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Biosorption of Precious Metal Ions by Chicken Feather

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ABSTRACT

Chicken feather (C-feather) is an intricate network of stable and water-insoluble protein fibers with high surface area and is an abundant bioresource. C-feather protein was found to accumulate various precious metal ions (gold and platinum metals) selectively from their dilute aqueous solutions in high yield and in short contact time, depending on pH and characteristics of the individual precious metal ions. Under certain condition, the sequestering level of precious ions, Au(III), Pt(II), and Pd(II) approaches about 17, 13, and 7% of dry wt of C-feather, respectively. Gold(III) potassium cyanade was also accumulated up to 5.5% at pH 2.0. The presence of 100-fold (mol) of coexisting cations, such as Na^+, Fe(III), Cu(II), and Ni(II), did not show a discernible effect on the precious metal uptake rate and capacity of C-feather. Experiment suggested C-feather is promising for use in the removal/recovery of precious metals as well as water pollution control. A qualitative discussion is given about the excellent adsorption behavior of C-feather.

Index Entries: Chicken feather; precious metal; biosorption.

INTRODUCTION

Gold and platinum metal ions are precious metal that have been in high demand for centuries. Despite continued threats of material substitution, consumption of these precious metals by the industry grew and is expected to increase further in the years to come. Gold is used extensively in many high-technology areas, particularly in computer applications, that demand the highest reliability. Platinum metals are used as a catalyst in organic synthesis and combustion gas treatment. Precious metals recovery from secondary sources, such as electronic scrap and catalyst, and waste electroplating solution, is therefore an important technology as well as good recovery from primary resources, such as leach solutions.

The recovery and collection of these precious metals from dilute solutions generally involves either zinc dust precipitation, carbon adsorption, solvent extraction, and usage of ion-exchange resin *(1)*. However, in most cases, these techniques have low selectivity and are likely to become increasingly expensive.

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Recently, some success has been achieved in the development of biosorbents for precious metals recovery. Certain types of biomaterials, such as microbial cells *(2–4)*, chitosan *(5)*, marine algae *(6–8)*, egg shell membrane *(9)*, possess the potential to sequester and accumulate metal cations, including precious metals in aqueous solution. Metal accumulation by biomaterials is termed "biosorption." In the present investigation, chicken feather (C-feather) was found to accumulate precious metal ions from their dilute aqueous solutions in high yield and in short contact time, but is dependent on the pH and characteristics of the individual metal ion. Biosorption is generally considered to be a rapid physical/chemical process and not expensive. C-feather is an abundant resource (byproduct of chicken industry), highly stable, water-insoluble, homogeneous, and has high surface area. It allows metal ions, as well as extremely large organic nutrient crosslinked protein molecule, to pass freely through it.

This article outlines some basic process parameters in the potential use of a new biomaterial, C-feather as a biosorbent, for sequestering and accumulating precious metals from aqueous solution.

MATERIALS AND METHODS

C-feather sample was obtained from the waste of a local chicken industry of Japan. The feather was washed twice with water and detergent by an electric washing machine, then washed with deionized distilled water, dried in air at room temperature, and then desiccated over phosphorus pentoxide under reduced pressure at room temperature. The powdered product was obtained by grinding the feather in the blender for approx 2 min.

Two procedures were utilized in experiments reported here. In the "batch" procedure, approximately the same weight of feather (around 30–40 mg) was precisely weighed, then placed directly in contact with aqueous solutions containing various metal ions. The feather was placed directly and soaked in the aqueous solutions containing metal ions in 40-mL stoppered glass test tubes. To prevent metal contamination during experiments, the test tubes were soaked with 10% HCl overnight. Then, they were washed and rinsed with distilled deionized water. This cleaning procedure was used throughout the experiments. The suspension volume was always 20 mL, unless otherwise specified. Precious metal solutions of desired concentrations (initial concentration of metal solution was always $3.0 \times 10^{-3}M$, unless otherwise specified) were prepared by dissolving Au(III) as $AuCl_4^-$, Pt(II) as $PtCl_4^{2-}$ and Pd(II) as $PdCl_2$ in deionized distilled water and shaken at 60 rpm with a shaker in a thermostated water bath at 25°C. The pH was adjusted with 0.1*N* HCl or 0.1*N* NaOH. Measurement of pH of solution was done by glass electrode pH meter type F-12 (Horiba Inc., Kyoto, Japan). The following chemicals—$NiCl_2 \cdot 6H_2O$, NaCl, $FeCl_3 \cdot 4H_2O$, and $CuCl_2 \cdot H_2O$—were chosen for coion effect experiments considering their high solubility in solutions at room temperature. All the reactions were terminated by the separation of the feather from the solution with tweezers, and then the feather was washed with the metal-ion-free aqueous solution of the same pH.

The kinetics of precious ion biosorption by the feather was investigated in a series of contact test tubes at the stated initial concentration at 25°C and at the desired pH. After desired durations of contact, the reactions were terminated, then the residual precious metal concentrations were determined, and the result was a time-dependent precious metal uptake profile. The biosorptive uptake capacity was determined as a function of residual metals concentration or by measurement of dry weight of feather complexed with metals. In order to confirm the retention of precious metal on the feather, the exposed feather was analyzed for precious metal content. For this purpose, the metal-laden feather was digested with an aqua regia solution.

Experimental scale of selective collection of gold and palladium from aqua regia digest of anode slime was carried out by feather powder-packed minicolumn (0.5 × 3.0 cm). The slurry of powdered feather was poured into a column, then aqua regia solutions of anode slime was passed through the column, and the effluent was analyzed for metal ions. For preparation of the aqua regia solution of metal ions from anode slime, 10 g of dried anode slime were digested with 30 mL of aqua regia. Gold and platinum adsorption was accomplished by passing the 10-times-diluted aqua regia solution through a column of the feather powder biosolvent.

Metal ion analysis was performed by using inductively coupled plasma atomic spectrometry (ICP AES: SPS 1200A, Seiko Instrument Inc., Tokyo, Japan).

RESULTS AND DISCUSSION

The feather exhibited a certain degree of biosorption of all metal ions tested. These included Ni(II), Zn(II), Cu(II), Ag^+, Hg(II), Au(III) as $AuCl_4^-$, Pt(II) as $PtCl_4^{2-}$, and Pd(II) as $PdCl_2$ (data for all not shown). The metal ions not specified were added as sulfate, nitrate, or chloride salts.

Figures 1A–C demonstrates the pH dependence of gold, platinum, and palladium at different soaking times of 1, 3, and 5 h at 25°C, respectively. These metal ions are bound to the feather much more strongly than any other metal ions tested, e.g., under certain conditions the feather has a binding capacity for gold(III) that is at most 17% of the dry wt of feather (about 0.7 mmol of gold/g of dry wt feather, for platinum that is 9%, and for palladium that is at most 6%. There are significant differences in behavior for each metal. For example, the maximum uptake values for gold , platinum, and palladium were obtained at pH 3.0, 1.8, and 2.2, respectively. This variation would enable one to perform selective elution of bound metal ions from feather for these ions.

In contrast to the behavior of most metal ions under these conditions, the binding of precious elements is not completely reversed by lowering the pH of the solution. We found a considerable amount of biosorption of all these precious elements to the feather takes place under the condition of 2% HCl solution (data not shown) and 10-times-diluted aqua regia solution with distilled water as described later. However, exposure of precious metal-bound feather, which was prepared by the treatment of the feather in the solution of precious metals at pHs ranging from 2–3, to 2% HCl solution was effective in stripping these metal ions from the feather. For example, roughly 55% of Au loaded at pH 3.0 was removed by the 2% HCl solution. Under the condition of 2% HCl at room temperature, the feather is stable and can be used repeatedly. However, exposure of precious metal-bound feather to high concentrations of sulfur-containing ligands, such as thiourea or mercaptoethanol, are effective at certain pHs (not shown) in stripping these metal ions from the feather surface.

Figure 2 illustrates the pH dependence of uptake of dicyanoaurate, $Au(CN)^{2-}$ at 25°C for 1 h soaked in $3.0 \times 10^{-3} M$ solution. And Figure 3 shows the relationships between contact time and uptake of $Au(CN)^{2-}$ on the feather at pH 2.5 and 25°C. The

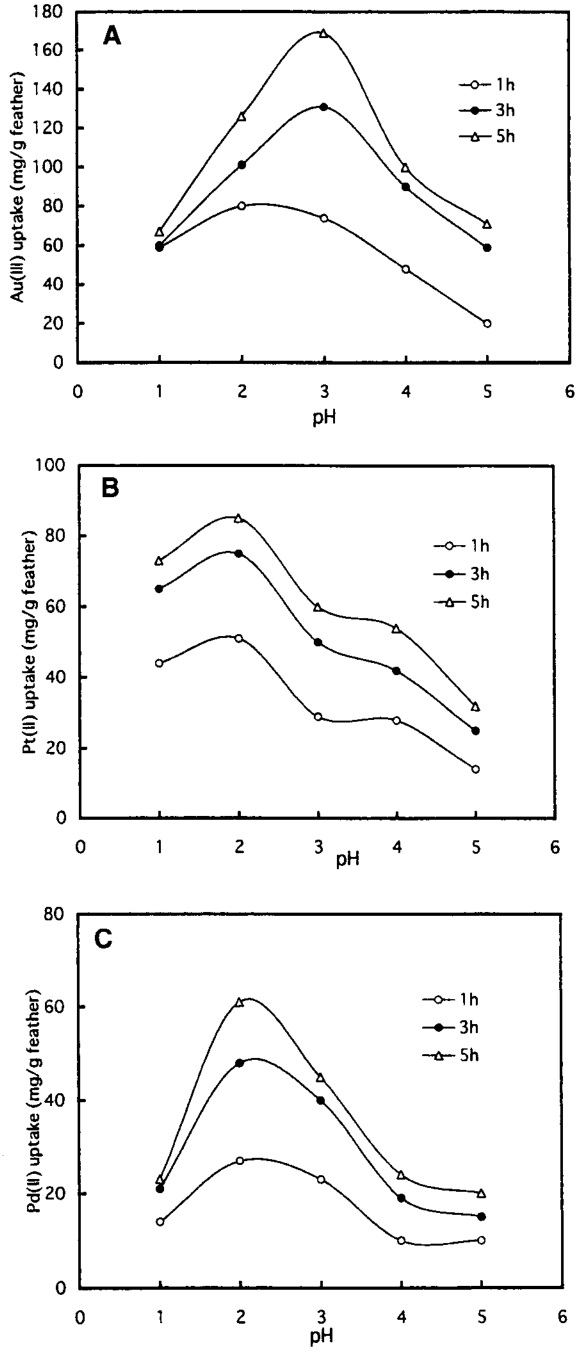

Fig. 1. **(A)** Effect of pH and soaking time on uptake of Au(III). Au(III): $3.0 \times 10^{-3}M$, temp.: 25°C. **(B)** Effect of pH and soaking time on uptake of Pt(II). Pt(II): $3.0 \times 10^{-3}M$, temp.: 25°C. **(C)** Effect of pH and soaking time on uptake of Pd(II). Pt(III): $3.0 \times 10^{-3}M$, temp.: 25°C.

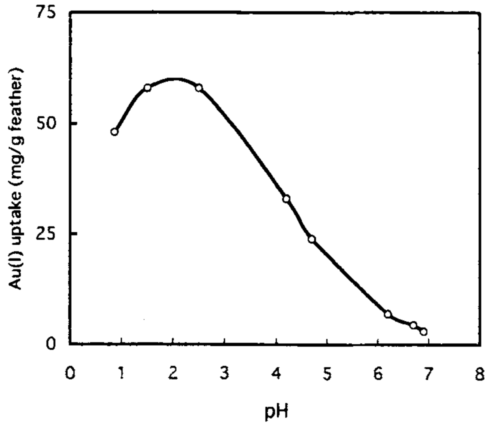

Fig. 2. Effect of pH on uptake of $Au(CN)^{2-}$. Au(III): $3.0 \times 10^{-3}M$, temp.: 25°C. Soaking time: 1 h.

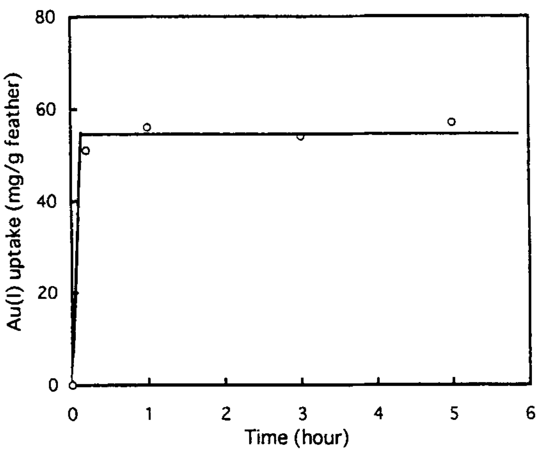

Fig. 3. Relationships between contact time and uptake of $Au(CN)^{2-}$ on chicken feather. Au(III): $3.0 \times 10^{-3}M$, ph: 2.5 at 25°C.

solution pH considerably affected the $Au(CN)^{2-}$ uptake. Interestingly, the feather shows unique behavior for $Au(CN)^{2-}$ to have high binding capacity and uptake equilibrated in extremely short contact time, i.e., under pH 2.5 the feather has binding capacity that is 5% of the dry wt of the feather within 15 min. Also the binding of $Au(CN)^{2-}$ is completely reversible when pH is increased to 6.0. From this behavior, we show that the feather could be used to the remove and/or recover gold from the effluent electroplating solutions.

The effect of the presence of coions in the solution on the precious metals biosorptive capacity of the feather was examined. Figure 4 shows the effect on palladium uptake, for example. Experiments were performed on $3.0 \times 10^{-3}M$ palladium solution with five times the concentration of coions, Fe(III), Cu(II) , Ni(II), and Na^+ as cations, which were tested because of their high probability of occurrence in solutions from industrial sources, at pH 2.0 for 5 h of soaking time. It was observed that no uptake of coions took place and there was a slight change in the uptake capacity of palladium. Gold and platinum also showed slight change

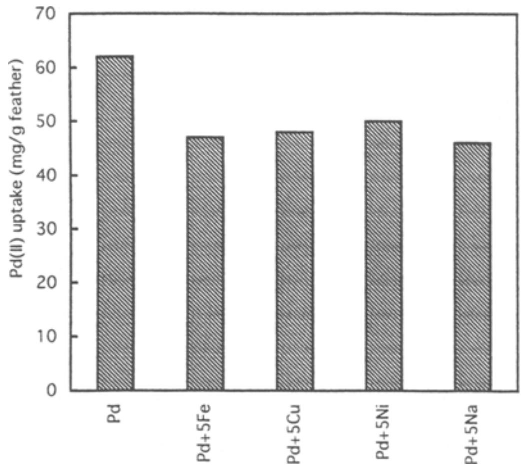

Fig. 4. Effect of cometal ions on uptake of Pd(II). Pd(III): $3.0 \times 10^{-3}M$, cometal ions Fe(III), Cu(II), Ni(II), Na^+: $1.5 \times 10^{-2}M$.

in the uptake rate and capacity in the presence of five times more (by mol) of these coexisting metal ions (data not shown).

Figure 5 shows the adsorption of palladium(II) on feather from the dilute (16 ppm) palladium solutions at pH 2.0 without and with 100 times more (by mol) coions, Fe(III), Cu(II), Ni(II), and Na^+. The results show no detectable amount of palladium found in all the aqueous solutions tested after 1 h of contact with the feather.

The different affinities of metal ions for binding to the feather can be used to develop a scheme whereby metal ions can be removed from solutions and can be selectively recovered. To demonstrate this, a solution that contained mixture of palladium ($1 \times 10^{-4}M$) and 10 times more (by mol) Cu(II) at pH 2.0 was applied to a column packed with feather powder. Copper ions eluted freely through the column, and palladium was retained completely. The result suggested that selective separation and recovery of precious metal ions may be possible. To confirm this, an aqua regia digestive solution of anode slime (Au: 0.4749, Ag: 9.4389, Cu: 0.7700, Se: 5.4, Pb: 46.17, and Pd: 0.0183 wt%) was charged on a column. Eluting solution was simply prepared by diluting with 10 times more (by volume) distilled water to the aqua regia solution. Figure 6 shows the elution profile of gold and palladium. The results suggested that precious metals can be separated and collected by feather biosorption.

The identities of the functional groups responsible for metal ion binding to the chicken feather are not known at this time. From the amino acid composition, sulfhydryl groups are involved in the binding for metal, but they are not the only groups responsible for precious metal binding. Precious metal ions have larger ionic radii than the coions tested in this research. This could conceivably be a part of the reason why they are so selectively sorbed from a solution of mixed cation. Further works are necessary to investigate the regeneration and multiple reuse potential of the biosorbent in many subsequent application cycles. Also further experiments are in progress to characterize for the binding sites and mechanisms of the binding of the precious metal ions. Whatever the nature of the binding sites, C-feather has a high affinity for the binding of precious metal ions.

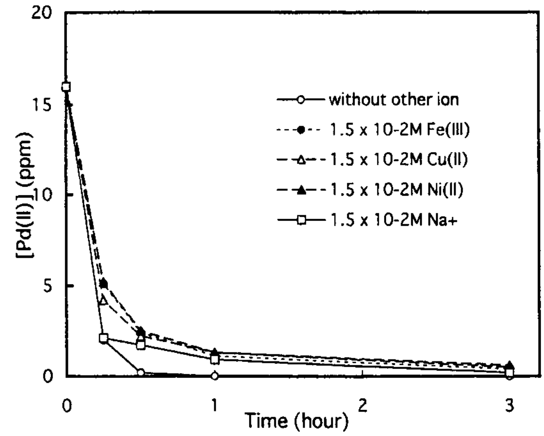

Fig. 5. Relationships between Pd(II) concentration and soaking times treated by batch method from the dilute Pd(II) solution in the presence of 100 times more (by mol) of cometal ions. Initial Pd(II) concentration and volume: 1.5 × $10^{-4}M$ and 20 mL. Feather: 50 mg, pH: 2.0 temp.: 25°C.

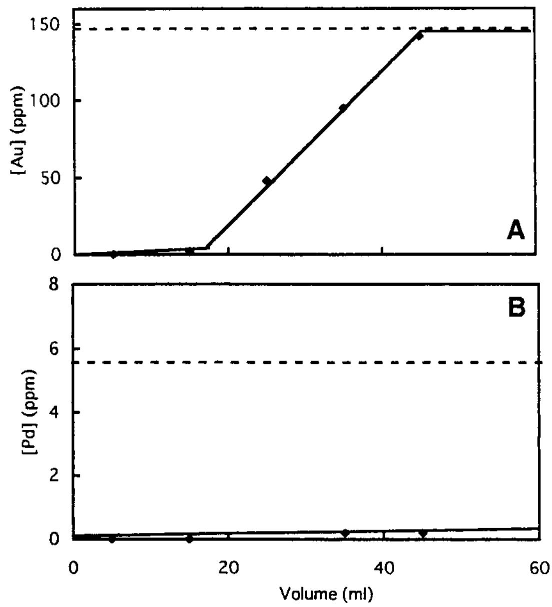

Fig. 6. Elution profiles of precious metal ions by minicolumn of the aqua regia solution of anod slime. **(A)** au, **(B)** pd. Anode slime was digested with three-fold increase (w/v) of aqua regia, then aqua regia solution was diluted 10-fold increase with water. Dilute solution was charged to feather minicolumn (5 × 30 mm: P 115 mg of feather powder). pH was not adjusted. -------: Initial concentration of Au and Pd.

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