F. Richter and A. J. Epstein, *Synth. Met.*, **18**, 285 (1987)

[3] A. Ray, G. E. Asturias, D. L. Kershner, A. F. Richter and A. G. MacDiarmid, *Synth. Met.*, **29**, E141 (1989)

[4] J. G. Masters, Y. Sun, A. G. Macdiarmid and A. J. Epstein, *Synth. Met.*, **41-43**, 715 (1991)

[5] P. M. McManus, S. C. Yang and R. J. Cushman, *J. Chem. Soc., Chem. Commun.*, 1556 (1985)

[6] C. F. Liu, D. K. Moon, T. Maruyama and T. Yamamoto, *Polymer Journal*, **25**(7), 775 (1993)

[7] M. Gill, F. L. Baines and S. P. Armes, *Synthetic Metals*, **55-57**, 1029 (1993)

[8] C. Dearmitt and S. P. Armes, *J.Colloid Interface Sci.*, **150**(1), 134 (1992)

[9] J. Stekskal, P. Kratochvil and N. Radhakrishnan, *Synthetic Metals*, **61**, 225 (1993)

[10] T. Nagaoka, H. Nakao, T. Suyama and K. Ogura, *Anal.Chem.*, **69**, 1070 (1997)

[11] N. Endo, M. Suma, M. Higa and K. Matsusaki, *Trans. Mat. Res. Soc. J.*, **27**[2], 431 (2002)

[12] N. Endo, Y. Takeda, M. Higa and K. Matsusaki, *Anal. Sci.*, **19**, 721 (2003)

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