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Adsorption and separation properties of gallic acid imprinted polymers prepared using supercritical fluid technology

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ABSTRACT

Molecularly imprinted technique is one of the methods to form specific memory sites in a polymer matrix with the template. For main objective of this work, we prepared molecularly imprinted polymers (MIPs) using supercritical fluid technique as an eco-friendly process. MIPs were synthesized using methyl methacrylate (MMA) as a third monomer, methacrylic acid (MAA) as a functional monomer, gallic acid (GA) as a template, and ethylene glycol dimethacrylate (EGDMA) as a crosslinking agent. The template was removed through the method of Soxhlet extraction, and the removal ratio was about 95–99%. The adsorption abilities of prepared MIPs was evaluated by binding kinetics, the binding isotherms, Scatchard analysis, the adsorption of materials with structures similar to templates, high performance liquid chromatography (HPLC) analysis, and the selectivity factor (a), The results of the evaluation indicate that the prepared MIPs have high separation abilities and selectivity. In addition, we identified that although there was a difference of adsorption quantities with the crosslinking agent contents (EGDMA contents), MIPs synthesized in this study had good adsorption selectivity in the presence of GA and its structure analogue materials. From this result, it could be found that the selectivity of MIPs was improved significantly by controlling the crosslinking agent.

1. Introduction

Supercritical fluids (SCFs) have specific properties which can be applied and increased by many sorts of preparation, analysis, and process operation for chemical engineering. SCFs is also that they can replace many environmentally harmful solvents currently used in industry. Especially, SCFs are a innovative replacement material to organic solvents to be used as additives in polymer processing or preparation. In other words, supercritical carbon dioxide (scCO2) is by far the most widely used SCF because its zero ozone-depletion potential makes it relatively cheap, nontoxic, nonflammable, eco-friendly, and acceptable. In addition, it has low critical constants of $T_c = 31\,^{\circ}C$ and $P_c = 74$ bar [1,2]. It is very easily removed from the polymeric product, avoiding the costly processes of drying or solvent removal, which is important in processing and preparing of polymeric materials because CO_2 is a gas under ambient conditions. As a polymerization medium, $scCO_2$ provides some advantages over the conventional solvents. High density of $scCO_2$ enable easy adaptation to reactions of polymerization, thus composed polymer chains precipitate from the solution after reaching a specific molecular weight. Furthermore, $scCO_2$ can be used to extract unreacted monomers, initiators, catalysts, and stabilizers from polymeric materials to accomplish high purity substance [3].

As a method of preparing ligand-selective cavities in a polymer matrix [4–7], molecular imprinting technique has been focusing on the possibility of creating molecular recognition sites that have high selectivity to the target molecule into polymeric materials. Ii has attracted important interest from chemistry and analytical sciences due to the ease with which these polymers may be prepared, to the range of target molecule (template) structures amenable to use, and to the apparent mechanical and chemical stability of the types of polymers generally synthesized [8]. The molecularly imprinted polymers (MIPs) are synthesized by the co-polymerization of functional vinyl monomers with a divinyl monomer as a cross-linker in the presence of template. After the removal of the template using appropriate solvents, the resulting polymers have a memory to selectively recognize the guest molecule using as a template through the footprint-like vacant spaces as a host [9]. MIPs are characterized by easy preparation, easy storage, and good stability. Therefore, MIPs are a good biomimetic materials that may replace biological macromolecules in some fields where molecular recognition is required. For example, MIPs have been used in chromatographic separation, solid phase extraction, sensors, and immunoassay [10].

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MIPs can be synthesized by the method of covalent or noncovalent [11,12], which is now widely used in bulk polymerization, in situ polymerization, suspension polymerization, precipitation polymerization, and multi-step swelling polymerization [13–16]. Common MIPs are prepared in a bulk formation by using bulk polymerization. They are crushed and ground to gain appropriately sized particles. The method has the advantages of ease for preparing MIPs. Nevertheless, heterogeneity of polymer can occur during the polymerization process. The crushing and grinding process causes also large loss and destruction of space in the shape of target molecule for the prepared MIPs. In order to overcome the weakness of bulk polymerization, various methods have been attempted to prepare MIP particles such as suspension, emulsion, dispersion, solution, and precipitation polymerization to gain easily the MIP particles. However, these methods are defective in selecting dispersion agent and mediums because the relation of combinations or solubility between components should be considered. Furthermore, in the case of dispersion, solution, and precipitation polymerization, MIP particles are prepared by using organic solvents. Use of organic solvents has an adverse effect not only on the environment, but also on the selective separation of target molecules. In order to resolve the disadvantages of these polymerization methods and to minimize the consumption of organic solvents, various works have been carried out using supercritical fluid assisted polymerization in $scCO_2$ as the reaction medium to prepare MIPs in a heterogeneous reaction system [17]. The preparation of MIPs by supercritical fluid assisted polymerization provides many advantages. First, High purity materials are easily gained. Second, They are prepared by CO_2 as an eco-friendly solvent. Third, the process of preparation for MIPs is relatively simple. Fourth, the MIPs synthesized by supercritical fluid assisted polymerization are obtained as free-flowing powders with controlled morphology and porosity [18].

In this study, gallic acid (GA) imprinted polymers (GA-IPs) were synthesized by using supercritical fluid assisted polymerization in $scCO_2$. GA is a naturally plant phenol obtained by the hydrolysis of tannins and is known to show some pharmacological activities such as antimutagenicity, anticarcinogenicity, antiviral activity, and antioxidative activity. Therefore, it was widely used in the pharmaceutical industry due to the prevention of some cardiovascular diseases and cancer [19]. In addition, GA is used in cosmetics, processed food, and packing materials to avoid decomposition or rancidity induced by lipid peroxidation and spoilage. However, it is necessary the selectively separation because GA used in various fields is wasted and discarded in nature. Puoci et al. [20] have prepared GA-IPs using bulk polymerization and investigated their adsorption properties. However, the results showed that the adsorption amount and selectivity for GA and its structure analogue materials was relatively low. In order to overcome this point, we prepared GA-IPs using supercritical fluid assisted polymerization in $scCO_2$. The binding characteristics of prepared GA-IPs are investigated by binding kinetics, adsorption isotherms, and Scatchard plot analysis. The selective separation abilities were analyzed by high performance liquid chromatography (HPLC) analysis, the adsorption of materials with structures similar to target molecules (aspirin (AS), benzoic acid (BA), and phenol (pH)), and the selectivity factor (α). The effects of various polymerization methods and different functional monomers were also investigated.

2. Experimental

2.1. Materials

Gallic acid (GA, $C_7H_6O_5$, CAS RN 149-91-7), aspirin (AS, $C_9H_8O_4$, CAS RN 50-78-2), benzoic acid (BA, $C_7H_6O_2$, CAS RN 65-85-0), phenol (pH, C_6H_6O, CAS RN 108-95-2), methyl methacrylate (MMA, $C_5H_8O_2$, CAS RN 80-62-6), ethylene glycol dimethacrylate (EGDMA, $C_{10}H_{14}O_4$, CAS RN 97-90-5), and methacrylic acid (MAA, $C_4H_6O_2$, CAS RN 79-41-4) were purchased from Sigma-Aldrich Chemical Company, Inc. (Milwaukee, WI, USA). The α, α'-Azobis(isobutyronitrile) (AIBN, $C_8H_{12}N_4$, CAS RN 78-67-1) was purchased from Junsei Chemical Co., Ltd (Tokyo, Japan). Ethanol was purchased from Duksan (Pharmaceutical Co., Ltd, Korea). Carbon dioxide (CO_2, CAS RN 124-38-9) was obtained from Deok Yang Gases Co. (Yeosu, Korea) and used as received. The specifications of all chemicals used are summarized in Table 1. Monomers used in this work were distilled under vacuum to remove inhibitors before polymerization. Distilled deionized water (DW) was used in all experiments.

2.2. Preparation of MIPs

The MIPs were synthesized by using supercritical fluid assisted polymerization in scCO2. GA was used as the template, MAA as a functional monomer, MMA as a third vinyl monomer, EGDMA as a cross-linker, AIBN as an initiator, and THF as a porogen solvent for the supercritical fluid assisted polymerization. Table 2 shows the composition of MIPs. 1.0 mol GA was weighed into a 50 mL vial. Added to it were 6.0 mol MAA, 20 mol MMA, 0–20 mol EGDMA, 1.0 wt% AIBN, and 2 mL THF were added, respectively. Dis-

Table 1
Specifications of the chemical used.

Chemical Name	Source	Mass Fraction Purity[a]	Purification Method	Analysis Method[a]
CO_2	Deok Yang Gas Co.	>0.999	None	–
MMA[d]	Aldrich-Sigma Co.	>0.985	Distillation	GC[b]
MAA[e]	Aldrich-Sigma Co.	>0.990	Distillation	Titration by NaOH
EGDMA[f]	Aldrich-Sigma Co.	>0.975	Distillation	GC[b]
GA[g]	Aldrich-Sigma Co.	>0.985	None	GC[b]
Aspirin	Aldrich-Sigma Co.	>0.995	None	–
BA[h]	Aldrich-Sigma Co.	>0.995	None	Titration by NaOH
Phenol	Aldrich-Sigma Co.	>0.990	None	GC[b]
Ethanol	Duksan Co.	>0.995	None	GC[b]
AIBN[i]	Junsei Chemical Co.	>0.980	Recrystallization	HPLC[c]

[a] Both the analysis method and the mass fraction purity were provided by the suppliers.
[b] Gas-liquid chromatography.
[c] High performance liquid chromatography.
[d] MMA = Methyl methacrylate.
[e] MAA = Methacrylic acid.
[f] EGDMA = Ethylene glycol dimethacrylate.
[g] GA = Gallic acid.
[h] BA = Benzoic acid.
[i] AIBN = α,α'-Azobis(isobutyronitrile).

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