



Poly(vinyl alcohol) and alginate cross-linked matrix with immobilized Prussian blue and ion exchange resin for cesium removal from waters

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HIGHLIGHTS

- Poly(vinyl alcohol) + alginate + Prussian blue + ion exchange resin granule was made.
- The granules are stable in fresh and sea waters with high cesium removal rates.
- Dosed ion exchange resin removed most hexacyanoferrate released from granules.
- Transport and reaction parameters for granules and for sand filter were estimated.

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ABSTRACT

Cesium (Cs) removal from contaminated water bodies is an emerging issue after the disaster at the Fukushima Daiichi Nuclear Power Plant. The Prussian blue (PB) is an effective Cs adsorbent but will release hexacyanoferrate fragments from the adsorbent matrix during adsorption. Alginate is an affordable biopolymer for PB particles immobilization. This study synthesized poly(vinyl alcohol) (PVA) and alginate cross-linked matrix for immobilization of PB nano-sized particles and a surface-modified styrene-ethyl styrene divinyl benzene resin and tested their swelling stability and Cs adsorption performance in fresh water and in seawater. The PVA–alginate granules have high structural stability in both fresh water and seawater, with the Cs adsorption capability higher for the former than the latter. The adopted resin effectively remove released PB fragments from the tested granules. The transport and reaction parameters for the granules and for the sand filter bed were estimated.

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1. Introduction

Nuclear accident such as the Fukushima Daiichi Nuclear Power Plant disaster could release mass quantity of radioactive nuclides, including long half-life radioactive cesium (Cs), to the environment (Namiki et al., 2012; Thammawong et al., 2013; Parajuli et al., 2013). The water bodies at nearby areas may be contaminated by the released radioactive fallout that needs intensive treatment for sufficient remediation (NRA, 2013). Conventional waterworks cannot remove dissolved Cs⁺ from contaminated water (Brown et al., 2008; Baeza et al., 2002).

Prussian blue (PB) has high Cs adsorption capability and ion selectivity since its Fe₇(CN)₁₈ matrix cage is of similar size to the

hydration radius of Cs⁺ (Ishizaki et al., 2013; Sasaki and Tanaka, 2012). The adsorbent matrix with embedded nano-sized PB crystals were tested for decontamination of Cs-polluted environmental samples (Kitajima et al., 2012; Vincent et al., 2015; Yasutaka et al., 2013, in press; Parajuli et al., 2016a; Lee et al., 2016). Chen et al. (2015a,b) demonstrated that both PB-embedded granules and PB-immobilized nonwoven fabric could be applied as effective Cs barrier for drinking waterworks. However, the PB matrix would release trace of PB fragments which poses a threat to the receiving water body (Chen et al., 2015b). Additionally, preliminary tests revealed that the PB granules applied in (Chen et al., 2015a) would disintegrate and dissolved in concentrated NaCl solution (Supplementary Materials), suggesting that the so-yielded PB granules cannot be applied for decontamination of radiocesium-polluted brackish waters or seawaters.

Biosorption of heavy metals have been intensively studied (Fomina and Gadd, 2014; Liu and Lee, 2014; He and Chen, 2014).

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Alginate (ALG) is a biopolymer of 1,4-linked β -D-mannuronic and α -L-guluronic acid residues with capability of forming hydrogels with divalent cations, which has been used as an immobilizing agent for PB particles (Majidnia and Idris, 2015; Mihara et al., 2016; Parajuli et al., 2016b) and other adsorbents (Tan and Ting, 2014). Parajuli et al. (2016c) synthesized the calcium alginate cohered granules of hexacyanoferrate and iron hexacyanoferrate for adsorption removal of radiocesium from waters. The main drawback of ALG matrix for practical use is its weak mechanical strength under shear. The PVA cross-linked with boric acid in the presence of calcium alginate produced granules were applied for cell immobilization with minimal agglomeration (Wu and Wisecarver, 1992). The PVA–ALG granules could have sufficient mechanical strength and reduced agglomeration tendency for applications (Hui et al., 2014; Wong et al., 2015).

This study synthesized PVA–ALG granules with boric acid and calcium chloride as cross-linking agents to immobilize PB nanoparticles as Cs adsorbents. These granules are proposed to overcome the two drawbacks for the currently available PB adsorbents: easy deterioration in seawater and high leakage of PB fragments. We noted that the newly synthesized granules are stable in seawater, and with incorporation of ion exchange resin particles in the synthesized granules, the PB release problem can be resolved. The so-produced granules were tested in batch adsorption tests and in stimulated sand filter tests for confirming its effectiveness as Cs adsorbents in both fresh and in seawater.

2. Experimental

2.1. Materials

For synthesizing ALG-alone granules, 10 g Prussian blue soluble (1% w/v) (Sigma–Aldrich, St. Louis, MO, USA) and 10 g sodium alginate (1% w/v) (Acros Organics, Geel, Belgium) were added into 1 L deionized water (DI water) with extensive stirring at 80 °C for 1 h. 20 g of calcium chloride (Fisher Chemical, Geel, Belgium) was added to another 1 L DI water for forming a 2% gelation solution. Then the previously prepared PB + ALG mixture was sprayed by a thin nozzle into the calcium solution with mild stirring. The formed PB–ALG granules were kept in the solution for another 12 h for complete gelation.

For synthesizing PB–PVA–ALG granules, 10 g 1% w/v Prussian blue soluble, 10 g 1% w/v sodium alginate and 10 g 10% w/v PVA (molecular weight 89,000–98,000, hydrolyzed, Sigma–Aldrich, St. Louis, MO, USA) were added into 1 L DI water with extensive stirring at 80 °C for 1 h. 20 g of calcium chloride and 40 g boric acid (Acros Organics, Geel, Belgium) was added to another 1 L DI water for forming the gelation solution. The PVA–ALG granules were formed by nozzle spraying the PB–PVA–ALG solution to the gelation solution with stirring and subsequent gelation for 12 h. In separate synthesis batch, the ion-exchange resin (IE) granules, the 500 μ m gel type styrene–ethyl styrene divinyl benzene resin with surface modified by trymethulanino chloride moiety synthesized according to (Parajuli et al., 2015), was used in the present study. Some IE granules were crushed by a commercial grain grinder to a mean size 80 μ m. 100 g of original or crushed IE resins were also added to the above PB + PVA + ALG mixture for making the PB–IE–PVA–ALG granules. The granules made were kept at the solution for 12 h to complete solidification. Then the granules were transfer to 0.9 M sodium sulfate solution for 12 h for dehydration.

The granules made were spheres of mean size of 3300 μ m (Supplementary Materials). The mean size of the PB particles herein synthesized was approximately 50 μ m.

2.2. Adsorption tests

2.2.1. Batch adsorption tests

Batch adsorption tests were conducted in polytetrafluoroethylene (PTFE) Erlenmeyer flasks. In each flask, 6 granules were added into 100 mL DI water or artificial seawater containing 60–45,000 ppb Cs⁺. The flasks were placed at 25 °C and shaken at 200 rpm in an orbital shaking incubator (OSI-511R, Double Eagle, Taipei, Taiwan). At fixed time intervals 5 mL samples were withdrawn from the flasks with its Cs⁺ concentration in solution being measured. Artificial seawater was made by mixing completely 10.82 g MgCl₂·6H₂O, 1.153 g CaCl₂, 0.761 g KCl, 0.4011 g Na₂SO₄, 24.06 g NaCl in 1 L DI water (Millero, 1986).

To reveal the interactions between bead swelling and the Cs adsorption behavior, independent tests were conducted with six granules first being immersed in each flask filled with DI water or 9 M sulfate solution. Then the granules were transferred to the flasks with seawater containing 30 ppb Cs⁺.

In independent adsorption-washing tests 12 granules were put into 100 mL 30 ppb Cs⁺-containing DI water and shaken at 200 ppm for 24 h and 25 °C. At the end of the test the granules were collected and washed with DI water and were placed in another 100 mL 30 ppb Cs⁺-containing DI water shaken for 24 h again. This process was repeated for six times.

2.2.2. Sand filter tests

A stimulated rapid sand filter modified from that used in Chen et al. (2015b) 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 or PB-IE granules. The schematic of the sand filter is available in Chen et al. (2015b). The tap water with 30 μ g/L Cs⁺ was the feed. The contact time for the tested granules was 33.3–200 s. The pressure drops over each layer of the packing materials were measured. All tests were conducted in triplicate at 25 °C.

2.3. Other analyses

The swelling ratio of the formed granules was measured by weighing the granules after 12-h 9 M sulfate solution soaking (W_0) and then after further soaking in DI water or sea water for another up to 24 h (W_e). The swelling ratio was defined as $(100(W_e - W_0)/W_0)$. This testing protocol was repeated for a few times to confirm the reversibility of the bead structure under hydration-dehydration cycles.

The water samples were pre-filtered with 0.45- μ m filter and then were measured on their Cs⁺ concentrations using inductively coupled plasma mass spectroscopy (model 7700 series ICP–MS, Agilent Technologies, Santa Clara, CA, USA). The sample pH was measured using a calibrated pH meter (WTW pH-315, Weilheim, Germany).

All analyses were conducted in triplicate to assure data quality.

3. Results and discussion

3.1. Swelling characteristics of granules

Fig. 1(a) shows the swelling kinetics for the PVA–ALG granules. In DI water or sea water, the granules could reach complete hydration within 2 h, the swelling ratio for former being around 58% and that for the latter, about 38%. Repeated hydration-dehydration cycles yielded swelling ratio of 45–58% in DI water and 32–38% in seawater (Fig. 1b), suggesting that the produced granules had satisfactory structural stability.

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