Separation and Purification Technology 153 (2015) 37–42

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Prussian blue non-woven filter for cesium removal from drinking water

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ARTICLE INFO

Article history:
Received 22 April 2015
Received in revised form 15 July 2015
Accepted 16 August 2015
Available online 17 August 2015

Keywords:
Cesium
Tap water
Prussian blue

ABSTRACT

Cesium (Cs) removal from tap waters is an emerging issue after the Fukushima Daiichi Nuclear Power Plant Disaster. Adsorbents highly specific to Cs in the presence of other alkali and alkali earth metals are desired to supply safe drinking waters to residents near the contaminated area. This work for the first time used Prussian blue (PB) nanoparticles implemented non-woven fabric as an efficient adsorbent for Cs removal. Adsorption isotherms were obtained using Langmuir equation at 288, 298 and 308 K, from which the maximum adsorption capacities were estimated as 216, 241, 260 mg/g. The studied PB-Cs adsorption was endothermic process while its capacity was lower in acid than in alkaline solutions. The column tests with synthetic raw water and pilot plant column with low and high-turbidity real raw waters revealed almost complete removal of Cs by sufficiently long contact time. All PB treatments had no noticeable effects on water quality while the produced water had no biological acute toxicities. Use of PB non-woven fabric for decontaminating Cs pollution in drinking water was discussed.

1. Introduction

The East Japan Earthquake seriously damaged Fukushima Daiichi Nuclear Power Plant, leading to release of 630,000–770,000 terabecquerels of radioactive nuclides to environment [30]. Japanese soils had been contaminated by the ^{137}Cs fallout [41,42,28]. The half live for ^{137}Cs is much longer than ^{131}I [37], hence left residual radioactivity to local residents at 1.8×10^{16} Bq ^{134}Cs and 1.5×10^{16} Bq ^{137}Cs one year after the Fukushima Disaster [32]. Radioactive fallout can lead to contaminated surface water and/or groundwater, eventually pollute the drinking water production chain [34,35]. At two years after the Fukushima Disaster trace of radiocesium was still found in drinking water of many cities in Japan [30].

Conventional coagulation–sedimentation processes can effectively remove particle-bound cesium but can hardly remove soluble cesium ions from waters. Cs behaves similarly with K and Na, hence leading to low removal efficiency by conventional drinking water treatment processes such as coagulation–sedimentation and sand filtration [39,27,13,12,2]. Brown et al. [4] commented that removal efficiencies of Cs in raw waters in coagulation–sedimentation and sand filtration stage ranged 10–40%. The best available technologies and the small system compliance technologies by Radionuclides Final Rule (December 7, 2000) by US Environmental Protection Agency for beta particle removal in drinking water are ionic exchange (IC) and reverse osmosis (RO). Hamasaki et al. [14] reviewed the methods proposed for Cs removal.

Adsorption efficiencies of Cs from waters using natural adsorbents are generally low [19,11,3,18,31,40,20]. Expensive synthetic adsorbents are proposed to remove Cs from waters [6,1,10,8,9,15,36]. Prussian blue (PB) is a pigment of dark blue color with chemical formula $Fe_7(CN)_{18}$, which has a simple face-centered crystal structure with eight water molecules forming a unit cell. PB crystal has a cage size similar to the hydration radius of Cs^+ (3.25 Å), which are smaller than those for Na^+ (3.6 Å), Ca^{2+} (4.1 Å) and Mg^{2+} (4.25 Å) [37]. Owing to the size screening effects, pharmaceutical-grade PB has been utilized for assisting Cs removal from patient body after the Chernobyl disaster. Ishizaki et al. [17] revealed that synthesized PB nanoparticles ($Fe_4(Fe(CN)_6)_3$ with hydrophilic defect sites has supreme Cs adsorption capability and proposed that the Cs^+ ions were adsorbed via the defect sites of nanoparticles by proton-elimination reaction from the coordinated waters.

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http://dx.doi.org/10.1016/j.seppur.2015.08.029
1383-5866/

The small size of PB nanoparticles provides them very large specific surface area for enhancing adsorption capability. The PB nanoparticles can effectively uptake Cs ions, however, their recovery after adsorption is an obstacle to field applications of these adsorbents [29,37]. The concept of using nanocomposites containing PB-type nanoparticles covalently linked to a matrix appears to be a promising route to the decontamination of cesium ions [7]. Kitajima et al. [25] adopted the ion-exchange technique (Na^+ to K^+) for immobilizing PB nanoparticles onto the cotton matrices, and applied the so-produced PB-matrices to adsorb Cs^+ from water at a decontamination factor of order of 10^6. Yasutaka et al. [43] applied PB impregnated nonwoven fabric to remove ^{134}Cs and ^{137}Cs from water streams. These authors noted that the radioactive cesium in water samples could be concentrated within 20–60 min by passing the sample through 10–12 columns, connected in series to recover 100–108% of isotopes. This method was used to concentrate the radionuclides in water samples in short period of time. Yasutaka et al. [44] adopted the cartridges with PB impregnated fabric to remove water with 0.005–5 Bq/L of Cs. The recovery of Cs ranged 83–98% when the water was passed through the cartridge. On the other hand, polymeric binder was commonly adopted to immobilize functional particles for specific applications. Vipin et al. [38] encapsulated Prussian blue in calcium/alginate beads and the beads were reinforced by carbon nanotubes. The so-yielded beads were used to adsorb cesium and revealed high affinity over wide range of pH and concentrations of potassium and sodium ions. These authors also demonstrated the use of these beads in large columns for large-scale water treatment. However, after adsorption of radioactive cesium, radiation heating may deteriorate the durability of polymeric matrix thus produced. Kawamoto et al. [24] filed the patent on the use of inorganic binder to form Cs-granules as adsorbent, which was used later by Chen et al. [5] for Cs removal from waters. Hu et al. [16] developed a spongiform adsorbent that contains PB for adsorbing cesium. This adsorbent was a quaternary (polyurethane/carbon nanotubes/diatomite/PB) composites. The caged PB after being permanently immobilized in polyurethane spongy showed a 167 mg/g capability for absorbing cesium.

This study applied the PB-non-woven fabric in batch and in column tests to remove soluble Cs^+ from waters. The cesium barriers applicable to waterworks have to be of high efficiency, cost-effective, stable in storage and compatible to the existing treatment processes. Additionally, impurities in drinking waters such as humic substances, residual coagulants (Al or Fe salts) and residual chlorine (if any) may interfere with Cs removal efficiency. Most existing literature works on Cs removal handled wastewaters or natural waters for non-potable purpose. As per our best knowledge, this is the first paper reporting the feasibility of using PB fabrics in waterworks for Cs removal from contaminated waters.

2. Experimental

2.1. PB adsorbent

The PB-immobilized nonwoven adsorbents used in the previous paper were prepared [23,43,26] (Fig. S1b). The PB density in the adsorbent is 3–6 wt%, depending on the Lot. No. The fabric was filled up the testing column of diameter 6.7 cm and height 10 cm and columns of diameter 35 cm and height 120 cm for lab test and field test, respectively.

2.2. Non-woven fabric tests

In lab tests columns of diameter 6.7 cm and length 10 cm were packed with the PB non-woven fabric (100 mm × 10 m) with 3% w/w PB. Tap water with 30 ppb dosed Cs and 0.40 NTU, pH 7.0 and 102 μS cm^{-1} was fed continuously at column bottom with flow rate controlled for contact time up to 400 s. The effluent samples were collected after 25 L of water had flowed through the column at each contact time. The filtered effluent was measured in its residual Cs concentration in the filtrate being measured using inductively coupled plasma mass spectroscopy (model 7700 series ICP-MS, Agilent Technologies).

In filed test, four identical columns (35 cm × 123 cm) were packed with 3% w/w PB non-woven fabric and were installed at Zhitan Waterworks, New Taipei City, Taiwan, which produces three millions metric tons of potable water per day (Fig. S1). Raw water received by the Zhitan Waterworks at the distribution wells was fed into the pilot plant facility, which had identical processes by the full-scale production chain. In brief, the raw water was first dosed with 30 ppb Cs^+ at receiving tank and then was dosed with polyaluminum chloride (PACl) as coagulant at rapid mixing basin, followed by a flocculation basin, sedimentation basin and a rapid filtration basin. (Note: The concentration chosen is to fit the detection limit of the applied ICP-MS (0.1 ppb) in water samples. Although in real scenario the radioactive Cs should be at much lower concentration, we believe the tests herein conducted provide a reference on the potential of applying the current fabrics in tap water treatment.) Flow rates into the four columns were controlled so the contact times of water to the PB fabric were initially at 100, 150, 200 and 375 s, respectively. Experiments were conducted in the period with a hit of a tropical typhoon with heavy shower and high turbidity of raw waters to demonstrate the effects of rapid change in raw water quality on cesium removal from waters. Water samples were collected at 2-h intervals after each process unit with their properties being measured.

2.3. Other analysis

The water samples were collected and filtered through 0.45 μm filters. The residual Cs concentrations (C_e) in the filtrate were measured using inductively coupled plasma mass spectroscopy (model 7700 series ICP-MS, Agilent Technologies), from which the adsorbed quantity on PB was evaluated (q_e). All tests were conducted in triplicate to assure data quality.

Zeta potential measurement of particles in suspensions was carried out in a Zetasizer (Nano-ZS, Malvern Co., UK). The cell repeated flushing by DI water and ethanol several times before the measurement. The pH of the samples was measured using a calibrated pH meter (WTW pH-315, Weilheim, Germany). The TOC data of water samples were analyzed by Aurora Model 1030 TOC analyzer (OI Analytical, Co., College Station, USA). The non-purgable dissolved organic carbon (NPDOC) is an index of organic composition concentration. The DOC data were averaged over triplicate analysis. Water quality were measured based on standard methods by Taiwan EPA (http://www.niea.gov.tw/analysis/method/ListMethod.asp?methodtype=WATER).

Biological acute tests with *Cyprinus carpio* and *Daphnia pulex* for collected water samples were performed using Standard methods by Taiwan EPA NIEA B904.13B and NIEA B901.14B, respectively.

3. Results and discussion

3.1. Batch adsorption

3.1.1. Adsorption equilibrium

The adsorption isotherms for PB nonwoven fabric in Cs^+ solution at 288, 298 and 308 K were shown in Fig. 1. At C_e < 2000 μg/L, the distribution coefficient (adsorbed amount (q_e) in μg/g PB to C_e in μg/mL solution can be greater than 4×10^4. At C_e = 30,000 μg/L,