

## Rapid Adsorption of Rh(III) by Polyamine-functionalized Cellulose Fiber Combined with Microwave Irradiation

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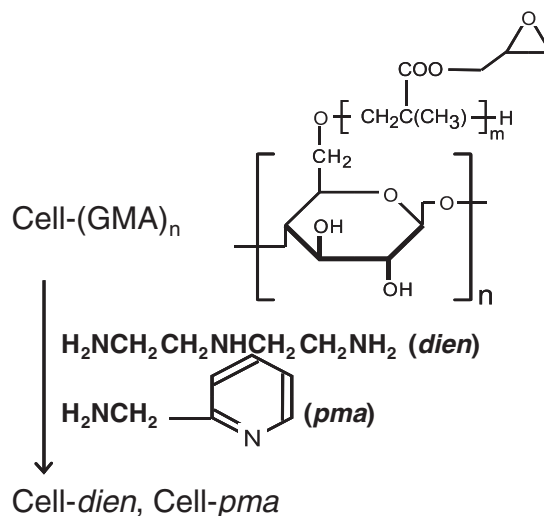
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New fibrous adsorbents were prepared by modification of cellulose fiber by graft polymerization of glycidyl methacrylate followed by introduction of diethylenetriamine and 2-pyridylmethylamine as the metal-binding site. Rapid and high adsorption of Rh(III) was achieved using the fibrous adsorbents, combining with microwave irradiation.

Rhodium is in great demand for use in various industries, particularly as a catalysts in automobile exhaust controls.<sup>1</sup> Because its natural deposits and locations of occurrence are few, recovery of rhodium from spent catalyst is important.<sup>2</sup> Adsorption processes using solid adsorbents present advantages because of their high enrichment efficiency from dilute solution, ease of phase separation, and operational simplicity.<sup>3</sup> Chelating resins immobilized with amines, aza-macrocyclic compounds, and -SH groups have been applied to the recovery of platinum group metals.<sup>4</sup> Nevertheless, rhodium (Rh(III) in aqueous solution) remains a difficult target of metal refining because of its complicated solution chemistry and kinetic inertness to complex formation.<sup>5</sup> Therefore, its recovery by adsorption and solvent extraction is often incomplete, and equilibrium is attained only over extremely long time periods.<sup>3</sup> Cellulose-based adsorbents provide advantages for attaining high adsorption rates because of their hydrophilic nature and fine fibrous morphology.<sup>6</sup> Moreover, because of the easy degradability of cellulose, metals can be recovered by simple incineration leaving very little ash. From an economic perspective, use of wastepaper as a cellulose resource has been attempted by chemical modification for recovery of platinum group metals.<sup>7</sup>

Microwave heating effectively accelerates the complex formation of "substitution-inert" metals including Rh(III), Ir(III), and Ru(II),<sup>8</sup> often enabling reduction of reaction time and dramatic improvement of the product yield. The possibility of the use of microwave irradiation for the intensification of adsorption was demonstrated previously for the preconcentration of platinum group metals.<sup>9</sup> In the present study, we prepared fibrous adsorbents by modification of cellulose fiber with glycidyl methacrylate (GMA), followed by introduction of polyamine ligands. We propose a facile and efficient recovery process for Rh(III) by use of these fibrous adsorbents combined with microwave heating.

Cellulose fiber (ARBOCEL BE00, TOA Kasei Co.) was initially activated by Fenton reaction using Fe(II) and hydrogen peroxide, which creates reactive radicals on the cellulose backbone.<sup>10</sup> Then, the cellulose fiber was modified by graft polymerization of GMA (Figure 1).<sup>10</sup> Finally, diethylenetriamine (*dien*) and 2-pyridylmethylamine (*pma*) were introduced to the fiber by epoxy ring opening of GMA (see Supporting Information<sup>14</sup>). Hereinafter, these fibrous adsorbents are desig-

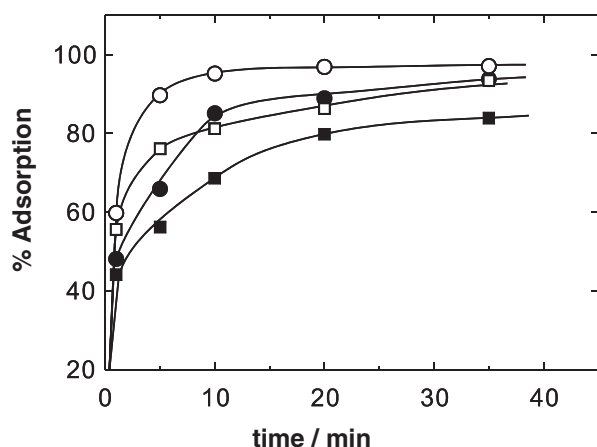


**Figure 1.** Introduction of ligands to fibrous cellulose modified with glycidyl methacrylate (GMA) polymer.

nated as Cell-*dien* and Cell-*pma*. Effective ligand contents of Cell-*dien* and Cell-*pma* were estimated to 0.69 and 0.43  $\text{mmol g}^{-1}$ , respectively by 24 h batch adsorption in the presence of excess Cu(II).

The adsorption measurements of Rh(III) (initial:  $10 \text{ mg L}^{-1}$ ) were conducted using a batch process in water throughout this work. The concentration of  $\text{Cl}^-$  was kept at 0.1 M. According to the speciation diagram of  $[\text{RhCl}_x(\text{H}_2\text{O})_y]$  in HCl solution,  $[\text{RhCl}_2(\text{H}_2\text{O})_2]^+$  and  $[\text{RhCl}(\text{H}_2\text{O})_5]^{2+}$  are predominant species in 0.1 M HCl.<sup>5</sup> Further aquation of coordinated  $\text{Cl}^-$  is accelerated by increase of pH.<sup>5</sup> Therefore, adsorption of Rh(III) proceeds by complex formation with the immobilized ligand and not by anion exchange between protonated ammonium cation and chloro complex anion. The percentage of Rh(III) uptake increases concomitantly with pH and reaches optimum level at above  $\text{pH} > 5.5$  for both Cell-*dien* and Cell-*pma*. Similar pH dependency of Rh(III) uptake was observed in the silica-supported chelating adsorbents containing nitrogen and sulfur donor atoms.<sup>11</sup> We also examined the effect of reaction temperature using conventional thermal heating in a water bath. The % adsorption of Rh(III) ( $10 \text{ mg L}^{-1}$ ,  $\text{pH} 6.5$ ) increased with increase of temperature in both adsorbents, indicating that the adsorption is endothermic.

Figure 2 presents a comparison of the time course for the adsorption of Rh(III) using microwave heating and conventional thermal heating at  $70^\circ\text{C}$ . In microwave heating, a glass tube used as the reaction vessel was placed at the center of the microwave chamber. The dispersion of fibrous adsorbent in



**Figure 2.** Time course of the adsorption of Rh(III) ( $10 \text{ mg L}^{-1}$ ,  $50 \text{ mL}$ ) with Cell-dien ( $\circ$ ,  $\bullet$ ) and Cell-pma ( $\square$ ,  $\blacksquare$ ) fiber at  $70^\circ\text{C}$ . The open symbol denotes the % adsorption attained by microwave heating, and closed symbol denotes that by conventional heating. Cell-dien ( $0.1 \text{ g}$ ), pH  $6.5$ .

aqueous solution was mixed well by bubbling air during the adsorption. The reaction temperature was measured using a Teflon-coated thermocouple inserted in the reaction solution. The measured temperature was fed back to the microwave generator (Green-Motif I,  $2.45 \text{ GHz}$ ,  $300 \text{ W}$ ; IDX Co.) so that the temperature was maintained at a constant value by the installed circuit. It appeared that microwave heating reduces the time required for equilibrium along with the increased % adsorption. Equilibrium was attained within  $20 \text{ min}$  with removal of  $97\%$  of Rh(III), although it required more than  $35 \text{ min}$  by conventional heating. The time course data were favorably expressed by the pseudo-first-order kinetics model. The calculated rate constants ( $k/\text{min}^{-1}$ ) of Cell-dien by microwave heating and conventional heating were  $0.197$  and  $0.091$ , respectively (see Supporting Information<sup>14</sup>). Consequently, the reaction rate by microwave heating was almost double that attained by the conventional heating. The magnitude of heating depends on the dielectric properties of the molecules in contrast to conventional heating. Water has high dielectric loss and efficiently converts microwave energy into thermal energy. Rapid mobility of Rh(III) and active molecular motion of ligands by selective absorption of radiation energy is one of the interpretations of rate enhancement.<sup>12</sup>

To elucidate the interference from foreign ions, competitive sorption of Rh(III) ( $10 \text{ mg L}^{-1}$ ) on Cell-dien ( $0.3 \text{ g}$ ) was examined in the presence of excess Cu(II), Ni(II), Mn(II), Fe(III), and Zn(II) ( $100 \text{ mg L}^{-1}$  each). The recovery of each metal ion at  $35 \text{ min}$  is listed in Table 1. Adsorption % of Rh(III) assisted by microwave heating reached  $83.7\%$ , whereas that by thermal heating remained  $40.1\%$ . Although its uptake was more or less interfered, Rh(III) is retained more strongly on Cell-dien than any other metal ions.<sup>13</sup> Rapidly complexed labile metal cations may obstruct access to Rh(III) and resist the metal metal substitution.

Remarkably stable complex formation inhibited the complete release of Rh(III) from the adsorbents even by use of strong acids. Thermogravimetric analysis of Cell-dien and Rh(III)-loaded Cell-dien under air flow indicated that the organic moiety

**Table 1.** Recovery of Rh(III) by the Cell-dien in the presence of foreign metal ions<sup>a</sup>

	Rh(III)	Cu(II)	Ni(II)	Mn(II)	Fe(II)	Zn(II)
Total amount/ $\mu\text{mol}$	4.9	78	85	91	90	76
Microwave/%	83.7	10.5	1.6	1.4	2.2	1.4
Thermal/%	40.1	15.8	1.8	1.7	2.4	1.8

<sup>a</sup>Cell-dien ( $0.3 \text{ g}$ ),  $50 \text{ mL}$ , pH  $5.0$ ,  $70^\circ\text{C}$ ,  $35 \text{ min}$ . Recovery of Rh(III) in the absence of metal ions:  $97\%$  (microwave),  $89\%$  (thermal).

was completely removed by combustion at above  $600^\circ\text{C}$ , leaving only rhodium as the residue. Therefore, rhodium can be recovered directly by incineration of the Rh(III)-loaded adsorbents.

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