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Application of acrylate gel having poly(ethylene glycol) side chains to recovery of gold from hydrochloric acid solutions

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Abstract

Hydrogel beads were synthesized from radical polymerization of poly(ethylene glycol) monoacrylate (PEGA) and poly(ethylene glycol) diacrylate (PEGDA), and applied for the recovery of Au(III) from hydrochloric acid solutions. The acrylate hydrogels had poly(ethylene glycol) units as side chain, and retained water as much as 70% of their dry-weight. Due to a strong interaction between Au(III) and poly(ethylene glycol) units in the hydrogel structure, the metal was adsorbed into the hydrogel beads with the percent adsorption of more than 90% irrespective of the acid concentration. The adsorption was well correlated with the Freundlich isotherm equation, and the adsorbed amount of Au(III) reached as high as 121 mg-Au/g-dry gel at maximum. Moreover, selective separation of Au(III) was attained since other heavy metals such as Cu(II), Zn(II), Fe(III) and Al(III) were excluded from the hydrogel beads. The present hydrogel beads were preferable in treating dilute acid solutions to avoid the hydrolysis of ester group in the gel structure at high acidities.

Keywords: Acrylate hydrogel; Gold recovery; Poly(ethylene glycol) unit; Freundlich isotherm equation

1. Introduction

Hydrogels are materials that retain a large amount of water in their three-dimensional network structure, and those made from natural polymers including gelatin, fibrin and polysaccharide are well-known. In recent decades, various kinds of hydrogels have also been prepared from synthetic polymers of (meth)acrylic acid, acryl amide, vinyl alcohol and their derivatives. They are now extensively used as water adsorbing material in medical and sanitary fields. Recently, sophisticated molecular design enables these hydrogels to find a wide range of novel application such as actuators [1,2], biointerfaces [3], drug delivery systems [4], chemical sensors [5,6] and removal of toxicities from wastewater [7]. The use of hydrogels as adsorbent for metals from dilute aqueous solutions is also attracting much attention [8–12]. Compared with conventional solid adsorbents like ion exchange and chelating resins, high wettability and high swelling of hydrogels might be advantageous to improving adsorption of target metals.

In aqueous media, ethylene oxide units are known to form complexes with various ions including alkaline earth elements [13]. Widely used non-ionic surfactants, poly(oxyethylene) nonyl phenyl ethers (PONPEs), have a number of ethylene oxide units in the molecules as hydrophilic moiety and show strong affinity to gold(III). Taking advantage of this interaction, we successfully recovered gold(III) using PONPEs in such operations as solvent extraction [14], cloud point extraction [15] and micellar-enhanced ultrafiltration [16]. In hydrochloric acid solutions, gold(III) exists in the form of tetrachloro auric acid ($HAuCl_4$) and this species interacts with electron-donating oxygen atoms in ethylene oxide units in the surfactants.

From the standpoint of handling, however, these liquid–liquid processes are inferior to solid–liquid ones like adsorption in many aspects, and this prompts us to construct the adsorbent containing poly(ethylene glycol) units in its structure. In this work, we have synthesized several hydrogels from mono- and di-acrylates with poly(ethylene glycol) units, and examined

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their availability as adsorbent for gold(III) from dilute aqueous solutions.

2. Experimental

2.1. Preparation of hydrogel beads

Poly(ethylene glycol) monoacrylate with number average molecular weight of 375 (PEGA) and poly(ethylene glycol) diacrylate with number average molecular weight of 575 (PEGDA) were purchased from Sigma–Aldrich Co. Ltd. An initiator, 2,2′-azobis(2-amidinopropane) dihydrochloride (AADP) was obtained from Wako Pure Chemical Industries Ltd. The above reagents were used without further purification.

A monomer solution was prepared by dissolving PEGA and PEGDA along with AADP (40 mg) in 40 ml deionized water in a 100 ml vial. The total volume of the two monomers was fixed at 40 ml. Aliquots (0.20 ml) of the monomer solution were poured into round-bottomed holes (i.d. 6.4 mm) of a 96-hole PTFE plate, and the plate was covered with a piece of PTFE film. Polymerization was carried out by keeping the samples at 80 °C for 16 h in an oven. The transparent bullet-shaped beads, thus, obtained were washed and stored in deionized water over 24 h before adsorption experiments.

2.2. Experimental procedure

Adsorption experiments were carried out in a batch mode at an ambient temperature. An aqueous stock solution of metals was prepared by dissolving an appropriate amount of each metal chloride ($HAuCl_4$, $CuCl_2{\cdot}2H_2O$, $ZnCl_2$, $FeCl_3{\cdot}6H_2O$ and $AlCl_3{\cdot}6H_2O$) in a HCl solution and its acidity was adjusted by adding a small amount of NaOH or HCl solution. A predetermined amount of the hydrogel beads was added into the metal solution (50 ml) in a 60 ml vial. The vial was rolled by a rotating mixer (Iuchi MIX-ROTAR MR-2) for 24 h, and aliquots (0.3 ml) of the supernatant liquid were taken out at appropriate time intervals. After appropriate dilution with deionized water, the metal concentrations in the aqueous phase were determined by using an inductively coupled plasma atomic emission spectrometry (ICP-AES, SEIKO SPS1500VR). The amounts of metals adsorbed on the hydrogel beads were calculated from the mass balance. The content of water in the hydrogel beads was determined by measuring a weight loss in drying at 110 °C for 24 h. After the adsorption experiments, the total concentration of organic carbon (TOC) in the aqueous phase was measured by a total organic carbon analyzer (Shimadzu TOC-V_{CSH}).

3. Results and discussion

Firstly, several kinds of hydrogel beads were synthesized from the monomer solutions containing various volumetric ratios of PEGA and PEGDA while keeping their total volume at 40 ml, as tabulated in Table 1. The other conditions were not changed. The synthesis was carried out in the presence of water to avoid cracking of the resulting beads. To obtain uniform and stable beads, both mono- and di-acrylates were found to be requisite; the synthetic beads polymerized from only PEGDA were too fragile and those from only PEGA were soluble in water. On the other hand, the beads synthesized from the mixtures of PEGA and PEGDA showed considerable mechanical stability and incohesivity, and were suitable for the following adsorption test. The beads obtained from the combination of 10 ml PEGA and 30 ml PEGDA were white, and the other three were colorless. The weight of each bead was ca. 0.24 g on a wet basis. Owing to the hydrophilic poly(ethylene glycol) units in the molecular structure, the synthetic beads show affinity to water and their percent water content ranges from 59 to 77%. The percent water content was defined as:

$$C = 100\frac{(W_w - W_d)}{W_d} \tag{1}$$

where W denotes the bead weight and the subscripts w and d stand for wet and dry condition, respectively. Thus, the present beads are categorized as hydrogel. Contrary to the expectation that the hydrogel beads become stiffer with increasing the degree of cross-linkage, the water content is not much affected by the ratio of PEGDA in the present system.

To overview the adsorption properties, the hydrogel beads (3.0 wet-g) were made contact with 0.1 M HCl solution (50 ml) containing 100 ppm Au(III). The mixing time was set to be 24 h. During the experiments, the beads sank in the aqueous solutions. The adsorbed amount of metal (q) was calculated according Eq. (2) from the metal concentrations in the aqueous phase before, $[M]_0$, and after, [M], the adsorption:

$$q = ([M]_0 - [M])\frac{V}{W} \tag{2}$$

where W and V denote the dry weight of the beads and the volume of the aqueous phase, respectively. All the hydrogel beads adsorbed Au(III) from the aqueous solutions and became yellow-tinted as the adsorption proceeded. As shown in Table 1, the q value reaches more than 4.0 mg/g in all the cases, and slightly increases with decreasing the PEGDA ratio. As will be explained in the following, the adsorption is ascribed to the strong interaction between Au(III) ions and poly(ethylene glycol) units in the hydrogels.

After the adsorption experiments, TOC in the aqueous phase was measured and summarized also in Table 1. Since the gel beads were washed and stored in deionzied water before the experiments to remove unreacted monomer, the TOC value represents the decomposition of the gels in solutions. The TOC values are relatively high for all the four beads and a secondary treatment such as activated carbon process might be necessary in practical situations. By decreasing the PEGDA ratio below

Table 1
Characterization of hydrogel beads prepared from PEGA and PEGDA

PEGA	PEGDA	C (%)	q (mg-Au/g-dry gel)	TOC (ppm)
0.25	0.75	59.0	4.05	495
0.50	0.50	70.9	4.50	337
0.75	0.25	67.5	4.68	762
0.99	0.01	76.6	4.74	783