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Prussian blue (PB) granules for cesium (Cs) removal from drinking water

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ABSTRACT

Cesium (Cs) removal from tap water has become an emerging issue after the disaster at the Fukushima Daiichi Nuclear Power Plant. Prussian blue (PB), a pigment crystal with a cage size similar to the hydration radius of Cs^+, is used in this study for the first time to remove Cs from drinking water. Adsorption isotherms of Cs on PB granules, which were determined at room temperature, fit Langmuir equations. The Cs-PB affinity was high, tolerating the challenge from competing ions and hypochlorite. Column tests and simulated rapid sand filter tests indicate that PB granules are highly efficient Cs adsorbents with low water head loss during applications. Possible scenarios for using PB granules as a Cs barrier in waterworks were discussed.

1. Introduction

The Fukushima Daiichi Nuclear Power Plant released 630,000–770,000 terabecquerels of radioactive nuclides into the environment after the East Japan Earthquake [1]. Since the half live of ^{137}Cs is much longer than ^{131}I [2], 1.8×10^{16} Bq ^{134}Cs and 1.5×10^{16} Bq ^{137}Cs residual radioactivity existed one year after the Fukushima Disaster [3]. The radioactive fallout contaminated drinking water in many Japanese cities [4]. Conventional drinking water treatment processes cannot effectively remove dissolved Cs from waters [5,6].

Adsorption efficiencies of cesium from water using natural adsorbents are generally inadequate [7–9]. Although efficient adsorbents have been synthesized, production costs are high [10–15]. Prussian blue (PB), a dark-blue pigment, has the formula $Fe_7(CN)_{18}$ and a crystal cage size similar to the hydration radius of Cs^+ [2,16]. Pharmaceutical-grade PB has been administered to assist in the removal of Cs from humans after the Chernobyl disaster. When binding to fixed carriers, nano-sized PB crystals have large specific surface areas for Cs decontamination from water [17,18]. For example, Kitajima et al. [19] applied an ion-exchange technique (Na^+ to K^+) to immobilize PB nanoparticles on cotton fabric. Yasutaka et al. [20] applied PB impregnated non-woven fabric to remove ^{134}Cs and ^{137}Cs from water streams. Additionally, Vipin et al. [21] encapsulated PB in calcium/alginate beads, which were reinforced with carbon nanotubes. Kawamoto et al. [22] filed a patent on the use of inorganic binders to form Cs granules as adsorbents.

This study applied the PB granules in batch tests and sand-bed filter tests to remove soluble Cs^+ from water. The cesium barriers applicable to waterworks must be high efficiency, cost-effective, stable in storage and compatible with existing treatment processes. To the best of our knowledge, this is the first study to apply PB granules to remove Cs from contaminated drinking water.

2. Experimental

2.1. PB granules

The PB adsorbents were produced following the patent by [23]. The formed PB nanoparticles had a mean diameter of about

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5–20 nm, equivalent to clusters of (5 × 5 × 5) or (20 × 20 × 20) unit cells. The synthesized PB nanoparticles were embedded into a binder matrix to make granules of size of 1 mm (Fig. S1a) following the patent by [24,25]. The weight percentage of PB in the granules was about 80%.

2.2. Granule tests

Batch tests of Cs adsorption were conducted by completely mixing tap water samples (turbidity 0.40 NTU, pH 7.4, residual chlorine 0.51 mg/L, total organic carbon 0.34 mg/L, conductivity 102 μS/cm) with 0.1375 g/L PB granules at 288, 298 or 308 K for 24 h. (Note: Preliminary tests revealed that 24 h was sufficient to reach adsorption equilibrium for the present PB-Cs system.) The dosed Cs had concentration of 3000–75,000 μg/L (ppb). Control tests with no PB granules were conducted to assure minimal loss of Cs during testing, sampling and measuring stages. To examine the effects of pH on Cs adsorption at 298 K, the pH of the tap water was adjusted to 5–9 by adding 1 M HCl or 1 M NaOH.

Laboratory columns (10 cm × 6.7 cm) packed with 350 g granules were prepared. The hydraulic permeability of PB packing was estimated by Darcy's law as 3.5×10^6 Pa s/m^2. The tap water with 30 μg/L Cs^+ was flowing from top to bottom. To examine the ion competition effects, NaCl, KCl, $CaCl_2$ and $MgCl_2$ salts were added in parallel tests with 900 ppb Cs^+ at 298 K. In all tests, the ionic strength of the tested samples were kept at 0.001 M. NaClO is a common disinfectant in Waterworks. In some tests, NaClO at 1 or 10 mg/L was dosed into the PB-Cs suspension to check whether the chlorine would attack the PB to release adsorbed Cs.

A stimulated rapid sand filter was composed of (from bottom) 10 cm cobblestone, 50 cm sand, 25 cm anthracite, and 10 cm Prussian blue granules (Fig. S1b). All packing except for PB granules was the same as those in use by Changxing Waterworks, Taipei, Taiwan. Two sets of tests were conducted with and without PB layer. Before Cs-testing, 800 l of tap water was first flowing through the sand bed at a filtration velocity identical to that applied in field application (7.7 m/h) to remove impurities. Then the tap water with 30 μg/L Cs^+ was flowing from top to bottom at prescribed superficial velocities to lead to contact times of PB granules of 46 s. Pressure drops across each layers of the packing were recorded. All filter tests were conducted in triplicate and at 298 K.

2.3. Other analyses

The water samples were first filtered using 0.45 μm filters and then measured on their Cs concentrations (Ce) using inductively coupled plasma mass spectroscopy (model 7700 series ICP-MS, Agilent Technologies). Based on the dosed quantity and measured Ce, the adsorbed quantity on PB (q_e) was calculated. 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 water quality were measured based on standard methods by Taiwan EPA (http://www.niea.gov.tw/analysis/method/ListMethod.asp?methodtype=WATER).

3. Results and discussion

3.1. Adsorption equilibrium

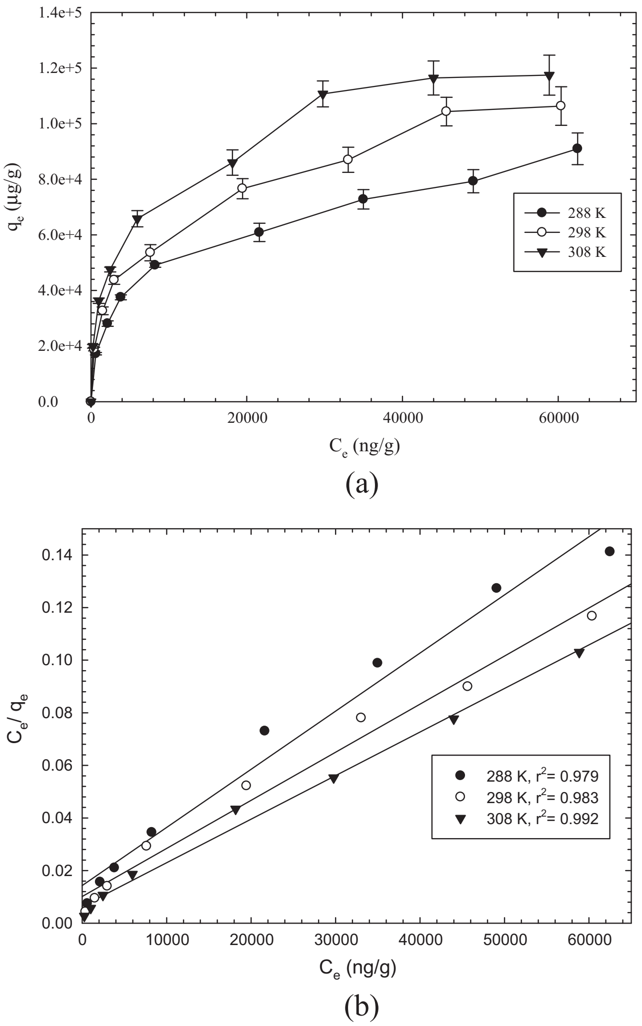

Fig. 1. Adsorption isotherms for Cs^+ adsorption on PB adsorbents. PB granules. pH: 7.4, contact time: 24 h. (a) Equilibrium data; (b) Langmuir fitting.

The adsorption isotherms for PB granules in Cs^+ solutions at 288, 298 and 308 K had Langmuir-like characteristics (Fig. 1a). The distribution coefficient (q_e/Ce) exceeded 50,000 for a low Ce regime. Restated, at <1000 ppb (μg/L), the PB granules were more effectively than at >10,000 ppb regime. Fitting data using the Langmuir equation ($q_e = q_{max}(K_{ad}C_e/(1 + K_{ad}C_e))$) (Fig. 1b) yielded the best-fit parameters (K_{ad}, q_{max}): (20,600 L/mol, 180 mg/g PB) at 288 K; (24,000 L/mol, 218 mg/g PB) at 298 K; and (34,500 L/mol, 241 mg/g PB) at 308 K. At a low Ce regime, approximation $q_e = q_{max}K_{ad}C_e$ holds. Ideally, assuming all treatments reach equilibrium within a short time and all active sites on granules can be used, 100 g of PB granules can remove 99.95% Cs^+ in 1 l of feed water with 30 ppb Cs^+ at 298 K, which can be used to decontaminate 1120 m^3 of feed water.

The plot of ln(K_{ad}) versus 1/T was linear at $r^2 > 0.99$ (plot not shown for brevity). The best-fit results indicate that the Cs adsorption process was $\Delta H = 18.9$ kJ/mole and $\Delta S = 148$ J/mole K. The Cs adsorption process can be characterized as a physical adsorption process. As stated by Liu and Lee [26], further discussion on the physical meanings of the obtained ΔH and ΔS data are not warranted.

Fig. 2a and b shows the influence of pH and concentration of competing ions on the quantities of adsorbed cesium (q_e). The q_e value peaked at pH 7. At an acidic pH, excess H^+ ions compete with cesium ions on the adsorption sites of PB *via* ion-exchange mechanisms. At an alkaline pH, q_e decreased slightly. Both Ca^{2+} and K^+ ions reduced the q_e value. However, in the presence of 145 mg/L