

## Research Article

# Synthesis of Hydrophilic Sulfur-Containing Adsorbents for Noble Metals Having Thiocarbonyl Group Based on a Methacrylate Bearing Dithiocarbonate Moieties

Haruki Kinemuchi and Bungo Ochiai 

Department of Chemistry and Chemical Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

Correspondence should be addressed to Bungo Ochiai; [ochiai@yz.yamagata-u.ac.jp](mailto:ochiai@yz.yamagata-u.ac.jp)

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Novel hydrophilic sulfur-containing adsorbents for noble metals were prepared by the radical terpolymerization of a methacrylate bearing dithiocarbonate moieties (DTCMMA), hydrophilic monomers, and a cross-linker. The resulting adsorbents efficiently and selectively adsorbed noble metals (Au, Ag, and Pd) from various multielement aqueous solutions at room temperature owing to the thiocarbonyl group having high affinity toward noble metals. The metal adsorption by the adsorbents was proceeded by simple mixing followed by filtration. The noble metal selectivity of the adsorbent obtained from DTCMMA and *N*-isopropylacrylamide was higher than that of the adsorbent obtained from DTCMMA and *N,N*-dimethylacrylamide due to the lower nonspecific adsorption.

## 1. Introduction

Noble metals such as Au, Pd, and Ag are essential in the modern life and applied in various fields such as jewelry [1], synthetic catalysts [2–5], and materials for electronic industry [6]. The amounts of noble metals in mines are inherently very low, and the recent increase in their use is shortening their reserves to production ratios. Therefore, recovery and reuse of these metals from various used materials is very essential. For example, the recycling from industrial wastewater and urban mines is promising owing to the high amounts and contents.

Typical methods for collection of noble metals from water are solvent extraction [7–12], adsorption [13–31], and electrochemical processes [32]. The collection by adsorption is advantageous owing to its low cost, safety, and high efficiency. By contrast, solvent extraction requires organic solvents, lots of eluents, and in some cases supercritical eluents to attain high extraction efficiency. As a result, tremendous amounts of wastes are produced. Electrochemical processes require a troublesome procedure to scrape off the deposited metals on the electrode. Adsorbents bearing sulfur substituents are one

of the most examined adsorption agents for noble metals owing to the excellent affinity of sulfur toward soft cations due to the soft Lewis basicity and the facileness of its introduction into various organic structures [30, 33–37]. Dithiocarbamic acids are the most popular sulfur adsorbents for heavy metals [38]. Dithiocarbamic acids effectively adsorb various metals, but the selectivity of the metal adsorption is low. The emission of toxic carbon disulfide is also a severe problem, although the emission rate is slow [39]. Adsorbents based on thiols and thiocarbonyl moieties are advantageous by eliminating the possibility of the leakage of sulfur compounds such as carbon disulfide. Thiols are effective scavengers for various metals by forming stable thiolates [40–46]. However, thiol groups are susceptible to oxygen-converting thiols into disulfides via oxidative coupling [44]. Thiocarbonyl moieties such as thioamide [26–30, 47–53], thiourethane [31, 33, 35, 37], and thiourea [11, 25, 54–60] have also been examined as stable adsorbents. We also have found that a polymer bearing *N,N*-dialkylthiourethane moieties has high adsorption ability to Pd and Au, but the adsorption from aqueous solutions only proceeded in the presence of organic solvents

such as chloroform due to the hydrophobic nature of the backbone [35]. Although these adsorbents bearing thiocarbonyl moieties certainly adsorb metals from aqueous or organic solvents, the effect of the structures adjacent to thiocarbonyl groups is still unclear.

In this study, we designed a hydrophilic adsorbent bearing thiocarbonyl moieties for selective adsorption of noble metals in an organic solvent free manner. As the source for thiocarbonyl groups, we focused on a methacrylate bearing dithiocarbonate moieties (5-(methacryloyloxy)methyl-1,3-oxathiolane-2-thione, DTCMMA) [61], which can be prepared via a simple reaction of glycidyl methacrylate with carbon disulfide. In order to adsorb noble metals from water in a facile manner, DTCMMA was copolymerized with hydrophilic monomers and a cross-linker to make the adsorbents swellable and insoluble. Selectivity of the adsorption was evaluated using three solutions containing multiple metal ions.

## 2. Materials and Methods

**2.1. Materials.** DTCMMA was prepared according to the reported procedure [61]. *N*-isopropylacrylamide (NIPAM) (Wako Pure Chemical, >98.0%) was purified by recrystallization from a mixed solvent of diethyl ether and *n*-hexane. *N,N*-dimethylacrylamide (DMAA) (Kanto Chemical, >97.0%) was dried over calcium hydride and distilled under reduced pressure. Dehydrated dimethyl sulfoxide (DMSO) (Wako Pure Chemical, >99.0%), *N,N'*-methylenebisacrylamide (MBAA) (Wako Pure Chemical, >97.0%), 2,2'-azobis(isobutyronitrile) (AIBN) (Tokyo Chemical Industry, >98.0%), palladium(II) chloride (Wako Pure Chemical, >99.0%), anhydrous copper(II) chloride (Wako Pure Chemical, >99.0%), nitric acid (Wako Pure Chemical, concentration: 60–61%), and hydrochloric acid (Kanto Chemical, concentration: 35.0–37.0%) were commercially available and used as received. Multielement solutions containing platinum elements (**A**) (10 mg/L of Sn, Ru, Rh, Pd, Sb, Te, Hf, Ir, Pt, and Au in 10% HCl/1% HNO<sub>3</sub> aq.), containing rare earth elements (**B**) (10 mg/L of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th in 5% HNO<sub>3</sub> aq.), and containing alkali metals, alkali earth metals, typical metals in groups 12–16, Ag, and U (**C**) (10 mg/L of Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, Tl, Pb, Bi, and U in 5% HNO<sub>3</sub> aq.) (PerkinElmer) were used for competitive adsorption experiments.

**2.2. Instruments.** IR spectra were recorded on a HORIBA FT-720 spectrometer. Inductive-coupled plasma mass spectrometry (ICP-MS) measurements were performed on a PerkinElmer ELAN DRC II spectrometer. Operating conditions were as follows: nebulizer gas flow, 0.91–1.01 mL/min; ICP RF power, 1.1 kW; lens voltage, 7.4 V; pulse stage voltage, 900 V; dwell time, 60 ns; sweeps, 3 times; readings per replicate, 3 times; and flow rate, 0.96 mL/min. The dissolution media for ICP-MS measurements of the samples after metal adsorption experiments were coincided with the multielement solutions, namely, 10% HCl aq. for **A**, 5% HNO<sub>3</sub> aq. for **B**, and 5% HNO<sub>3</sub> aq. for **C**.

**2.3. Hydrophilic Sulfur-Containing Adsorbent from DTCMMA and NIPAM (1).** A solution of DTCMMA (96.4 mg, 442 μmol), NIPAM (500 mg, 4.42 mmol), MBAA (6.8 mg, 4.4 μmol), and AIBN (21.8 mg, 133 μmol) in DMSO (3.0 mL) was stirred at 60°C for 24 h under a nitrogen atmosphere. The resulting precipitate was washed with a large amount of methanol and dried under reduced pressure at 50°C to obtain a hydrophilic sulfur-containing adsorbent (**1**) (586 mg, yield = 97.2%). IR spectra (KBr, cm<sup>-1</sup>): 3438 (NH in C(=O)NHCH(CH<sub>3</sub>)<sub>2</sub>), 3303 (NH in C(=O)NHCH<sub>2</sub>), 1730 (C=O in C(=O)OCH<sub>2</sub>), 1657 (C=O in C(=O)NH), and 1192 (C=S).

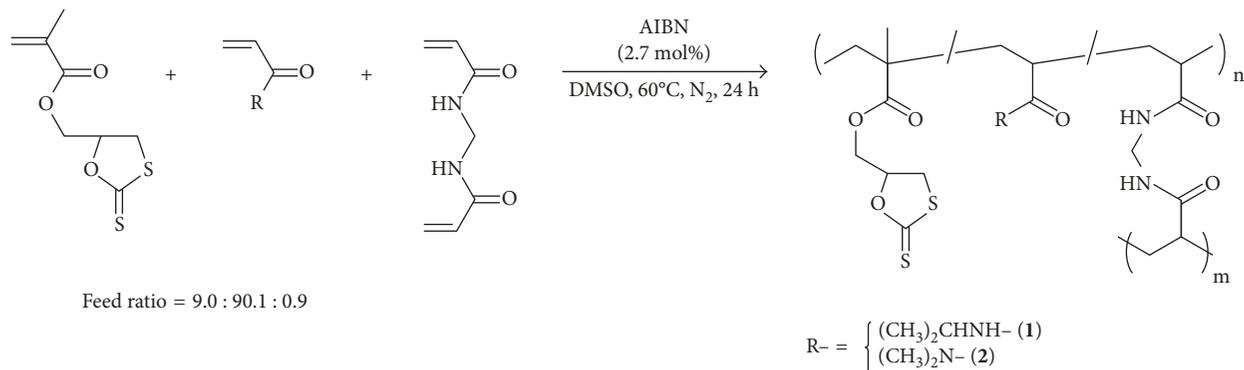
**2.4. Hydrophilic Sulfur-Containing Adsorbent from DTCMMA and DMAA (2).** A solution of DTCMMA (96.4 mg, 442 μmol), DMAA (438 mg, 4.42 mmol), MBAA (6.8 mg, 4.4 μmol), and AIBN (21.8 mg, 133 μmol) in DMSO (3.0 mL) was stirred at 60°C for 24 h under a nitrogen atmosphere. The resulting precipitate was washed with a large amount of methanol and dried under reduced pressure at 50°C to obtain a hydrophilic sulfur-containing adsorbent (**2**) (524 mg, yield = 96.8%). IR spectra (KBr, cm<sup>-1</sup>): 3473 (NH in C(=O)NH), 1732 (C=O in C(=O)OCH<sub>2</sub>), 1631 (C=O in C(=O)N(CH<sub>3</sub>)<sub>2</sub>, C(=O)NH), and 1192 (C=S).

**2.5. Metal Adsorption from Multielement Solution with Hydrophilic Sulfur-Containing Adsorbents (Typical Procedure).** A multielement solution (2.0 mL, 10 mg/L of metal ions) and a hydrophilic sulfur-containing adsorbent ([C=S]/[total metal] = 4.5/1) were stirred in a glass vial at room temperature for 1.5 h. Then, the adsorbent was removed by filtration and washed 2 times with 100 mL amounts of water. The amounts of adsorbed metals were calculated from the concentrations of metals in the filtrate measured by ICP-MS.

**2.6. Competitive Metal Adsorption from Pd/Cu Mixed Solution with 2 (Typical Procedure).** CuCl<sub>2</sub> (54.9 mg/mL) in 1 N HCl solution (2.0 mL), PdCl<sub>2</sub> (0.36 mg/mL) in 1 N HCl solution (2.0 mL), and adsorbent **2** (50.0 mg) were added to a glass vial and stirred at room temperature for 1.5 h. Then, the adsorbent was removed by filtration and washed 2 times with 100 mL of water. The amounts of adsorbed metals were calculated from the concentrations of metals in the filtrate measured by ICP-MS.

## 3. Results and Discussion

**3.1. Synthesis of Hydrophilic Sulfur-Containing Adsorbents.** Hydrophilic sulfur-containing adsorbents were synthesized by the radical terpolymerization of DTCMMA, hydrophilic monomer NIPAM or DMAA, and a cross-linker MBAA (feed ratio, [DTCMMA]<sub>0</sub>: [hydrophilic monomer]<sub>0</sub>: [MBAA]<sub>0</sub> = 9.0:90.1:0.90) in DMSO at 60°C using AIBN (2.7 mol%) under a nitrogen atmosphere (Scheme 1). Products insoluble in common organic solvents and water were obtained in excellent yields. The products obtained using NIPAM and DMAA were denoted as **1** and **2**,



SCHEME 1: Synthesis of hydrophilic sulfur-containing adsorbents 1 and 2.

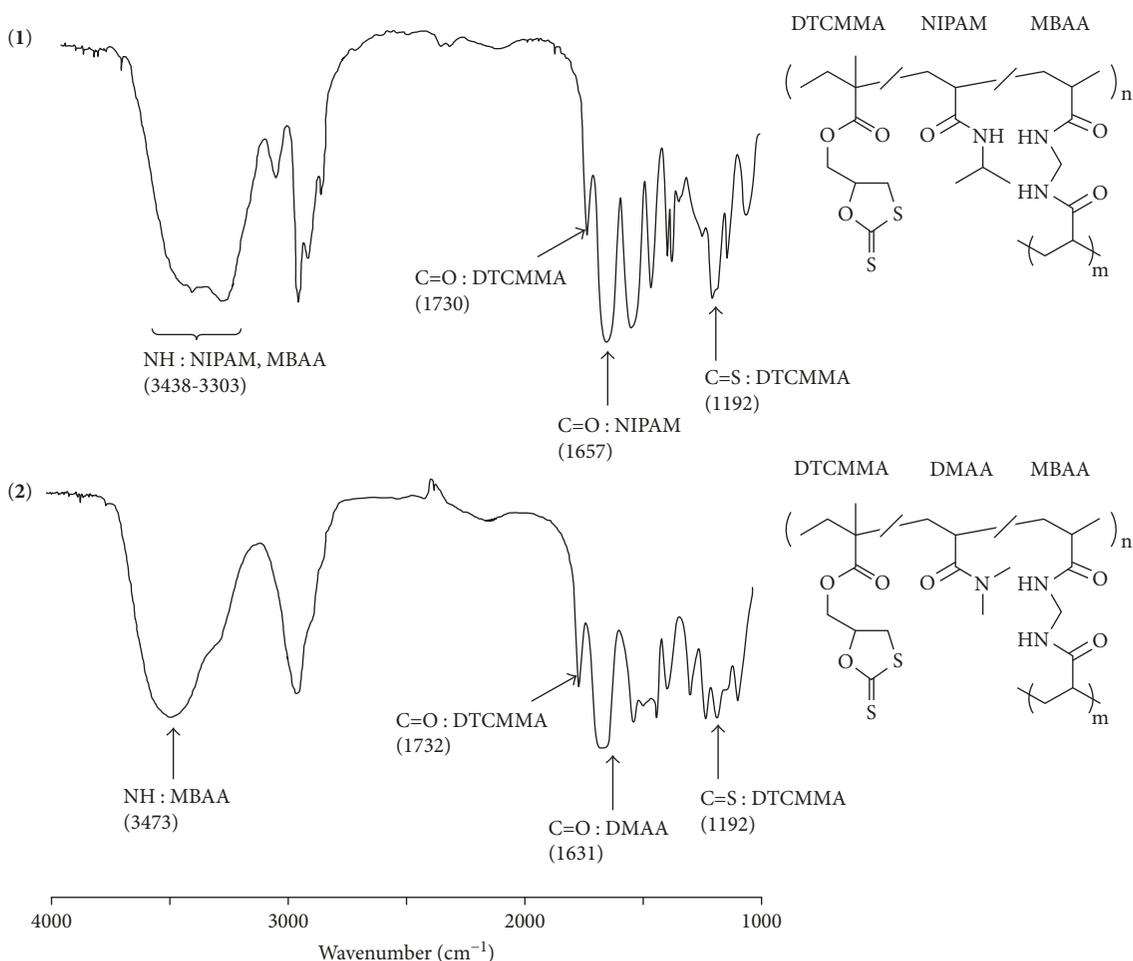


FIGURE 1: FT-IR spectra of hydrophilic sulfur-containing adsorbents (1) and (2).

respectively. The products could be swelled by water to yield soft gels. The structures were confirmed by FT-IR spectroscopic analysis (Figure 1). Characteristic peaks assignable to C=S moieties in the DTCMMA unit were observed at  $1192\text{ cm}^{-1}$  [60]. Peaks assignable to the amide moieties and carbonyl group in the units originating from the hydrophilic monomers and MBAA were also observed (1:  $3438\text{ cm}^{-1}$  for NH in NIPAM,  $3303\text{ cm}^{-1}$  for NH in MBAA,

$1730\text{ cm}^{-1}$  for C=O in DTCMMA, and  $1657\text{ cm}^{-1}$  for C=O in NIPAM; 2:  $3473\text{ cm}^{-1}$  for NH in MBAA,  $1732\text{ cm}^{-1}$  for C=O in DTCMMA, and  $1631\text{ cm}^{-1}$  for C=O in DMAA). The contents of the DTCMMA unit in the hydrophilic sulfur-containing adsorbents were estimated by elemental analysis. The contents of DTCMMA units in 1 and 2 were calculated to be  $68.3\text{ }\mu\text{mol}$  and  $73.0\text{ }\mu\text{mol}$  of DTCMMA units per  $100\text{ mg}$  of the adsorbents, respectively, which almost agreed

with the feed ratio (theoretical values for **1** and **2**: 73.3 and 81.6  $\mu\text{mol}$ ).

**3.2. Metal Adsorption Experiments to Find the Metals Adsorbed by the Hydrophilic Metal Adsorbents Using Multi-element Solutions.** The hydrophilic metal adsorbents were used at the molar ratio of  $[\text{C}=\text{S}]/[\text{total metal}] = 4.5/1$ . The metal adsorption experiments were conducted by dispersing the adsorbents in multi-element solutions, and the adsorbents adsorbing metals were separated by filtration. The amounts of the adsorbed metals were calculated by measuring the amounts of the metals in the filtrates by ICP-MS.

The metal adsorption ratios of some metals were calculated to be negative values, possibly because the apparent metal concentrations after the adsorption increased by uptake of water by the adsorbents resulting in increase in the concentration of metals.

First, a multi-element solution **A** was employed for metal adsorption experiments at room temperature for 1.5 h and 24 h (Figure 2). As a result, Au was adsorbed almost quantitatively by both of the metal adsorbents in 1.5 h. Pd was also adsorbed quantitatively in 24 h, but the adsorption ratios at 1.5 h were differed to be 52.3 and 98.7% for **1** and **2**, respectively. The faster adsorption by **2** can be ascribed to the hydrophilicity of the DMAA unit higher than that of the NIPAM unit. Other metals were negligibly adsorbed. The selectivity of the metal adsorption by the sulfur-containing metal adsorbents can be ascribed to the very soft Lewis basicity of the thiocarbonyl group in the dithiocarbonate moieties having high affinity with the very soft Lewis acids Pd and Au.

Second, a multi-element solution **B** was employed for the adsorption at room temperature for 24 h (Figure 3). As a result, all the adsorption ratios were below 10%. The low adsorption originated from the low affinity between the very soft thiocarbonyl group and the hard rare earth elements.

Third, a multi-element solution **C** was employed for the adsorption at room temperature for 1.5 and 24 h (Figure 4). The exact metal concentrations of Na, Mg, Al, K, Ca, Fe, Zn, and Ba could not be obtained using the standard curves based on this multi-element solution, probably due to the leakage of these metals from the vials used in this experiment. As a result, Ag was adsorbed almost quantitatively by both of the metal adsorbents within 1.5 h. Se, originating from  $\text{SeO}_2$  and existing as selenous acid, was also adsorbed at 36.2 and 31.4% by **1** and **2**, respectively, and the adsorption ratios were increased to ca. 60% at 24 h. We presume that selenous acid coordinated to the Lewis basic carbonyl groups in **1** and **2** as a hard Brønsted acid. The selectivity of **1** was excellent by the negligible adsorption of other metals, but that of **2** was lower due to the slight adsorption of most of the elements, suggesting nonspecific adsorption described later. The experiments using these three multi-element solutions proved that the hydrophilic sulfur-containing adsorbents, especially **1**, are effective adsorbents for noble metals with high selectivity and efficiency even in the presence of various elements.

We considered the excellent selectivity of the thiocarbonyl group in DTCMMA for noble metals. The

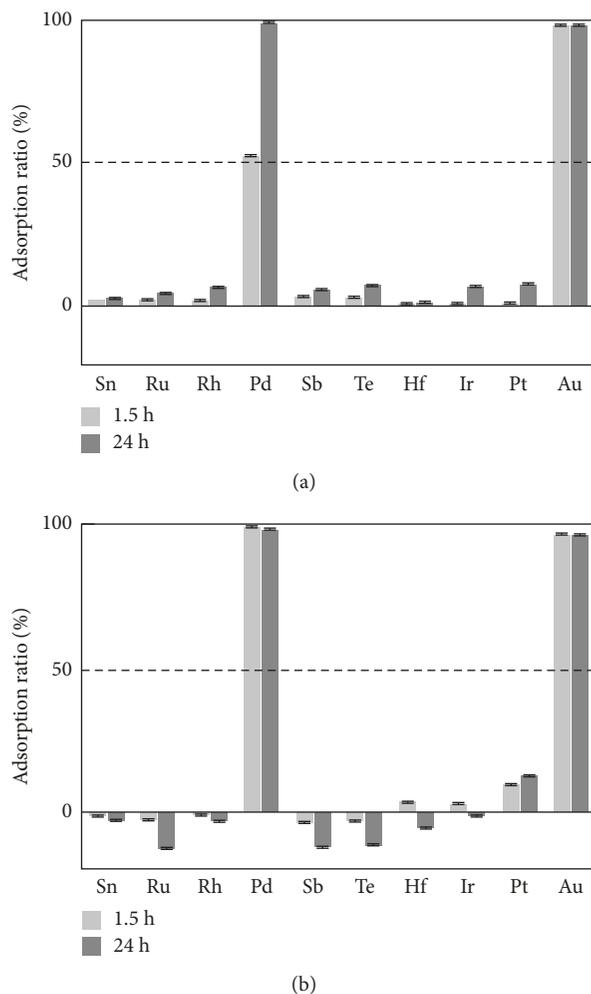


FIGURE 2: Metal adsorption from multi-element solution **A** with hydrophilic sulfur-containing adsorbents **1** (a) and **2** (b) (feed molar ratio of  $[\text{C}=\text{S}]/[\text{total metal}] = 4.5/1$ ).

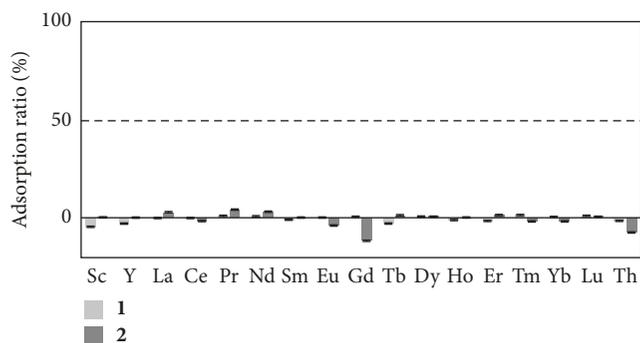


FIGURE 3: Metal adsorption from multi-element solution **B** with hydrophilic sulfur-containing adsorbents **1** and **2** (feed molar ratio of  $[\text{C}=\text{S}]/[\text{total metal}] = 4.5/1$ ).

selectivity of **1** and **2** toward Pd, Au, and Ag is higher than conventional adsorbents having thiocarbonyl groups such as thioamide [26–30, 46–52], thiourethane [32, 34, 36], and thiourea [11, 25, 53–59] including a commercial adsorbent QuadraPure™ TU (Aldrich) with the  $\text{R}-\text{NH}(\text{C}=\text{S})\text{NH}_2$

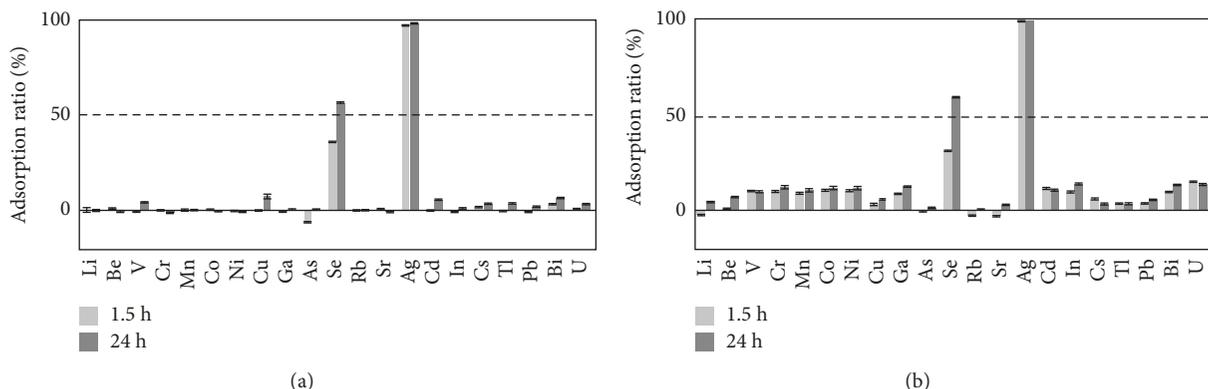
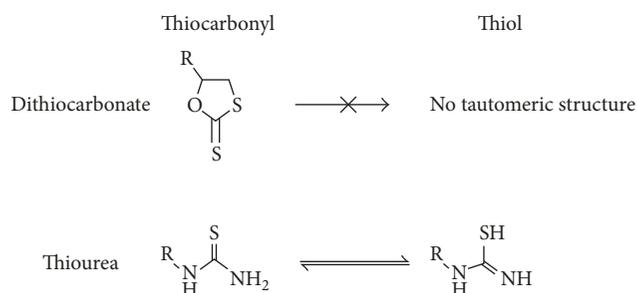


FIGURE 4: Metal adsorption from multielement solution C with hydrophilic sulfur-containing adsorbents **1** (a) and **2** (b) (feed molar ratio of [C=S]/[total metal] = 4.5/1).

structure [61]. The lower selectivity of these thiocarbonyl structures can be ascribed to the tautomerism between thiocarbonyl and thiol. For example, the thiourea structure in QuadraPure TU can take the tautomeric iminothiol structure (Scheme 2) [62]. The thiol group is a harder ligand than the thiocarbonyl group and has higher affinity with metals with harder Lewis acidity. By contrast, the selectivity of DTCMMA for the noble metals is higher by the dithiocarbonate moiety without taking harder tautomeric structures.



SCHEME 2: Tautomeric structures of thiocarbonyl and thiol.

**3.3. Control Experiment Using Cross-Linked Polymers without DTCMMA Unit.** We confirmed the effect of the DTCMMA unit using analogous cross-linked polymers without DTCMMA unit. The cross-linked polymers were synthesized by the radical copolymerization of the hydrophilic monomers NIPAM (**1'**) and DMAA (**2'**) with MBAA in DMSO at 60°C under a nitrogen atmosphere. Control experiments with **1'** and **2'** were conducted using the multielement solutions A and C, which contain the metals adsorbed by **1** and **2**. The metal adsorption experiments were conducted at room temperature for 24 h in a similar manner with the adsorption experiments using the sulfur-containing adsorbents. Most of the elements in A were hardly adsorbed as the cases of **1** and **2**, but the adsorption ratios of Au by **1'** and **2'** were slightly higher (19.0% and 16.7%, resp.) (Figure 5). A plausible reason for the adsorption of Au is the adsorption with the amide moieties as reported for poly(NIPAM), poly(DMAA), and poly(*N,N*-diethylacrylamide) gels [63], which should be occurred for the amide moieties in **1'** and **2'** leading to the nonspecific adsorption. In the adsorption from the multielement solution C, **1'** negligibly adsorbed metals, indicating that nonspecific adsorption is ignorable (Figure 6). Contrary to **1'**, **2'** adsorbed most of the metals though to lesser extents. These control experiments supported the excellent selectivity of **1** toward noble metals than **2**. A possible reason is the harder Lewis basicity of the carbonyl group in DMAA units that is likely to be responsible for nonspecific adsorption. The difference in the Lewis basicity was supported by FT-IR absorption of the carbonyl groups in **1'** and **2'** appeared at 1635 cm<sup>-1</sup> and

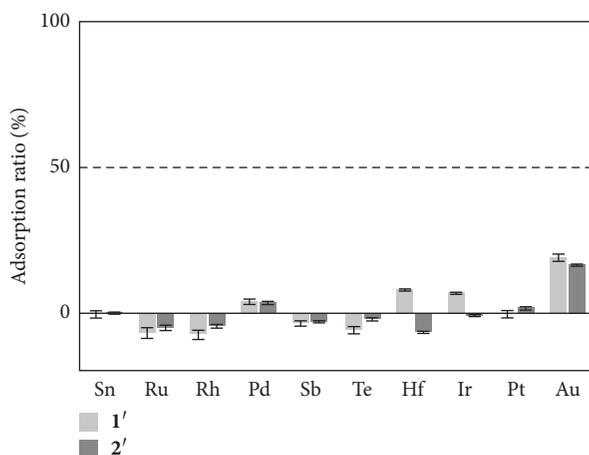


FIGURE 5: Metal adsorption from multielement solution A with hydrophilic gels **1'** and **2'**.

1610 cm<sup>-1</sup>, respectively. This result convinced us that the DTCMMA unit in the sulfur-containing adsorbents served as the important group for adsorption of noble metals.

**3.4. Competitive Metal Adsorption from Mixed Solution of Pd and Excess Amount of Cu by **2**.** Pd is a noble metal, and the concentration in nature is very low. In addition to the content in Pd mines, Pd is slightly contained in ores of other metals such as Cu. In industrial and catalytic uses of Pd, Pd are often

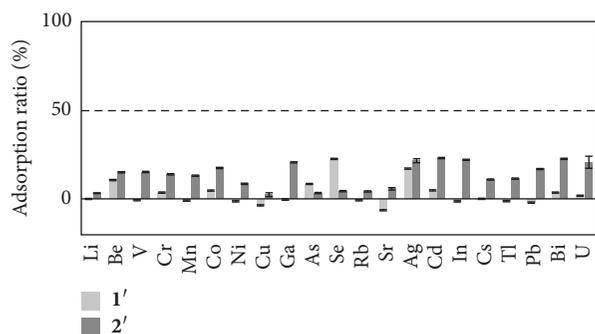


FIGURE 6: Metal adsorption from multielement solution C with hydrophilic gels 1' and 2'.

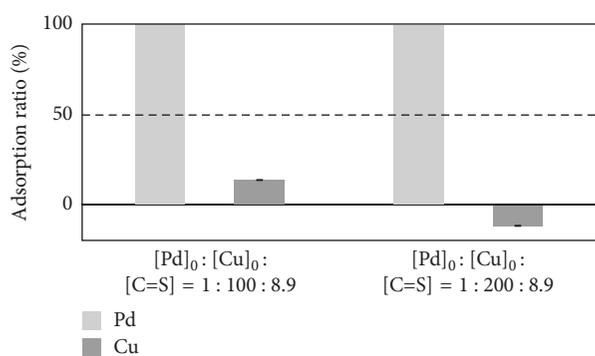


FIGURE 7: Competitive metal adsorption from mixed solutions of Pd and excess amount of Cu by 2.

used with other metals such as catalysts for Sonogashira coupling reaction combined with copper halides [64]. For this reason, extraction of Pd from mixtures containing excess amounts of other metals such as Cu is an important subject. Accordingly, we conducted competitive adsorption experiments for Pd from mixtures containing excess amounts of Cu with 2. The feed molar ratios of the C=S moieties in 2 and the metals examined were  $[C=S]:[Pd]_0:[Cu]_0 = 8.9:1:100$  and  $8.9:1:200$ . The experiment was conducted for 1.5 h in a similar manner with the case of the multielement solutions. As a result, 2 adsorbed Pd in an effective and selective manner at both of the feed ratios in spite of the excess amounts of Cu (Figure 7). This result suggested the excellent selectivity of 2 as a Pd adsorption agent from solutions containing various base metals such as wastewater from Cu mines and waste solutions after Pd-catalyzed reactions [65].

#### 4. Conclusions

We developed hydrophilic sulfur-containing adsorbents having thiocarbonyl groups based on a methacrylate bearing dithiocarbonate moieties and investigated the effect of the structure adjacent to the thiocarbonyl group. The hydrophilic sulfur-containing adsorbents 1 and 2 could selectively adsorb noble metals, Au, Ag, and Pd, from multielement aqueous solutions A and B. Au and Ag were adsorbed within 1.5 h by 1 and 2. The adsorption of Pd from multielement solution A with 2 proceeded faster than 1 owing to the

higher hydrophilicity of DMAA than NIPAM but 1 also quantitatively adsorbed Pd for 24 h. Selective adsorption of Pd could be achieved with 2 in the presence of excess amounts of Cu by the high noble metal selectivity. The selectivity of 1 to noble metals was higher than 2 due to the lower nonspecific adsorption. The high selectivity of the hydrophilic sulfur-containing adsorbents is advantageous for practical recycling of noble metals from industrial and mining wastewater.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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