Journal of Hazardous Materials 203–204 (2012) 213–220

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

The synthesis of poly(vinylphosphonic acid-*co*-methacrylic acid) microbeads by suspension polymerization and the characterization of their indium adsorption properties

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ARTICLE INFO

Article history:
Received 1 September 2011
Received in revised form
16 November 2011
Accepted 2 December 2011
Available online 14 December 2011

Keywords:
Suspension polymerization
Ion exchange
Microbeads
Indium adsorption

ABSTRACT

Poly(vinylphosphonic acid-*co*-methacrylic acid) microbeads were synthesized by suspension polymerization, and their indium adsorption properties were investigated. The obtained microbeads were characterized by Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The microbeads were wrinkled spheres, irrespective of the components, and their sizes ranged from 100 to 200 μm. The microbeads were thermally stable up to 260 °C. As the vinylphosphonic acid (VPA) content was increased, the synthetic yields and ion-exchange capacities decreased and the water uptakes increased. The optimum synthetic yield, ion-exchange capacity and water uptake were obtained at a 0.5 mol ratio of VPA. In addition, the maximum adsorption predicted by the Langmuir adsorption isotherm model was greatest at a 0.5 mol ratio of VPA.

1. Introduction

Indium and its compounds have a wide range of industrial applications whose rapid development has increased their consumption [1]. However, indium is widely dispersed in nature and only typically found at low concentrations in some zinc, copper and lead sulfide ores. Therefore, the development of indium recovery technology is in demand. Furthermore, indium wastewater is suspected to be carcinogenic to humans, and it is known that indium and its compounds induce cytotoxicity in several animal experiments [2,3]. Hence, the interest in indium recovery is not only increasing in the field of rare metal recovery but also in that of heavy metal elimination.

Several studies on methods for indium recovery have been reported, including liquid–liquid extraction (LLE) [4], co-precipitation [5], solid-phase extraction [6], electroanalytical techniques [7,8] and ion exchange methods. The primary disadvantage of LLE is the loss of extractant into the aqueous phase, which may result in economic limitations and environmental hazards. The other indium recovery technologies also exhibit disadvantages, such as a high solvent-recovery cost, environmental and health hazards and time-consuming processing methods. Ion exchange methods are simpler than the other technologies and have the advantage of a low recovery cost.

A few investigations on metal recovery using ion exchange have been reported. Fortes et al. reported indium adsorption onto ion exchangers that contained different organic functional groups, such as iminodiacetic acid, diphosphonic acid and aminophosphonic acid [9]. Mendes and Martins reported the adsorption of nickel and cobalt onto some commercially available chelating ion-exchange resins [10]. However, most researchers involved in indium recovery using ion exchange have only reported its adsorption properties on commercially available ion exchange resins. In this study, microbeads were prepared as ion exchangers by suspension polymerization, and their adsorption properties were investigated.

Suspension polymerization has been widely used in industrial applications to produce specialty polymer particles, such as ion-exchange resins, chromatographic separation media and supports for enzyme immobilization. Suspension polymerization is a suitable polymerization technique for the production of large polymer beads, typically in the range of 5–1000 μm [11]. Numerous reports on the preparation of ion-exchange resins by suspension polymerization have appeared in the literature. Lin et al. reported the synthesis of *p*-(ω-sulfonic-perfluoroalkylated)polystyrene ion-exchange resin by suspension polymerization [12], and Coutinho et al. described the preparation of a pellicular ion-exchange resin [13].

In this study, the microbeads were synthesized by suspension polymerization using vinylphosphonic acid (VPA) and methacrylic

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doi:10.1016/j.jhazmat.2011.12.020

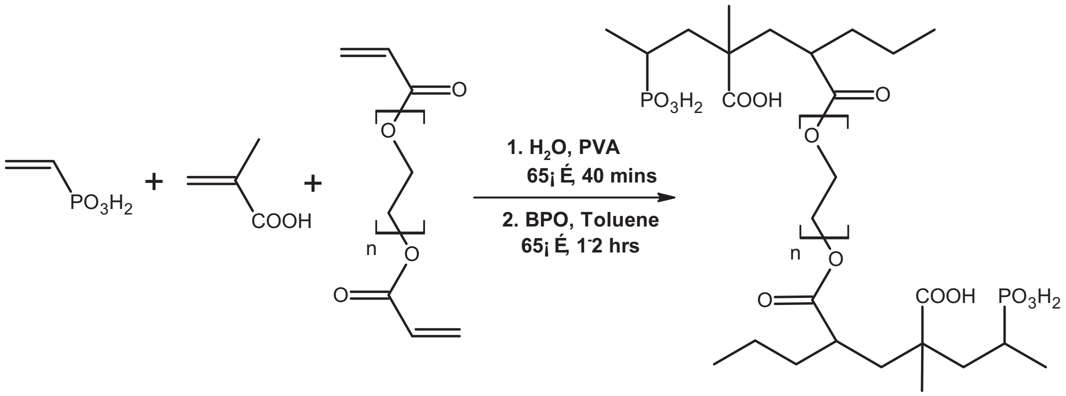

Fig. 1. A schematic mechanism for the synthesis of poly(vinylphosphonic acid-*co*-methacrylic acid).

acid (MAA) as monomers and poly(ethylene glycol) diacrylate (PEGDA) as a crosslinking agent. VPA has a chelate which allows exchanging In^{3+} and it is possible to synthesize by radical polymerization due to its vinyl group. However, VPA is very expensive and VPA alone make a synthesis yield decrease. On the contrary, MAA allows a yield to increase and furthermore its weak acid group, —COOH, helps ion-exchange capacity to increase. Therefore, in this study, the basic properties of ion exchange beads at a different VPA content were investigated. Furthermore, the adsorption properties and thermodynamic properties of the best condition's sample were examined. The structure and morphology of the microbeads were confirmed by Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM).

2. Experiment

2.1. Materials

VPA (90%) and MAA (99.5%) (used as monomers) and PEGDA ($M_w = 258$) (used as the crosslinking agent) were obtained from Sigma–Aldrich Co. (New York, USA). Benzoyl peroxide (BPO, 75%) (used as an initiator) and poly(vinyl alcohol) (PVA) (used as a stabilizer) were purchased from Lancaster (Morecambe, England) and Junsei (Tokyo, Japan), respectively. 1-(2-Pyridylazo)-2-naphtol (PAN) and ethylene diamine tetraacetic acid (EDTA) (used as an indicator and as a titrant, respectively) were purchased from Sigma–Aldrich Co. (New York, USA) and Samchun Co. (Seoul, Korea), respectively. Twice-distilled water, toluene and ethanol were used as solvents.

2.2. Preparation of poly (VPA-co-MAA) ion-exchange microbeads

Different monomer ratios of poly(VPA-*co*-MAA) were synthesized by suspension polymerization. Fig. 1 shows the structures of the monomers and poly(VPA-*co*-MAA). The polymerization was conducted in a 500 mL three-neck round-bottom flask equipped with a mechanical stirrer (IKA® RW20 digital, IKA company, Osaka, Japan), a condenser, a nitrogen inlet, a thermometer and a dropping funnel. VPA, MAA and PEGDA were dissolved in a mixture of distilled water and PVA at 65 °C. The solution was placed under continuous strong agitation until all of the monomers were completely dissolved. BPO (as an initiator) and toluene were then added to the solution with a dropping funnel. The polymerization was performed in airtight equipment at 65 °C and maintained for 1–2 h with stirring (750 rpm). Table 1 shows the mole ratios of the syntheses.

The synthetic yield of the microbeads was determined by Eq. (1):

$$\text{Synthetic yield (\%)} = \frac{W_d}{W_m} \times 100 \quad (1)$$

where W_d is the weight of the clean and dry polymer beads (g), and W_m is the initial weight of the monomer (g).

2.3. The characterization of poly(vinylphosphonic acid-co-methacrylic acid)

The structures of the poly(VPA-*co*-MAA) samples were characterized using FT-IR (IR Prestige-21, Shimadzu, Kyoto, Japan). Discs containing 1 mg of sample and 150 mg of KBr were prepared on a press using a 60–70 kN compression force. The FT-IR spectra were collected over a wavenumber range of 4000–600 cm^{-1}; the resolution was 4 cm^{-1}, and 20 scans were taken.

The elemental analysis of poly(VPA-*co*-MAA) was performed with energy-dispersive X-ray spectroscopy (EDS, JSM-7000F, JEOL, Akishima, Japan), which was attached to the scanning electron microscope (SEM). Incident electron-beam energies from 0.5 to 30 keV were used. In all cases, the beam was at a normal incidence to the sample surface and the measurement time was 100 s. All of the surfaces of the samples were covered with osmium using the ion sputtering method.

The thermal decomposition behaviors of the microbeads were investigated using TGA (TA Instruments Q500, New Castle, DE, USA)

Table 1
Synthesis conditions of poly (vinylphosphonic acid-*co*-methacrylic acid).

Sample code	Monomer (mole ratio)		Crosslinking agent	Stabilizer	Initiator
	VPA	MAc	PEGDA	PVA	BPO
VMP00-3	0.00	1.00	30 wt%	0.01 wt%	0.01 wt%
VMP02-3	0.25	0.75			
VMP05-3	0.50	0.50			
VMP07-3	0.75	0.25			
VMP10-3	1.00	0.00			
VMP00-4	0.00	1.00	40 wt%		
VMP02-4	0.25	0.75			
VMP05-4	0.50	0.50			
VMP07-4	0.75	0.25			
VMP10-4	1.00	0.00			
VMP00-5	0.00	1.00	50 wt%		
VMP02-5	0.25	0.75			
VMP05-5	0.50	0.50			
VMP07-5	0.75	0.25			
VMP10-5	1.00	0.00			