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ARTICLE

A Facile, Selective, High Recovery System for Precious Metal Based on Complexation between Melamine and Cyanuric Acid

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We developed a facile, selective, high recovery system for precious metal based on complexation between melamine and cyanuric acid (denoted as MC) through hydrogen bonding. The addition of melamine to an aqueous solution of metal ions allows for homogeneous coordination to metal ions with high efficiency at a high rate. After coordination, subsequent addition of cyanuric acid to the metal-melamine complexes results in precipitation of metal-MC complex, which can be separated by filtration. The recovery of Pd^{II} using MC system was fast and the recovery efficiency was greater than 90% within 1 min. The maximum amount of Pd recovered by the MC system (0.595 g_{Pd}/g_{MC}) was greater than other materials in the literature. The system was also capable of selective recovery of Pd^{II} from other metal solutions. Pd recovered by the MC complex could be separated quantitatively by reductive treatment, and the MC system was recyclable at least 4 times. This system is therefore promising as a selective and high recovery system for precious metals.

1. Introduction

Precious metals (in other words, 'rare metals') such as Pd, Pt, Rh, Nd, and Dy are globally scarce, and for applications in which they are utilized, it is often difficult to find suitable alternatives. For example, precious metals are essential for high-tech industries such as auto mobiles, digital consumer electronics, and ICT devices.^{1,2} The demand for precious metals, known as the 'vitamins of industry', is increasing in line with the development of such industries. However, due to weak supply, the international price of precious metals has increased markedly. Therefore, the efficient recovery of precious metals from nature, wastewater, and discarded high-tech products has been of increasing importance both in terms of ensuring their supply, and the general desirability of resource recycling and environmental sustainability.

Conventional methods for the recovery of metals from water and wastewater include reduction,³ oxidation,⁴ solvent extraction,^{5,6} precipitation,^{7,8} and adsorption.⁹⁻¹¹ Adsorption using polymer sorbents is one of the most suitable techniques in the recovery of metals due to its low cost, safety, and high efficiency.^{12,13} Various sorbents have been developed and are now commercially available as metal scavengers,⁹⁻¹³ however, because nearly all polymers are insoluble in aqueous solutions of metal ions, adsorption must proceed heterogeneously, resulting in low recovery amounts and rates, which represent a hurdle to practical use.

To solve this problem, we developed a facile, high-recovery material for precious metals based on a polymer consisting of thiocarbonyl groups for metal-complexation groups and amino groups as water-soluble groups.¹⁴ Because the polymer is soluble in aqueous solutions of metal ion, complexation proceeds

homogeneously and efficiently. As complexation progresses, cross-linking takes place between the complexation groups and the metal ions, precipitating the polymer complex, which can be separated by filtration. Good solubility in aqueous solution allows for efficient recovery, providing a maximum Pd^{II} recovery amount (0.508 g_{Pd}/g_{polymer}) greater than those for other polymers reported in the literature. However, although selectivity from a mixture of metal ions in low-concentration solution is essential in practical use, this polymer shows a low selectivity, because the amino groups also contribute to metal complexation. Furthermore, the metal-coordinated polymer cannot be recovered from a low-concentration solution due to the relative lack of cross-linking points between complexation groups and metals. Additionally, synthesis of the polymer involves a cumbersome process and toxic reagents. These points represent a serious hurdle to practical use for metal recovery.

In this article, we describe a new recovery system which solves the problems detailed above while retaining the merits of the system. Our new system involves the utilization of a ligand (i.e., melamine), for recovery of metals. Melamine is known to associate with cyanuric acid through hydrogen bonding, affording a 1:1 complex of melamine and cyanuric acid (denoted as MC complex).^{15,16} In this study, we utilized the complexation of melamine and cyanuric acid for recovery of precious metals. Fig. 1 shows a schematic representation of our design. The addition of melamine to an aqueous solution of metal ions results in homogeneous coordination to metal ions with high efficiency and at a high rate. After coordination, subsequent addition of cyanuric acid to the metal-melamine complexes results in precipitation of a metal-MC complex, which can be easily separated by filtration. Compared with

metal recovery by polymers, our system using ligands has significant advantages: 1) Many water-soluble ligands are present, allowing homogeneous and efficient coordination to metal ions; 2) the proportion of coordination sites in the molecular structure is greater than that for a polymer, resulting in a larger recovery amount per unit weight; 3) the selection of an appropriate ligand suitable to a target metal can result in the construction of a number of selective recovery systems. Since the melamine-coordinated metals are precipitated through hydrogen bonding with cyanuric acid, this system can be used for metal recovery from a low-concentration solution. To the best of our knowledge, utilization of ligands for recovery of metals in aqueous solution is a first example. It represents a solution to the aforementioned problems and is a simple and efficient recovery system for precious metals.

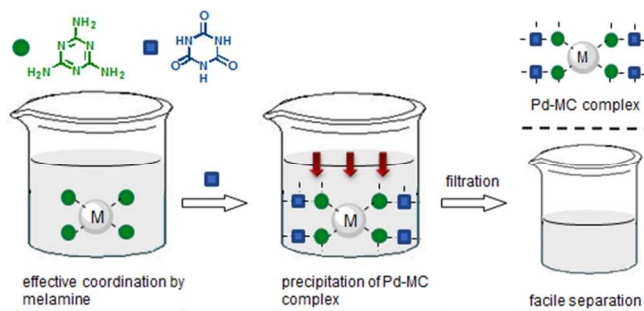


Fig. 1 Schematic representation of facile, selective, high recovery system based on complexation between melamine and cyanuric acid.

2. Experimental Section

2.1 Materials

Melamine (Tokyo Kasei Kogyo, >98.0 %) and cyanuric acid (Tokyo Kasei Kogyo, >98.0 %) were commercially available and used as received. Sodium tetrachloropalladate (II) (Na_2PdCl_4 , Tokyo Kasei Kogyo, >98.0 %), manganese (II) chloride tetrahydrate (Kanto Chemical, >99.0 %), iron (III) chloride hexahydrate (Wako Pure Chemical, >99.0 %), cobalt (II) chloride hexahydrate (Kanto Chemical, >99.0 %), nickel (II) chloride hexahydrate (Kanto Chemical, >98.0 %), copper (II) chloride (Wako Pure Chemical, >95.0 %), zinc (II) chloride, sodium tetrachloroaurate (III) dihydrate (Wako Pure Chemical, >95.0 %), and hydrogen hexachloroplatinate (IV) (Wako Pure Chemical, >98.5 %) were commercially available and used as received. Hydrochloric acid (Wako Pure Chemical, 35.0–37.0 %), sodium hydroxide (Wako Pure Chemical, >97.0 %), and sodium boron hydride (Wako Pure Chemical, >90.0 %) were commercially available and used as received.

2.2 Instruments

Flame atomic absorption spectrometry was carried out using a Hitachi polarized zeeman atomic absorption spectrometer (AAS) Z-2310. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was carried out using a model ICP575II Nippon Jarrell-Ash instrument. ^{13}C cross-polarization magnetic angle scanning (CP-MAS) NMR measurements were performed using a Bruker DSX300 spectrometer operating at 75 MHz equipped with a CP-MAS probe. IR spectra were recorded with a Jasco FT/IR-5000 spectrometer and the values were given in cm^{-1} . X-ray photoelectron spectroscopy (XPS) spectrum was measured with a KRATOS AXIS-NOVA

instrument. Wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) measurements were carried out using the beamline BL40B2 at the synchrotron radiation facility Spring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan). The wavelength (λ) of the synchrotron beam was 1.00 angstrom. Camera lengths were 51.4 mm for WAXD and 2220 mm for SAXS measurements. Scanning electron microscopy (SEM) was performed using a Hitachi S3000N instrument at an acceleration voltage of 1.5 kV. Energy dispersive X-ray analysis (EDX/SEM) measurement was carried out with Horiba EX-200K/Hitachi S3000N instruments. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was carried out using a model ICP575II Nippon Jarrell-Ash instrument.

2.3 Metal recovery (typical procedure)

Melamine (40 mg, 0.31 mmol) was added into a 0.2 mM of an aqueous sodium tetrachloropalladate (II) solution (20 mL, pH 5.5), and stirred at ambient temperature for 1 h. An addition of an aqueous 15.5 mM cyanuric acid solution (20 mL, pH 5.5) into the resulting mixture allowed an instant precipitation. The resulting precipitation was separated by filtration (pore sized of filter; 0.45 μm), and an aliquot (0.250 mL) of the filtrate was removed for sampling. After appropriate dilution, the metal concentration in the solution was determined by AAS. The recovery amount was calculated based on the following equation:

$$\text{Recovery amount (g}_{\text{metal}}/\text{g}_{\text{MC}}) = M \text{ of metal} \times \text{recovery amount (mmol)}/\text{weights of melamine and cyanuric acid used (g)}$$

Anal. Found for Pd-MC complex: C, 27.99; H, 3.73; N, 48.43.

2.4 Competitive Recovery of Metal Ions

Melamine (40 mg, 0.31 mmol) was added into a mixed solution (20 mL, pH 5.5) containing 10 ppm of each metal ion, namely, Pd^{II} , Mn^{II} , Co^{II} , Ni^{II} , Cu^{II} , and Zn^{II} metal ions, and stirred at ambient temperature for 1 h. An addition of an aqueous 15.5 mM cyanuric acid solution (20 mL, pH 5.5) into the resulting mixture allowed an instant precipitation. The resulting precipitation was separated by filtration (pore size of filter; 0.45 μm), and the filtrate was analyzed using ICP-AES to determine the concentration of unrecovered metal ions.

2.5 Separation of Pd from Pd-MC Complex

To examine the separation of Pd from Pd-MC complex, recovery experiment was first conducted. Melamine (40.0 mg, 0.310 mmol) was added into a 0.200 mM of aqueous sodium tetrachloropalladate (II) solution (20.0 mL, pH 5.5), and stirred at ambient temperature for 1 h. An addition of 15.5 mM aqueous cyanuric acid solution (20.0 mL, pH 5.5) into the resulting mixture allowed an instant precipitation, which was separated by filtration (pore size of filter; 0.450 μm) and the concentration of Pd^{II} in the filtrate was measured by AAS to determine the recovery amount (1.96×10^{-2} mmol). The precipitates were washed with distilled water and they were added into a 0.200 M aqueous NaOH solution (7.00 mL) to dissolve them. An addition of sodium boron hydride (0.200 g, 5.29 mmol) to the mixture and stirring for 15 min provide the precipitation (black powder, Pd). The resulting precipitates were separated by filtration (pore size of filter; 0.450 μm) and dried *in vacuo*.

2.6 Recycle of MC Complex for Pd^{II} recovery

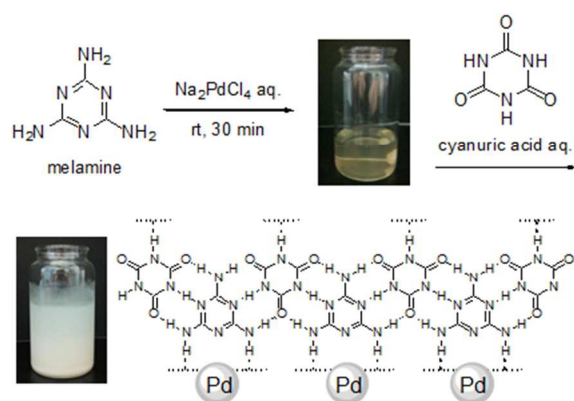
The filtrate obtained in the above section was neutralized by an aqueous 1.00 M HCl solution, precipitating the MC complexes.

The separated MC complexes were dissolved in a mixed aqueous solution of 0.200 mM Pd^{II} and 1.00 M NaOH (20.0 mL), and the mixture was stirred at ambient temperature for 1 h. Subsequent neutralization by aqueous 1.00 M HCl solution precipitated the Pd-MC complexes, which were separated by filtration and dried in *vacuo* for the next separation of Pd.

3. Results and Discussion

3.1 Metal recovery behavior of MC system.

We initially investigated the recovery of Pd, a metal that is the subject of increasing attention due to its application in automotive catalysis,¹⁷ electronic devices,¹⁸ dental materials,¹⁹ and accessories.²⁰ Melamine (40 mg, 0.31 mmol) was added to a 0.2 mM aqueous solution of sodium tetrachloropalladate(II) (Na₂PdCl₄, 0.2mM, 20 mL, pH 5.5), and the mixture was stirred at ambient temperature (Scheme 1). A subsequent addition of a 15.5 mM aqueous solution of cyanuric acid (20 mL, equimolar with melamine, pH 5.5) to the mixture resulted in instant precipitation. The precipitate was separated by filtration, and the concentration of Pd^{II} in the filtrate was measured by atomic absorption spectrometry (AAS), yielding a high recovery efficiency (98%). This demonstrated that melamine coordinates efficiently to Pd^{II}, and the coordinated Pd in the MC complex can be separated by filtration.



Scheme 1. Recovery of Pd^{II} by MC complexation

The resulting Pd-MC complex was characterized structurally. Elemental analysis of the complex showed that the ratio of melamine to cyanuric acid was 1:1. Based on this result and the amount of Pd^{II} recovered, as determined by AAS, the ratio of Pd/melamine/cyanuric acid was 1:82:82. To examine the coordination site, the ¹³C CP-MAS (cross-polarization magnetic angle scanning) NMR spectra before and after the recovery were measured (Fig. 2). The NMR signal corresponding to the imine group in melamine around 163 ppm was shifted to the higher magnetic field, while the signal corresponding to the carbonyl group in cyanuric acid around 153 ppm was hardly shifted. IR spectra before and after the recovery (recovery amount: 0.122 g_{Pd}/g_{MC} and 0.264 g_{Pd}/g_{MC}; MC refers to the amount used for recovery) showed the similar tendency (Table 1, Figure S1). The absorption peak corresponding to C=N (1536 cm⁻¹) was shifted, while those corresponding to NH₂ (3392.6 cm⁻¹) and C=O (1736.6 cm⁻¹) were shifted only slightly. These results indicated that the imine groups in melamine coordinate to Pd^{II} predominantly. This tendency is well consistent with the nucleophilicity: the nucleophilicity of the imine group in melamine is higher than those of the primary

amine group in melamine and the carbonyl group in cyanuric acid. XPS analysis of the MC complex showed a Pd3d_{5/2} peak at 337.9 eV, which is assigned to Pd^{II} species (Fig. 3A). EDX/SEM measurement showed the presence of Pd and Cl species (Fig. 3B). The Cl species was ascribed to Na₂PdCl₄; therefore, Pd^{II}Cl₂ is contained in the complex. Wide-angle X-ray diffraction (WAXD) measurements of the MC and Pd-MC complexes showed peaks, indicating that both complexes were crystalline (Fig. S2). The reflection peak intensities were reduced for Pd-MC complex, suggesting that the crystallinity decreased with the introduction of Pd ions into the complex. Small-angle X-ray scattering (SAXS) measurements of the MC and Pd-MC complexes showed no peaks, demonstrating the absence of a regular structural pattern in the nanometer region (Fig. S3). The WAXD results were consistent with the SEM analysis: the homogeneity of needle crystal in the Pd-MC complex decreased compared to the MC complex (Fig. 4).

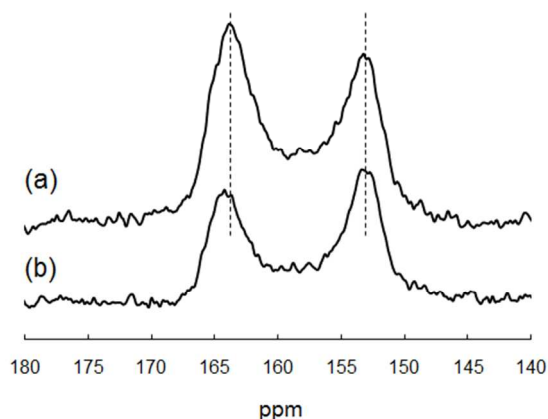


Fig. 2 ¹³C CP-MAS NMR spectra (a) before the recovery and (b) after the recovery (recovery amount: 0.160 g_{Pd}/g_{MC}).

Table 1. IR peak positions of Pd-MC complexes with different recovery amounts.

entry	recovery amount of Pd ^{II} (g _{Pd} /g _{MC})	stretching vibration of NH ₂ (cm ⁻¹)	stretching vibration of C=O (cm ⁻¹)	stretching vibration of triazine ring (cm ⁻¹)
1	0	3392.6	1736.6	1536.3
2	0.122	3393.4	1736.2	1537.2
3	0.264	3393.4	1736.5	1541.1
shift (cm ⁻¹)	–	+0.8	-0.1	+4.8

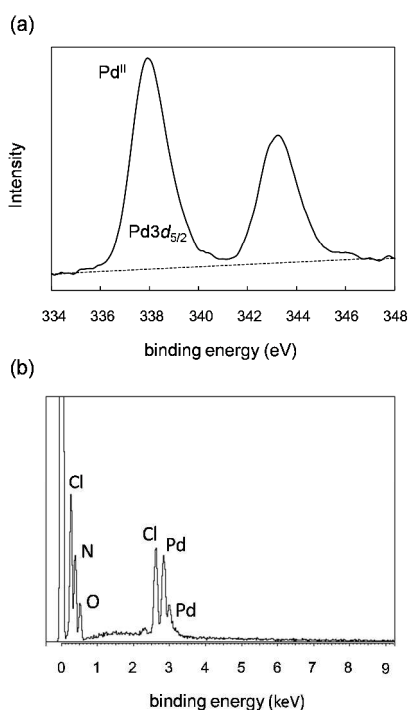


Fig. 3 (A) XPS spectrum of Pd-MC complex (recovery amount: 0.122 g_{Pd}/g_{MC}). (B) EDX spectrum of Pd-MC complex (recovery amount: 0.122 g_{Pd}/g_{MC}).

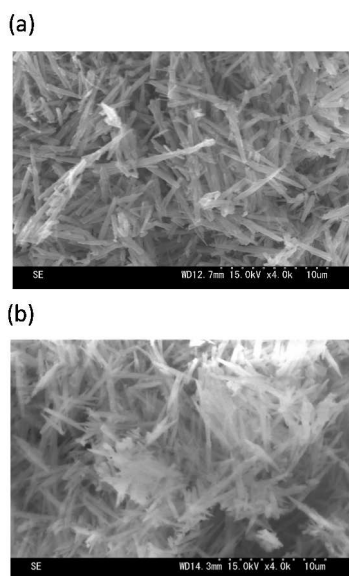


Fig. 4 SEM images of (A) MC complex. (B) Pd-MC complex. Prepared conditions: melamine: 40 mg (0.31 mmol); aqueous solution of Pd^{II}: 20 mL (0.2 mM); aqueous solution of cyanuric acid: 20 mL (15.5 mM, molar equimolar to melamine); ambient temperature; reaction time: 1 h.

MC complexation is affected by pH, because acidic and basic conditions may cause the dissociation of hydrogen bonds. Accordingly, we examined the effect of pH on the recovery of Pd^{II} through MC complexation (Fig. 5A). Under acidic conditions (pH 1 and 3), the recovery efficiency decreased due

to the scission of hydrogen bonds between melamine and cyanuric acid, leading to low precipitation of the Pd-MC complex. Also, under basic conditions (pH 7 and 9), the recovery efficiency and precipitation amounts of the Pd-MC complexes were slightly lower than those at pH 5.5. Therefore, the subsequent experiments were conducted at pH 5.5.

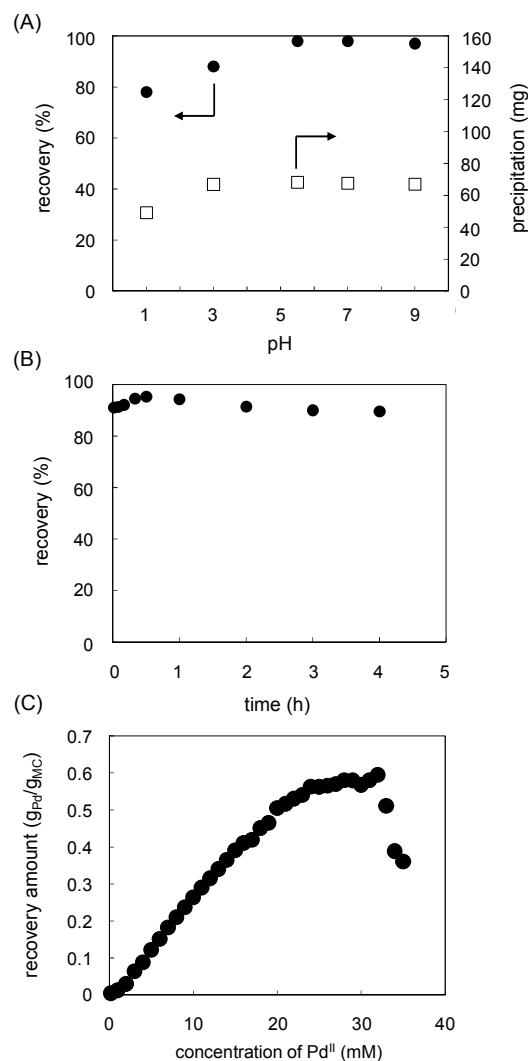


Fig. 5 (A) Effect of pH on recovery of Pd^{II} by MC complexation. Conditions: melamine: 40 mg (0.31 mmol); aqueous solution of Pd^{II}: 20 mL (0.2 mM); aqueous solution of cyanuric acid: 20 mL (15.5 mM, molar equimolar to melamine); ambient temperature; reaction time: 1 h. (B) Changes in recovery of Pd^{II} as a function of mixing time. Conditions: melamine: 40 mg (0.31 mmol); aqueous solution of Pd^{II}: 20 mL (0.2 mM, pH 5.5); aqueous solution of cyanuric acid: 20 mL (15.5 mM, molar equimolar to melamine); ambient temperature; reaction time: 1 h. (C) Recovery amounts as a function of initial concentration of Pd^{II}. Conditions: melamine: 40 mg (0.31 mmol); aqueous solution of Pd^{II}: 20 mL (appropriate concentration, pH 5.5); aqueous solution of cyanuric acid: 20 mL (15.5 mM, equimolar to melamine); ambient temperature; reaction time: 1 h.

Because the homogeneous recovery system is expected to achieve recovery at a high rate, the kinetics was examined. The efficiency of Pd^{II} recovery by MC complexation was greater than 90% within 1 min, but a slight decrease in the recovery efficiency was observed after 30 min (Fig. 5B). This high rate is one of the significant advantages of this system for use in wastewater treatment processes. The experimental kinetic data were fitted with a pseudo-first-order kinetic equation:

$$\log(Q_e - Q_t) = \log Q_e - kt/2.303 \quad (1)$$

where Q_e is the equilibrium recovery amount of Pd^{II} (g_{Pd}/g_{MC}), Q_t is the recovery amount (g_{Pd}/g_{MC}) at time t , and k is the rate constant (h^{-1}). For the recovery of Pd^{II} by MC complexation, k was estimated to be $3.412 h^{-1}$ (correlation coefficient $R^2 = 0.9841$). The slight decrease in the recovery efficiency after 30 min was ascribed to the formation of melamine aggregates around Pd^{II} ions, which hinders the formation of a complex with cyanuric acid.

The effect of the initial concentration of Pd^{II} on the recovery amount was examined to determine the maximum recovery amount in the MC system. As shown in Fig. 5C, the recovery amount increased with increasing Pd^{II} concentration, reaching a maximum value around 32 mM, followed by a decrease. Based on the maximum value, the maximum recovery amount for the MC system was evaluated as $0.595 g_{Pd}/g_{MC}$. Table 2 compares the maximum recovery amounts for different types of recovery material. The MC system had a higher recovery amount (Q_{max}) than any other material reported in the literature we obtained. The decrease in the recovery amount at more than 32 mM was attributed to excess coordination of Pd^{II} ions around melamine, which inhibited the formation of complexes with cyanuric acid. The recovery of Au^{III} and Pt^{IV} was also examined. In each case, melamine was added to an aqueous solution of the metal ion (32 mM, which is optimum concentration of Pd^{II} recovery), and stirred for 30 min at ambient temperature. Subsequent addition of cyanuric acid aqueous solution resulted in precipitation of the complex. The recovery amounts of Au^{III} and Pt^{IV} were very high ($0.500 g_{Au}/g_{MC}$ and $0.394 g_{Pt}/g_{MC}$, respectively).

Table 2. Comparison of the maximum recovery capacities of palladium ions on different recovery materials.

entry	recovery material	Q_{max} ($g_{Pd}/g_{poly.}$)	ref.
1	PA-lignin	0.010	24
2	Thiourea-modified MA resin	0.015	25
3	Amberlite IRC 718	0.059	26
4	Lysin modified chitosan	0.101	27
5	Glycine modified chitosan	0.120	27
6	Glutaraldehyde modified chitosan	0.180	28
7	Dimethylamine-modified paper	0.224	29
8	Thiourea modified chitosan	0.278	30
9	Amine-modified polystyrene	0.280	31
10	Rubanic acid modified chitosan	0.352	30
11	Thiourea-modified Polyallylamine	0.508	14, our work
12	MC system	0.595	this work

The MC system showed high selectivity for Pd^{II} from a mixture of metal ions in low concentration solution. To demonstrate this, competitive recovery of Pd^{II} from a mixture of metal ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, each at 10 ppm) was investigated. The MC system selectively recovered Pd^{II}, leaving the other metal ions almost unrecovered (Fig. 6). This is explained by the hard soft acid base (HSAB) principle. The tertiary amine group in melamine is categorized as a soft base, which preferentially coordinates to a soft acid such as Pd^{II}.²¹⁻²³ On the other hand, Mn^{II} and Co^{II} are hard acids, and Ni^{II}, Cu^{II}, Zn^{II} are borderline acids, which are not preferentially coordinated by melamine. These results showed that MC system acts as a selective recovery system for soft metal ions such as platinum group metals.

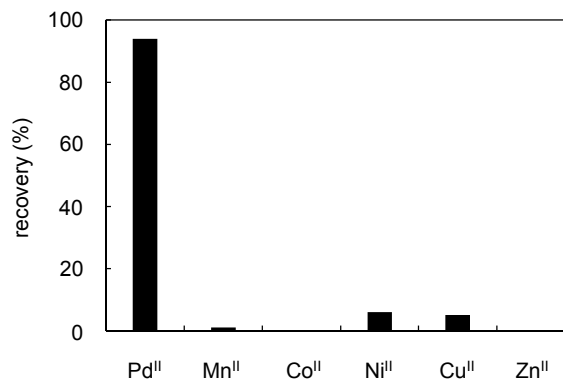


Fig. 6 Competitive recovery of metal ions. Conditions: metal ion aqueous solution (20 mL, pH 5.5, each metal ion at 10 ppm); melamine 40 mg (0.31 mmol); aqueous solution of cyanuric acid 20 mL (15.5 mM, molar equivalent to melamine); ambient temperature; reaction time = 1 h.

3.2 Separation of Pd and reuse of MC system.

In practical use, Pd recovered through an MC complex must be quantitatively separated, allowing the MC system to be reused. Initially, separation of Pd from the MC complexes was examined (Fig. S4). A Pd-MC complex whose recovery amount had been confirmed by AAS was added to a 0.2 M aqueous solution of NaOH, resulting in dissolution of the complex via hydrogen bond scission (Fig. S4A). Subsequent reductive treatment with NaBH₄ precipitated the reduced Pd, which was separated by filtration (Fig. S4D). That the precipitate was elemental Pd was confirmed by XRD spectroscopy (Fig. S5). In order to recover the MC complexes, the filtrate was neutralized with a 1.0 M aqueous solution of HCl, resulting in precipitation of the MC complex via the regeneration of hydrogen bonds (Fig. S4C). The separated MC complex was recycled for further use in Pd^{II} recovery (Fig. S4E), because melamine and cyanuric acid could not be separated. The MC complexes were dissolved in a mixed solution of 0.2 mM Pd^{II} and 1.0 M HCl aq., and the mixture was stirred at ambient temperature for 1 h. Subsequent neutralization with 1.0 M HCl aq. resulted in precipitation of the Pd-MC complex, which was treated with NaBH₄ in 0.2 M NaOH aq. to separate the reduced Pd. The recyclability of the MC complex is summarized in Table 3. The method could be used for effective separation of Pd from the MC complex; the separation of Pd was quantitative over five cycles. The recovery capacity was almost unaffected by the cycles, which means that the MC system can be used effectively over at least five cycles, adding more economic and environmental benefit to the process.

of metal recovery. This recovery system possesses essential recoverabilities for precious metal recovery, i.e., high recovery, high rate, selectivity, and recyclability.

Table 3. Recovery and separation of Pd in MC system.^a

cycle	Pd ^{II} recovery (mmol) ^b	Pd separation (mmol) ^b	recovery (%) ^c
1	1.96×10^{-2}	1.96×10^{-2}	>99
2	1.90×10^{-2}	1.90×10^{-2}	>99
3	1.87×10^{-2}	1.87×10^{-2}	>99
4	1.86×10^{-2}	1.86×10^{-2}	>99
5	1.74×10^{-2}	1.72×10^{-2}	99

^aRecovery conditions: melamine: 40 mg (0.31 mmol); aqueous solution of Pd^{II}: 20 mL (0.2 mM); aqueous solution of cyanuric acid: 20 mL (15.5 mM, molar equimolar to melamine); ambient temperature; reaction time: 1 h. Separation conditions: NaBH₄: 200 mg (5.29 mmol); 0.200 M aqueous NaOH solution (7.00 mL). ^bDetermined by AAS analysis. ^cPd^{II} recovery (mmol)/Pd separation (mmol).

4. Conclusions

In conclusion, we have successfully developed a facile, selective, high recovery system for precious metal based on MC complexation. Pd^{II} recovery was fast and the recovery efficiency was greater than 90% within 1 min. The maximum amount of Pd recovered by the MC system (0.595 g_{Pd}/g_{MC}) was greater than other materials reported in the literature. The system was also capable of selective recovery of Pd^{II} from other metal solutions. Pd recovered by the MC complex could be separated quantitatively by reductive treatment, and the MC system was recyclable at least 4 times. This system is therefore promising as a selective, high recovery system for precious metals. We are now challenging to develop various selective recovery systems by varying the combination of ligands.

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