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Short Communication

Cesium removal from drinking water using Prussian blue adsorption followed by anion exchange process

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ABSTRACT

Prussian blue (PB) was proposed to be an effective cesium (Cs) adsorbent for drinking waterwork; however, the release of PB fragments from PB adsorbent matrix poses threat to water quality. This study examined the feasibility of a PB+anion exchange (AE) process for decontamination of Cs-polluted drinking water. Two scenarios were tested: AE granules over PB granules in a stimulated sand filter and PB column followed by AE column in a full-scale waterworks. Both scenarios revealed complete removal of Cs and PB fragments from the treated drinking waters, suggesting that the PB+AE unit can be the core of emergency response plan for typical drinking waterworks at nuclear accident threat.

1. Introduction

The disaster of Fukushima Daiichi Nuclear Power Plant disaster released huge quantities of radioactive cesium (Cs) with long half-life to environment [1–3]. The so-released radioactive fallout had contaminated nearby raw water sources, since conventional waterworks cannot satisfactorily remove dissolved Cs^+ from water [4,5], the so-produced drinking water was reported to be contaminated with radionuclides [6].

Prussian blue (PB)-based adsorbents were demonstrated as an efficient Cs scavenger since the $Fe_7(CN)_{18}$ matrix has a crystal cage size similar to the hydration radius of Cs^+ [2,7,8]. The nano-sized PB crystals are fixed to binding matrix for providing a mass transfer unit that can be applied for field applications [9–15]. For instance, PB particles were bound to nonwoven fabric as carrier [16]. The PB particles was also embedded in calcium/alginate beads [8,17–19], in polyarylacetylene resin [20], in chitosan sponge [21], or in inorganic binders [22]. Chen et al. [23,24] for the first time showed that both PB-embedded granules and PB-immobilized nonwoven fabric are effective Cs barrier for drinking waterworks. However, a major concern of these applications is the release of PB fragments from the tested granules or nonwoven fabric that pose a threat to drinking water quality.

Anion exchange resin can be used to remove anions from waters. This study examined the feasibility of a PB+anion exchange (AE) process for decontamination of Cs-polluted drinking water. Two scenarios were tested: AE granules over PB granules in a stimulated sand filter and a PB column and an AE column in a full-scale waterworks. Both scenarios revealed satisfactory removals of Cs and PB fragments from the treated drinking waters.

2. Experimental

2.1. PB adsorbents and AE granules

The PB granules were synthesized according to [25–27]. These granules were made by embedding 5–20 nm PB nanoparticles with inorganic binders to form granules of size of 1 mm. Details for the Cs adsorption behavior by these 80% w/w PB granules was

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described by [23]. These granules were used in the present stimulated sand filter tests (described latter).

The 3–6 wt% PB-immobilized nonwoven adsorbents used in [24] was synthesized according to [28,10] adopted in the present column tests. The non-woven fabric was filled up the testing column (diameter 35 cm and height 120 cm) for field test.

The AE granules were gel type styrene-ethyl styrene divinyl benzene resin, with surface modified by trymethylanino chloride moiety [29]. The AE resins are yellow spherical granules of size 0.3–1.2 mm and of apparent density 670–750 g/L (Fig. S1). At 25 °C, this resin can remove 99% of hexacyanoferrate anions ($[Fe(CN)_6]^{3-}$) in water in 20 h contact time [29].

2.2. Flow tests

A stimulated rapid sand filter was modified from [23], which composed of (from bottom) 10 cm cobblestone, 50 cm sand, 25 cm anthracite, 10 cm PB granules and 10 cm AE granules (Fig. S2). All packing materials except for PB and AE granules were collected from those in use by Taipei City Waterworks and all testing hydraulic parameters for the stimulated sand filter were identical as those adopt in real applications. The sand filter tests with or without the AE layer were conducted. The tap water with 30 μg/L Cs^+ was the feed. The contact times (t_c) for PB granules and AE granules were 50 s or 150 s (each). The pressure drop over each packing layer was measured. All tests were conducted in triplicate at 25 °C.

In column test, a 3% w/w PB non-woven fabric column (35 cm × 123 cm) identical to the ones adopted by [24], which was set up at Zhitan Waterworks, New Taipei City, Taiwan. An AE column of size 26.7 cm × 40 cm, filled with the AE granules produced in Section 2.1, was connected to the exit of the PB column (Fig. S3). The raw water received by the Zhitan Waterworks had a turbidity of a mean value of 10–40 Nephelometric turbidity units (NTU), which was fed to the pilot plant facility with polyaluminum chloride (PACl) as the coagulant (Fig. S4). Details of the pilot plant facility are available in [23]. 30 μg/L Cs^+ was dosed to the raw water before entering the pilot plant. The flow rates to the PB column was controlled to reach a contact time of water to the PB column and AE column at 100 and 19 s, respectively. All tests were conducted in triplicate at field temperature.

2.3. Other analyses

The collected water samples were filtered by 0.45 μm filters. The filtrate was then measured on its Cs concentrations using inductively coupled plasma mass spectroscopy (model 7700 series ICP-MS, Agilent Technologies, Santa Clara, CA, USA). The zeta potentials of water samples were measured by a Zetasizer (Nano-ZS, Malvern Co., UK). The water quality were measured based on Taiwan EPS Standard Methods (http://www.niea.gov.tw/analysis/method/ListMethod.asp?methodtype=WATER). The concentrations of total cyanide and weak acid dissociable cyanide in water samples were measured via Taiwan EPA Standard Methods NIEA W410.53A. The biological acute toxicities of water samples were measured by Taiwan EPA Standard Methods NIEA B904.13B (carp) and NIEA B901.14B (daphnia).

All analyses were conducted in triplicate to assure data quality.

3. Results and discussion

3.1. Sand filter tests

Table 1 shows the head loss of each layer of the sand filter at t_c = 50 or 150 s. At 50 s contact time the total water head loss was 0.42–0.44 m; while at 150 s contact time, the head loss was about 0.16 m. In these tests, the AE layer only contributed 0.02–0.07 m head loss, an affordable loss in field applications.

The PB layer in the stimulated sand filter effectively removed the dosed Cs^+. With 50 s contact time, the Cs removal rates were all above 98% (Fig. 1a); while at 150 s contact time the effluent Cs concentration was below the detection limit (0.1 μg/L) (Fig. 1b). The presence of AE layer did not affect the removal rates of Cs^+ ions (Fig. 1). Additionally, at 50 or 150 s contact time, the AE layer had minimal impacts on the turbidities (Fig. S5), solution conductivity (Fig. S6), solution pH (Fig. S7), or cation concentrations (Figs. S8 and S9) of the filtrate. The AE layer slightly reduced the solution pH from around neutral to about 6.5, not a concern for drinking water quality.

Correlating with the findings of [24], the PB granule layer had increased the concentrations of Fe in filtrate: from nearly zero to 0.22–0.26 mg/L at 50 s contact time or to 0.26–0.38 mg/L at 150 s contact time. The associated total cyanide concentrations in PB effluents at 50 s contact time ranged 1.08–0.87 mg/L (Table 2). The adopted AE granules completely removed the ferricyanide ions from filtrate (Fig. 2). One thing to be mentioned is that although total cyanide was presented in PB effluents, there were no biological acute toxicity to carp or to daphnia (LC_{50} > 100%, detailed data not shown), suggesting that the PB fragments (which is assumed non-toxic to living species) rather than dissolved cyanide were present in the tested water samples.

3.2. Field column tests

Removal rates for Cs^+ using the conventional coagulation-sedimentation-sand filtration process were negligible (data not shown), correlating with the conclusions by [24] that traditional drinking waterworks cannot remove dissolved Cs^+ from water.

The effluent from PB column contained Cs^+ ions below detection limits at the first 7 h of operation (Fig. 1a); while the removal rate was slightly dropped after 27-h operation. The AE column did not affect the cesium removal rates from waters. Additionally, neither PB column nor AE column affected the turbidities (Fig. S10), conductivity (Fig. S11), pH (Fig. S12), or cation (except for Cs^+) concentrations (Fig. S13), of filtrate.

As noted in [24], the PB column released ferricyanide ions to water (Fig. 3b), around 0.38 mg/L at the start of test and was reduced to 0.09 mg/L at the end of 27-h operation. Meanwhile, the total cyanide concentration in PB effluent was 1.14 mg/L at the start of test and became 0.3 mg/L at the end of 27-h test (Table 2). The AE column completely removed these released ferricyanide ions (Fig. 3b) and total cyanide (Table 2) in produced water. Although with detectable total cyanide concentrations, all PB effluents revealed no biological acute toxicity to carp or daphnia (LC_{50} > 100%, detailed data not shown).

Table 1
The water head loss of each packing layer (m) of stimulated sand filter tests.

PB+AE layers							
t_c = 50 s							
Time (h)	<1	1	2	3	4	5	6
AE layer	0.07	0.06	0.06	0.06	0.06	0.06	0.07
PB layer	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Anthracite	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Sand	0.28	0.27	0.27	0.27	0.27	0.27	0.28
Cobblestone	0.03	0.03	0.03	0.03	0.03	0.03	0.03
t_c = 150 s							
Time (hr)	<1	1	2	3	4	5	6
AE layer	0.02	0.02	0.02	0.02	0.02	0.02	0.02
PB layer	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Anthracite	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Sand	0.10	0.10	0.10	0.09	0.10	0.10	0.10
Cobblestone	0.01	0.01	0.01	0.01	0.01	0.01	0.01