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## Removal of mercury ions in a simulated wastewater using functionalized poly(glycidyl methacrylate)

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### ABSTRACT

Porous poly(glycidyl methacrylate) (PGMA) was prepared via water-in-oil (W/O) emulsion polymerization and was grafted with thiol groups. The removal of mercury (Hg) ions from water was evaluated using the functionalized PGMA. First, PGMA was synthesized and functionalized. Then, FTIR was used to assess the bonding of thiol groups with PGMA. SEM was used to analyze the porous characteristics of the material. To determine the effect of the pH on the Hg adsorption to functionalized PGMA, Hg adsorption tests were performed by varying the solution pH from 2 to 10. Additionally, a Hg adsorption test was performed by changing the initial Hg concentration.

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### Introduction

Mercury (Hg) exists in various forms as metallic Hg, inorganic Hg salts and organic Hg compounds in the environment. Hg bioaccumulates up the food chain. Hg accumulation beyond a certain level in the human body damages the nerves and kidneys and causes other harmful effects. Therefore, efforts to suppress the discharge of Hg into the environment are underway. The Minamata Convention on Mercury was ratified in 2013 and is expected to be operational in 2016 [1–3]. Therefore, a safe management plan for Hg and Hg compounds is required in response to this agreement.

It is difficult to separate heavy metal ions in wastewater discharged as the anthropogenic emissions from industrial facilities from water. Chemical, biological and physical treatments have been used to separate the heavy metal ions in wastewater. Adsorption is a physical method and is the most effective in terms of efficiency, stability and cost [4]. Various types of inorganic adsorbents have been studied, such as activated carbon [5–7], zeolite [8,9], and silica gel [10,11], in addition to biochemical organic materials from seaweed [12], wood [13], and polymer adsorbents [14]. Adsorption efficiency is determined by the physical structure of the pore, the specific surface area, and the porosity. Physical adsorption involves the combination with adsorbates through van der Waals forces, forming weak bonds

with the adsorbates. Chemical adsorption is caused by moving electrons, and the resulting bonding force is stronger than physical adsorption bonding [15].

In this study, porous poly(glycidyl methacrylate) (PGMA) was developed as a polymer adsorbent. PGMA forms pores via emulsion polymerization, which can control the structure and properties of the polymer material in the fabrication process. In addition, thiol groups that form stable bonds with Hg were used to functionalize PGMA [16]. A polymeric material with porous PGMA is easily functionalized with other materials because it contains highly reactive epoxy groups [17]. Epoxy groups are reactive with amines or carboxylic acids. Based on these facts, PGMA was functionalized with L-cysteine, which possesses carboxyl groups, amine groups and thiol groups [18,19]. High selectivity and efficiency are expected for the removal of Hg ions from water when using thiol groups as the PGMA functional groups. The chemical bonds between the thiol groups and PGMA were measured using Fourier transform infrared (FTIR) spectroscopy. The physical characteristics of the functionalized PGMA were identified using field emission scanning electron microscopy (FESEM) and N<sub>2</sub> sorption analysis, and the properties of Hg ion adsorption were determined.

### Materials and methods

#### Reagents

Glycidyl methacrylate (95%, Daejung, Siheung, Korea), divinylbenzene (80%, Sigma Aldrich, Saint Louis, USA), Span80 (Daejung,

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Siheung, Korea), potassium sulfate (99%, Daejung, Siheung, Korea), potassium persulfate (99%, Sigma Aldrich, Saint Louis, USA), magnesium chloride (98%, Siheung, Daejung, Korea), L-cysteine (95.5%, Sigma Aldrich, Saint Louis, USA), ethyl alcohol (94.5%, Daejung, Siheung, Korea), Hg(II) chloride (99.5%, Samchun Chemical, Seoul, Korea), stannous chloride dihydrate (Junsei Chemical Co., Ltd., Tokyo, Japan), and SRM3133 (9.954 mg/kg  $\pm$  0.053, NIST, Gaithersburg, USA) were used.

#### Preparation of porous PGMA

The water phase was prepared by mixing 0.11 g of potassium persulfate ( $K_2S_2O_8$ ), 0.55 g of potassium sulfate ( $K_2SO_4$ ) and 45 mL of water. The organic phase consisted of 3.0 g of glycidyl methacrylate (GMA), 2.0 g of divinylbenzene (DVB), and 4.0 g of Span80. The organic phase was stirred at 600 rpm, and during stirring, the water phase slowly formed small droplets in the organic phase. The two-phase materials were mixed to result in an emulsion polymerization process, and the material formed a white emulsion. The emulsion was introduced into a mold and was polymerized at 60 °C in an oven for 48 h. After 48 h, the product was washed with ethyl alcohol and water and dried in an oven at

100 °C for 48 h. Using this process, monolith PGMA was obtained. The preparation scheme for porous PGMA is shown in Fig. 1.

#### Preparation of functionalized porous PGMA

After mixing 0.5 g of L-cysteine, 0.1 g of  $MgCl_2$ , and 1 g of PGMA in 100 mL of water, the mixture was reacted for 24 h at 100 °C. After 24 h, the product was washed and dried at 60 °C.

#### Preparation of the Hg ion solution and measurements

A Hg(II) chloride ( $HgCl_2$ ) solution was used in the Hg adsorption test. A stock solution was prepared at a concentration of 1,000 mg/L, which was diluted to 50, 100, 200, 300, 400, and 500 mg/L. A volume of 50 mL of the Hg solution was used in the adsorption experiments. After adding 0.1 g of the adsorbent to the 50 mg/L Hg solution while stirring, the Hg concentration in the solution after adsorption was analyzed using a CVAAS (Cold Vapor Atomic Absorption Spectrometry)-type Hg analyzer (RA-915<sup>+</sup>/RP-91, Lumex Ltd., St. Petersburg, Russia). The amount of Hg adsorbed by the adsorbent was obtained by measuring the Hg concentration of the Hg solution before and after the adsorption.

#### Hg analysis

A solution of 10% stannous chloride was added to reduce all the Hg(II) ions in the solution to  $Hg^0$  prior to the measurement. The concentrations before and after Hg adsorption were measured in triplicate. The adsorption amount was calculated using Eq. (1):

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

where  $q_e$  is the amount of Hg adsorbed at equilibrium,  $C_0$  is the initial Hg ion concentration (mg/L),  $C_e$  is the equilibrium Hg ion concentration (mg/L),  $m$  is the weight of adsorbent (g), and  $V$  is the volume of the Hg solution (L).

The concentration range of the calibration curve was from 0 to 10,000 ng/L for the Hg solution, prepared by SRM3133. The calibration curve was only used when the coefficient of determination ( $R^2$ ) was greater than 99%. Each concentration in the calibration reflects the average value obtained by measuring the Hg solution three times.

## Results and discussion

#### Characteristics of the thiol-grafted porous PGMA

##### Chemical structure

FTIR spectroscopy (Spectrum 100 Series, PerkinElmer, Waltham, USA) was used to identify the presence of thiol groups in PGMA (Fig. 2). For PGMA, peaks of an epoxy and an OH group are observed at 910 and 3400  $cm^{-1}$ , respectively [20,19]. Meanwhile, new peaks, such as a C–O stretching vibration (1345  $cm^{-1}$ ) [21], a C–N bond (1095  $cm^{-1}$ ) [22,23], a C–S bond (665  $cm^{-1}$ ) [24], and a –SH group (2540  $cm^{-1}$ ) [22], are observed in the functionalized PGMA spectrum. The peak for C–O stretching appeared due to bond breakage in the epoxy group during the L-cysteine grafting process. A C–N bond and a C–S bond are also formed, and a –SH group bond is clearly formed via a reaction with L-cysteine, verifying that PGMA is functionalized with thiol groups.

##### Morphology and specific surface area

The morphologies of PGMA were characterized by FESEM (Model 7001F, JEOL Ltd., Tokyo, Japan). Because pores were produced by emulsion polymerization, two samples were confirmed in the form of a porous open cell structure possessing a shape

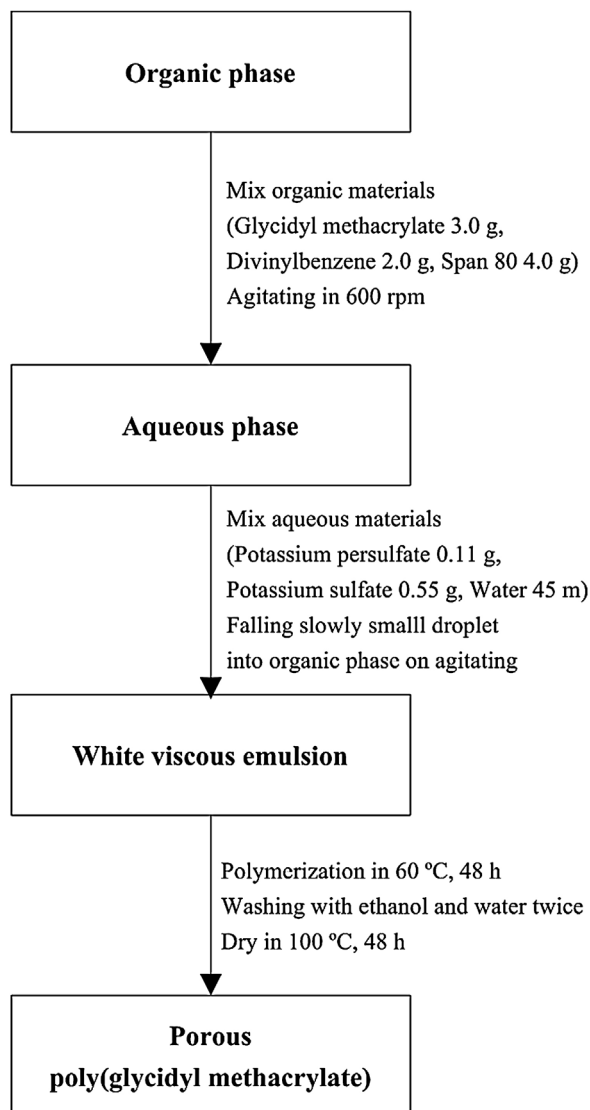


Fig. 1. Preparation of porous PGMA.

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