Journal of the Taiwan Institute of Chemical Engineers 84 (2018) 142–148

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Poly (methyl methacrylate) matrix with immobilized Prussian blue for cesium removal from waters

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ARTICLE INFO

Article history:
Received 1 December 2017
Revised 2 January 2018
Accepted 10 January 2018

Keywords:
Cesium
Prussian blue
PMMA
Beads

ABSTRACT

Prussian blue (PB) is an effective adsorbent for cesium (Cs) ions from contaminated water. Ideal PB adsorbents for Cs removal should be able to spontaneously adsorb Cs^+ ions without significant release of hexacyanoferrate fragments and can be stably stored in dry condition. This study synthesized poly(methyl methacrylate) (PMMA) beads using suspension polymerization with PB-rich shell as Cs adsorbents, which presents less than 2% water swelling in water and can be stored at dry condition. In batch and sand filter tests the PB-PMMA beads reveal spontaneous and endothermic Cs adsorption behavior with minimal release of the hexacyanoferrate fragments.

1. Introduction

The nuclear accident like Fukushima Daiichi Nuclear Power Plant disaster discharged radioactive nuclides to the environment [1–3]. The long-life nuclides such as Cs^{137} can be detected in contaminated areas for many years after the disaster [4]. Use of conventional coagulation-filtration treatment process cannot effectively remove dissolved Cs ions from drinking water [5,6]. Prussian blue (PB) is lattice of formula $Fe_7(CN)_{18}$ that has cage size similar to the hydrated Cs^+ ions, hence having been utilized to adsorb Cs^+ in the presence of competing ions [7,8]. Numerous organic/inorganic matrices were proposed to immobilize nano-sized PB crystals as efficient Cs adsorbents [9–14].

Chen et al. [15,16] applied the inorganic binding PB granules and PB-immobilized nonwoven fabric for decontamination of Cs-polluted drinking water. The PB adsorbents can effectively remove dissolved Cs from waters [17]. Dechojarassri et al. [18] coated chitosan containing immobilized PB to adsorb Cs^+ from contaminated waters. Jia et al. [19] produced PB nanoparticles inside porous polyacrylonitrile membranes for direct removal of Cs during filtration. These carriers are of high strength for water shear in use. However, the produced drinking water may contain hexacyanoferrate fragments eroded from the PB matrix [16]. Restated, the binding strength between the immobilization matrix and the PB nanoparticles needs enhancement to yield quality PB adsorbents for drinking water production. Parajuli et al. [20] synthesized the calcium alginate cohered granules of hexacyanoferrate and iron hexacyanoferrate for adsorption removal of radiocesium from waters. The main drawback of alginate matrix for practical use is its weak mechanical strength under shear [21].

Poly(methyl methacrylate) (PMMA) is a thermoplastic with chemical formula of $(CH_3O(CO)C(CH_2)(CH_3))_n$ and glass transition temperature of about 100 °C. PMMA matrix can be produced using emulsion polymerization. The structure of PMMA is sufficiently strong to provide high mechanical strength of the polymerized blocks, which leads to low intra-block diffusion rates for poor ion transport between the blocks and the surroundings. Hasell et al. [22] synthesized the Fe_3O_4-PMMA polymer particles with Fe_3O_4 nano-particles being stabilized outside the PMMA polymer matrix. Using a similar synthesis scheme, this study yielded PMMA beads with PB enriched outer layer as Cs adsorbent. The so-produced beads are stable in seawater and can be stored at dry condition. Also, since the binding between PMMA and PB-rich layer is strong, the hexacyanoferrate fragments erosion noted in granules by [16] and in [23] is not noted. The so-produced granules were then tested in batch adsorption tests and in stimulated sand filter tests for confirming its effectiveness as Cs adsorbents in waters.

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https://doi.org/10.1016/j.jtice.2018.01.012
1876-1070/

Table 1
Parameters for polymerization reaction to synthesize the PB-PMMA beads.

No.	DI water (mL)	PVA	PB	$MgCO_3$ basic	NaCl	MMA (mL)	BPO	EGDMA	W/O ratio	Temperature (°C)	bead size (mm)
1–1	350	3%	0.57%	0.21%	4%	50	0.61%	0.30%	7:1	76	0.222 ± 0.012
1–2	350	3%	0.57%	0%	4%	50	0.61%	0.30%	7:1	76	0.260 ± 0.044
2	300	3%	1.30%	0%	4%	50	0.61%	0.30%	6:1	76	0.314 ± 0.060
3	250	3%	1%	0%	4%	50	0.61%	0.60%	5:1	76	0.659 ± 0.027
4	230	3%	1%	0%	4%	70	0.61%	0.60%	3.29:1	76	0.607 ± 0.044
5–1	250	3%	1%	0%	4%	45	0.61%	1.33%	5.56:1	76	0.366 ± 0.011
5–2	250	3%	1%	0%	4%	45	0.61%	1.33%	5.56:2	76	0.382 ± 0.023
6	300	3%	1%	0%	4%	50	0.61%	1.33%	6:1	76	No bead formed
7	**250**	**3%**	**1%**	**0%**	**4%**	**40**	**0.61%**	**1.33%**	**6.25:1**	**76**	**1.160 ± 0.500**
8	250	3%	1%	0%	4%	40	0.61%	1.33%	6.25:1	58	0.911 ± 0.093
9	250	3%	1%	0%	4%	40	0.61%	1.33%	6.25:1	64	0.924 ± 0.072
10	250	3%	1%	0%	4%	40	0.61%	1.33%	6.25:1	70	0.931 ± 0.191
11	500	3%	1%	0%	4%	100	0.61%	1.33%	6.25:1	76	1.220 ± 0.157
12	250	3%	1%	0%	4%	40	0.61%	1.33%	6.25:1	80	0.976 ± 0.019

2. Experimental

2.1. Bead synthesis

2.1.1. Materials and reaction

The methyl methacrylate monomer was purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA; CAS no. 80-62-6), and was purified by batch distillation at 150 °C under atmospheric pressure.

The organic phase was prepared by pre-polymerizing 50 mL purified MMA with 0.3 g benzoyl peroxide (BPO) as initiator and 0.45 mL ethylene glycol dimethylacrylate (EGDMA) as cross-linking agent under 80 °C for 1 h.

Aqueous phase was prepared by mixing 3 g 4% sodium chloride (NaCl), 0.5 g PB powders, and 2.25 g 3% w/w poly (vinyl alcohol) as stabilizer in 75 mL double-distilled water.

The two phases were put into the double-neck flask reactor in N_2 atmosphere at prescribed temperature 70 °C with agitation 170 rpm. After polymerization the suspension was centrifuged at 8000 rpm at 4 °C. The sediment was heated to 90 °C for 12 h for removing moisture, un-reacted monomers and the dispersing agents. The following five factors were varied: species and quantity of the dispersing agents, stirring speed, monomer/water ratio, species of monomers, and temperature (Table 1). The dried powders were grinded and screened to remove fine fragments.

All the chemical information was noted in Appendix A.

2.1.2. Bead characterization

The reaction yield of PB-PMMA bead is defined as follows: $Y(\%) = (W_p/\Sigma W_r) \times 100\%$, where W_p is the total weight of solid bead and ΣW_r is the total weights of feed reactants.

The bead sizes were characterized by US standard testing sieve with mesh number 14, 16, 18, 25 and 35. The density (ρ) of the PB-PMMA beads was measured by Pycnometer (Accupyc II 1340, Micrometritics, Norcross, GA, USA).

The PB loading rate for the beads was determined by dissolving 1.44 g PB-PMMA beads in 10 mL 8% w/w nitric. The solution was then mixed with 20 mL DI water and 1000 mL 2% w/w nitric acid for filtration with 0.22 µm membrane. The concentration of iron ions in the solution was then determined by inductively coupled plasma mass spectrometry (model 7700, ICP-MS, Agilent Technologies, Inc., Santa Clara, CA, USA). The PB weight (W_{PB}) was calculated from the measured iron contents by $W_{PB} = M_{Fe} \times Mw_{PB}/7$, where M_{Fe} is the moles of iron in the solution (mol) and MW_{PB} is the molecular weight of PB (859.2 g/mol). The loading rate was calculated by the weight of PB divided by the bead weight.

The swelling ratios of beads in waters were defined as follows: $SR(\%) = D_f/D_i \times 100\%$, where D_f and D_i are the bead diameters before soaking and after soaking, respectively. 3 g PB-PMMA bead was placed in 125 mL water in PTFE Erlenmeyer flask and their diameters at different soaking times were recorded.

Five randomly selected beads were embedded in 1-chloro-2,3-epoxypropane (0.027 g) and bisphenol A (0.009 g) after solidification at room temperature for five days (provide detailed recipes). The solidified bead was polished in sequence by no. 600, 1200, and 2000 sandpaper to expose the cross-section of the beads. The enlarged images of tested beads were determined by field emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDS) (Nova^{TM} NanoSEM 230, FEI Company, Hillsboro, Oregon, USA).

The X-ray diffraction (XRD) spectra of tested samples were conducted by D2 phaser X-ray diffractometer (Bruker, Congleton, UK) with a Cu anode (40 kV and 30 mA) and canning from 5° to 90°.

2.2. Adsorption tests

2.2.1. Batch adsorption tests

The PB-PMMA bead was dried at 80 °C for 12 h before adsorption tests. The used beads were collected and dried again at 80 °C without washing for repeated adsorption test. Batch adsorption tests were conducted in polytetrafluoroethylene (PTFE) Erlenmeyer flasks. In each flask, 0.25–6 g PB-PMMA beads were added into 125 mL DI water containing 60 µg/L Cs^+. The flasks were placed at 25 °C and shaken at 200 rpm in an orbital shaking incubator (OSI-511R, Double Eagle, Taipei, Taiwan) for 24 h. At fixed time interval 5 mL samples were withdrawn from the flasks with addition of 2% w/w nitric acid. The collected samples were filtered by 0.45 µm membrane with their filtrate being measured by its Cs^+ concentration.

Kinetic measurements revealed that the adsorption equilibrium can be achieved in 24 h testing. The adsorption isotherm was presented by measuring the surface concentration of Cs on bead equilibrated for 48 h at original concentration (C_o) of 100, 200, 400, 600, 800, 1000, 1500, or 2000 ppb and at 15, 25, 35 or 45 °C.

2.2.2. Sand filter tests

A stimulated rapid sand filter modified from that used in [16] was applied for the present tests. The sand bed was composed of (from bottom) 10 cm cobblestone, 50 cm sand, 25 cm anthracite and 10 cm PB-PMMA beads (1.53 g in mass, porosity (ε) equals to 0.89). In parallel tests, the columns with bead thickness of 2, 4, 6, or 8 cm were also tested. The schematic of the sand filter is available in [16]. The tap water with 60 µg/L Cs^+ was the feed. The contact time for the tested granules was set at 50–200 s. All tests were conducted in triplicate at 25 °C.