

Collection of Trace Ions by Use of Conducting Polymer Colloid

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For the collection of metal ions, the colloidal powder consisting of Polyaniline, poly(vinylalcohol) and silica gel powder was prepared. The colloidal powder acts as an anion exchanger in acidic solution, because of the protonation of polyaniline. In the aqueous solution containing with anionic ligands, the metal ions was incorporated into colloidal powder in the form of anionic complex. The adsorption property of metal ions is influenced by the complex stability and the formation of the composite colloidal matrix formed in the polymerization. The latter was resulted form the sieve effect between the size of metal complex and mesh of the colloidal matrix determined by the coexisting dopant anion sizes in synthesis. Thus, the selectivity of metal adsorption on the PANI/PVA colloidal powder can be controlled by the selection of the coexisting dopant anions. Then, the optimization of PANI/PVA colloidal powder for the selective collection of particular metal ions was examined.

Key Words: Polyaniline, 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 may vary 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 atom in the oxidation and reductive PANI units is easily protonated in strongly acidic solution. Then, anions in the solution are incorporated with protonation of PANI as a dopant anion. On account of the replacement of the dopant anion from another anions in the immersed solution at equilibrium,⁶ polyaniline acts as the ion exchanger. In the basic solution, the dopant anion is released with the deprotonation.⁷ Thus, polyaniline is expected to use a functional ion separator.

In the copolymerization of aniline with the appropriate polymer surfactant, such as poly(vinylalcohol) (PVA), the PANI/PVA composite colloidal particle can be prepared.⁸⁻¹¹ Colloidal particle of PANI indicates higher hydrophilicity and surface area due to the relatively uniform pillar morphology with an average diameter of 150-220 nm.¹² In previous paper,^{13,14} the difference of the ion exchange property on the PANI/PVA colloidal powder and commonly ion exchange resins. 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. The purpose of this work is the development of optimized preparation of PANI/PVA colloidal powder for the selective collection of particular metal ions from aqueous solutions. It should be useful for the development of the designable ion exchange separator.

2. EXPERIMENTAL

2.1 Apparatus

The concentration of metal ions in the 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 copper, cadmium and lead were purchased from Hitachi Co. Ltd. A deuterium-arc background correction was used throughout.

2.2 Reagents and Chemicals

Poly(vinylalcohol) (PVA) was purchased from Ishizu 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 by adsorption on silica gel powder of the PVA/PANI composite colloidal particle. Colloidal particle incorporated with Cl^- (PVA/PANI(Cl^-)) was synthesized by the chemical method. One hundred milliliter mixture solution of 0.2 mol l^{-1} HCl dissolved with 0.03 mol aniline and 3.52 g PVA were stirred with silica gel powder (15 ml). To this mixture, 0.01 mol of 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 $1.0 \times 10^{-3} \text{ mol l}^{-1}$ HCl solution until the washings were no longer colored. This powder was kept in $1.0 \times 10^{-3} \text{ mol l}^{-1}$ HCl solution. PVA/PANI colloid powder incorporated with another dopant anion were also prepared and washed by same method in corresponding acid solution of same concentration.

2.4 Procedure

Two milliliters of PVA/PANI(Cl^-) was introduced into a 100 ml flask and several washings were made with $1.0 \times 10^{-3} \text{ mol l}^{-1}$ HCl solution. After that, sample solution containing of the various concentration of copper nitrate, $3.6 \times 10^{-3} \text{ mol l}^{-1}$ KI 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 taken out by decantation, and shaken for 30 min. in 0.8 mol l^{-1} HNO_3 solution for elutriation. The concentrations of copper ions in adsorbed and eluate solution were measured using GFAAS. A $10 \mu\text{l}$ aliquot of sample solution injected by autosampler. The durations and temperature were 15 sec. at 120°C for drying, 30 sec. at 528°C for ashing and 5 sec. at 2800°C 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°C) for 3 sec. after measuring each samples in order to cleaning any residue from surface of furnace.

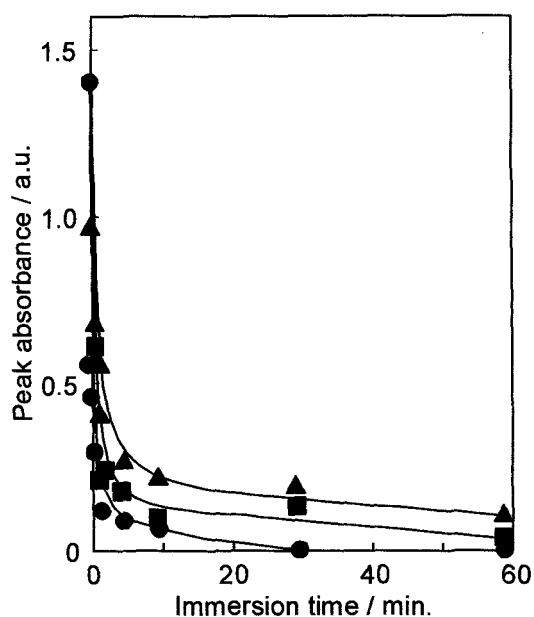


Fig.1 Adsorption rate of Cu^{2+} (●), Pb^{2+} (▲) and Cd^{2+} (■) from 25 ml of $2.5 \times 10^{-6} \text{ mol l}^{-1}$ solution onto 2 ml PANI/PVA colloidal powder.

In another metals, these experiments were also carried out using optimized similar method.

3. RESULTS AND DISCUSSION

3.1 Condition of the adsorption and desorption process

The determination of various metal cation using PANI/PVA colloidal powder was optimized for the concentration of coexisted ligand and immersion time for adsorption and desorption. The adsorption rate of the various metal ions onto PANI/PVA colloidal powder was measured. In Fig.1, copper ion was adsorbed quickly onto PANI/PVA colloidal powder and all ions were adsorbed at 30 minutes. In the lead and cadmium ions, the most part of metal ions was adsorbed at 60 minutes. The difference of adsorption rate is attributable to the stability and ionic radii of the metal complexes. Further details describe below part. In this experiment, The flask introduced sample solution and PANI/PVA colloid was shaken for 30 minutes in copper ions, and 60 minutes in lead and cadmium ions.

The optimum concentration of ligands in absorption process was examined. The amounts of copper eluated from PANI/PVA colloidal powder immersed into sample solution containing with various concentration of KI was determined. In this results, the peak absorption of eluate solution increases as KI

concentration rises to $2.5 \times 10^{-3} \text{ mol l}^{-1}$, above which it was constant. It means that the sufficient amounts of ligand was added at that time and the determination of metal ions was not influenced by too many ligand in the solution. In this experiment, potassium iodide was added $3.6 \times 10^{-6} \text{ mol l}^{-1}$ as sufficient ligand concentration. The concentration of eluate solution and shaking time of elutriation, described above, was determined by same procedure. These optimized values were used in subsequent studies.

3.2 Effect of pH on the adsorption of metal ions

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 $2.5 \times 10^{-6} \text{ mol l}^{-1} \text{ Cu}^{2+}$ and adjusted at various pHs. This colloidal powder was taken out and immersed into eluate solution for elutriation. The similar experiments on lead and cadmium ions were carried out using sample solutions containing $1.2 \times 10^{-5} \text{ mol l}^{-1}$ and $5.0 \times 10^{-8} \text{ mol l}^{-1}$, respectively. The concentrations of metal ions in eluate solution was shown in Fig.2. The recovery of Cu^{2+} increases as the concentration of hydrogen ions

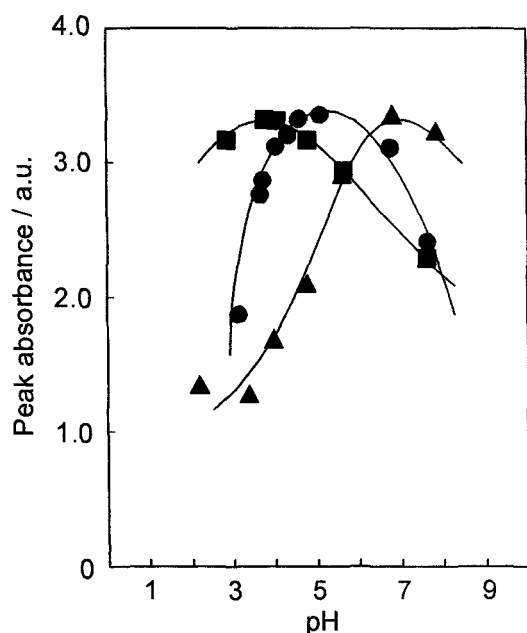


Fig.2 Effects of pH on the collection using PANI/PVA colloidal powder from 25ml of $2.5 \times 10^{-6} \text{ M Cu}^{2+}$ (●), $1.2 \times 10^{-5} \text{ M Pb}^{2+}$ (▲) and $5.0 \times 10^{-8} \text{ M Cd}^{2+}$ (■) solutions.

decreases to pH5, below which it decreases. The maximum recovery of Cu^{2+} was 0.96. It is consider that the formation of anionic iodide complex was influenced by the concentration of hydrogen ions in the sample solution in adsorption. In Pb^{2+} and Cd^{2+} , the maximum recoveries of metal ions were obtained at pH7 and pH4, respectively. The metal ion is complexed with iodide ions and incorporated into colloidal particle in the form of the anionic iodide complex. It is consider that the metal-iodide complex is decomposed in the acidic solution, and hydrolyzed or alternated to hydroxide metal complex in the basic solution. Thus, the recovery of metal ion is decreased by the decomposition of anionic complex. Hence, the adsorption of copper, cadmium and lead ions were carried out in the sample solution adjusted 5.0, 4.0 and 7.0, respectively.

3.3 Influence of dopant anions in the polymerization

In previous paper,^{13,14} the ion exchange properties of PANI/PVA colloidal powder is influenced by the coexisting dopant anions in polymerization. In the ion exchange on the colloidal particle, the exchangeable ions pass through the mesh of colloidal network and migrate to the ion exchange site. The mesh of polymer network is influenced by the coexisted dopant anions. Thus, the recovery using PANI/PVA colloidal powder prepared with the various dopant anions were measured. In order to exclude the effect of the hydrophobic interaction, dopant anions were replaced NO_3^- by washing with $1.0 \times 10^{-3} \text{ mol l}^{-1} \text{ HNO}_3$ solution. The colloidal powder prepared in HCl solution and pretreated in HNO_3 is referred to here as PANI/PVA($\text{Cl}^- \rightarrow \text{NO}_3^-$). In table 1, the sequence of recovery on the dopant anions incorporated into PANI/PVA colloidal powder in synthesis is $\text{Cl}^- > \text{ClO}_4^- > \text{BS}^-$. This sieve effects was then examined with respect to the adsorption selectivity and the ionic radii of the exchangeable ions for PANI/PVA colloidal powder. The molar equivalent conductivity in an infinite dilute aqueous solution is often substituted for the ionic radius in aqueous solution. The molar equivalent conductivity of Cl^- and ClO_4^- are 0.007631 and 0.00673 $\text{m}^2 \text{ S mol}^{-1}$, respectively.¹⁵ The decrease in the molar equivalent conductivity corresponds to the increase in the radius of the hydrated ion. Thus, the PANI/PVA colloidal particle polymerized with the hydrophobic

Table 1 Recovery from various metal samples using PANI/PVA colloidal powder synthesized with various dopant anions.

Adsorbant ^{a)}	Recovery		
	Cu ^{b)}	Cd ^{c)}	Pb ^{d)}
PANI/PVA(Cl ⁻ →NO ₃ ⁻)	0.96	0.97	0.77
PANI/PVA(ClO ₄ ⁻ →NO ₃ ⁻)	0.87	0.93	0.72
PANI/PVA(BS ⁻ →NO ₃ ⁻) ^{e)}	0.76	0.90	0.72

a) PANI/PVA prepared with various dopant and replaced to NO₃⁻

b) 2.5 × 10⁻⁶ mol l⁻¹ Cu²⁺ + 3.6 × 10⁻⁶ mol l⁻¹ KI solution was used.

c) 5.0 × 10⁻⁸ mol l⁻¹ Cd²⁺ + 3.6 × 10⁻⁶ mol l⁻¹ KI solution was used.

d) 1.2 × 10⁻⁵ mol l⁻¹ Pb²⁺ + 3.6 × 10⁻⁶ mol l⁻¹ KI solution was used.

e) BS, benzenesulfonic acid

dopant anions is formed closely polymer network and smaller opening in the colloidal matrix, because of the smaller hydrated ion sizes of the coexisted dopant anions. Consequently, the mobility of metal complex into colloidal matrix is decrease as the mesh of colloidal matrix becomes closely.

A comprehensive understanding of the ionic sizes of organic compounds in aqueous solution such as benzenesulfonic acid is still lacking. But, colloidal powder prepared with BS⁻, that is regarded as the greater compounds, indicates smaller recoveries than with Cl⁻ and ClO₄⁻. It means that the more closely mesh was formed in the PANI/PVA(BS⁻) colloidal particle. It is predicted that the incompletely replacement of the incorporated benzenesulfonic acid with nitrate ions. The incorporated benzenesulfonic acid on the inner doping site in the colloidal particle is difficult to exchange with nitrate ions because of the greater sizes of itself. Hence, more closely colloidal matrix was formed by the colloidal polymer chain and benzenesulfonic acid compounds. Thus, the influence of recovery on the various dopant anions is attributable to the density of polymer matrix formed in the polymerization.

As compared with the variation amounts of recovery on the Cu²⁺, Cd²⁺ and Pb²⁺, the recovery of Cu²⁺ was obviously decreased. It is explained by the high stability and bulky formation of metal complex consisting of copper and iodide. The metal complex consisting of copper and iodide is more stable than one of cadmium and lead. Thus, the tightly and bulky compound of metal complex is difficult to diffuse into the closely colloidal matrix. The decrease of a number of ion exchange sites in the PANI/PVA colloidal particle leads to the decrease of distribution ratio in

adsorption, because of apparent ion exchange capacity. In contrast, the recoveries of Cd²⁺ and Pb²⁺ were decreased slightly. It is consider to the contributions to ligand substitution reaction between fixed ligands on the doping site in the colloidal particles and metal complex. Consequently, the recovery of metal ions using PANI/PVA colloidal powder is influenced by the density of polymer chains formed in synthesis and selection of ligand. For the selective recovery of particular ions in aqueous solution, these parameter can use to control of the ion adsorption properties.

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