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Polyvinyl alcohol-borate hydrogel containing magnetic adsorbent for surface decontamination

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ABSTRACT

A stimuli-sensitive, strippable coating material that consisted of a magnetic field-sensitive adsorbent with excellent ^{137}Cs adsorption and a temperature-sensitive, elastic Poly vinyl alcohol (PVA)-borate hydrogel was developed for the decontamination of ^{137}Cs-contaminated surfaces. The viscous solution of adsorbent/PVA-borate complex can easily be applied to a surface at 50 °C, subsequently forming an adsorbent/PVA-borate hydrogel film that is strippable from the surface at room temperature. The film displayed a good removal efficiency of 83.46% and the decontamination factor (DF) of 6.05 from the ^{137}Cs-contaminated surface due to the presence of the adsorbent, which had a large distribution coefficient for Cs (3.34×10^4 mL/g). Moreover, the PVA-borate complex can be reused following a simple addition of water via the magnetic separation of the adsorbent, which can capture 99.071% of the ^{137}Cs in the used hydrogel film. These findings suggest a new eco-friendly volume-reduction method for radioactive waste after surface decontamination.

1. Introduction

The radioactive cesium isotope ^{137}Cs is the most dangerous contaminant among the nuclear fallout and radioactive waste generated by nuclear facility including nuclear power plants due to its long half-life (30.2 years), high-energy gamma ray (γ-ray) emissions, and similar biological behavior similar to potassium (Calarese, 2011). The nuclear accident at the Fukushima Daiichi nuclear power station in 2011 released large amounts of radioactive cesium into the environment, which affected various urban structures such as roofs, building exterior surfaces, and roads (Kinoshita et al., 2011). Thus, decontaminating various surfaces of objects that now contain ^{137}Cs is a critical issue for people who lived in the urban area surrounding the site of the nuclear accident.

Various methods for the surface decontamination of nuclear facilities, including aggressive chemical agents such as strong acids, physical removal of the surface using scabbling tools, or strippable coatings, have been extensively investigated (International Atomic Energy Agency, 2011; Serre and Drake, 2009). However, these methods are not suitable for exterior use in the treatment of ^{137}Cs-contaminated surfaces after a nuclear accident due to the hazards involved and to the costs of both specialized equipment and large-scale operations (Kaminski et al., 2016). Moreover, water-based washing processes require an additional water treatment system to prevent a secondary environmental contamination; further, the conventional strippable coatings are often toxic because they include both carcinogenic solvents and chelators, and they can become radioactive waste after use, which will require costly waste disposal (Gray et al., 2011).

Our group recently reported a magnetic adsorbent embedded in Ca-alginate hydrogel beads as a new surface decontaminant for the volume reduction of the radioactive waste that is generated after surface decontamination via the magnetic separation of the adsorbent capturing ^{137}Cs from the beads (Yang et al., 2016a). Although these beads exhibited an effective Cs removal performance of 90.51% from contaminated surfaces, the surface decontamination procedure requires two steps because the dried adsorbent/hydrogel beads must be deposited on a contaminated surface to capture the desorbed ^{137}Cs after the surface is treated with washing solution. Moreover, the procedure needs a harmful chelating agent such as EDTA, which can cause a secondary environmental contamination, to break the Ca^{2+}-alginate cross-linking for the magnetic separation of adsorbent (Yang et al., 2016a). Consequently, new surface decontaminants are still desired for a convenient surface decontamination procedure that includes a one-step application and an eco-friendly volume reduction method for radioactive waste that does not use toxic additives such as EDTA.

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In this paper, we present a new surface decontaminant that consists of magnetic adsorbents and a PVA-borate complex-based hydrogel for the one-step decontamination of ^{137}Cs-contaminated surfaces and the eco-friendly volume reduction method of radioactive waste after use. It is well known that PVA solutions, in the presence of a borate compound (e.g., borax), form a thermally reversible polymeric dispersion via the borate ester cross-linking with hydroxy groups on the PVA. Furthermore, with the PVA-borate complex exhibits a high elastic modulus that is tunable by changing either the temperature or total wt% of PVA and borate (Robb et al., 1997; Koga et al., 1999). The temperature-sensitive elastic property of the PVA-borate hydrogels allows them to be easily applied on a surface due to their low elasticity at high temperatures, but they can be peeled from a surface easily due to their high elasticity at low temperatures (Carretti et al., 2009, 2010; Natali et al., 2011). The adsorbent capturing the ^{137}Cs in the PVA-borate hydrogel is then magnetically separated from the hydrogel without using any harmful chemical agents for the volume reduction of radioactive waste after use. To the best of our knowledge, the utility of PVA-borate hydrogel as a coating material for the removal of ^{137}Cs from the surface have not been previously investigated, although PVA-borate-based hydrogels were shown to be effective cleaning agents in art conservation treatments (Carretti et al., 2009, 2010; Natali et al., 2011).

2. Materials and methods

2.1. Fabrication of adsorbent/PVA-borate-based surface decontaminant

Magnetic adsorbents were synthesized by following the procedure previously reported by our group (Yang et al., 2016b). Briefly, 2.7 g of $FeCl_3{\cdot}6H_2O$ and 7.2 g of sodium acetate were dissolved in 100 mL of ethylene glycol. Then, the mixture solution was transferred to a Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated to 200 °C for 8 h. After washing with excess ethanol and deionized water several times, the aqueous solution of magnetic nanoparticles (0.5 mg/mL) at pH 2 was reacted with a 2.5 mM $K_4[Fe(CN)_6]$ solution. After stirring for 1 h, the black particles were washed with deionized water several times. Finally, the product was dried in vacuum at 60 °C overnight.

For the fabrication of the surface decontaminant, the desired amount of sodium borate decahydrate was first dissolved in water or 0.1 M NH_4Cl solution. Then, the PVA (99 + % hydrolyzed, avg M_w 13,000–24,000) was dissolved by stirring and heating at 80 °C in sealed vials to prevent water from evaporating (Carretti et al., 2009). The wt% of PVA ranged from 4 to 6 wt%, and the wt% of borax was fixed at half that of PVA. Finally, the magnetic adsorbents were added to the PVA-borate hydrogel solution.

Oscillatory shear measurements were performed on a rotational rheometer (ARES-G2, TA instrument) in a parallel plate geometry with a plate diameter of 4 cm. Frequency sweeps were carried out within the linear viscoelastic range, as determined by a dynamic strain sweep. The storage and the loss shear moduli, G'(w) and G" (w), of the samples were measured over a frequency range of 0.05–100 rad/s at 20 °C and 50 °C. A controlled humidity chamber was used to prevent solvent evaporation.

2.2. Surface decontamination procedure

Cement was deposited on the surface of a planchet (diameter = 4 cm) and then coated with paint (Ilshin Co. Ltd., South Korea) to serve as a model surface. The painted cement was contaminated with ^{137}Cs by dropping and evaporating a known amount of ^{137}Cs solution on the surface (Yang et al., 2016a). While the temperature of decontamination solution was maintained at 50 °C, the contaminated surface was treated with 2.5 g of decontamination solution. Within a few minutes, an adsorbent/PVA-borate hydrogel film was generated and then peeled off the surface 3 h later. The radioactivity (counts per minute, cpm) of the painted cement before and after treatment was measured using an automatic low-background Alpha/Beta counting system (Tennelec series 5-XLB, Canberra, USA). Then, the adsorbent/PVA-borate hydrogel film was added to 20 g of water, and the adsorbent was magnetically collected using an external magnet. The radioactivity of the aqueous solutions before and after magnetic separation of the adsorbent was measured using an HPGe detector (Canberra, USA).

3. Results and discussion

Scheme 1 demonstrates the surface decontamination procedure using our stimuli-sensitive adsorbent/PVA-borate hydrogel. Our stimuli-sensitive surface decontaminant, which consists of a temperature-sensitive PVA-borate complex and a magnetic Cs adsorbent, can be brushed onto a surface due to its low viscoelasticity at temperatures higher than room temperature (Koga et al., 1999). Upon reaching room temperature, it forms an adsorbent/PVA-borate hydrogel film with a high elastic modulus that can easily be peeled from the surface (Carretti et al., 2009, 2010). When the hydrogel is applied to a contaminated surface, the ^{137}Cs begins to be solubilized and is captured by the magnetic adsorbent within the PVA-borate hydrogel. The subsequent removal of the adsorbent/PVA-borate hydrogel film with the captured ^{137}Cs results in some degree of surface decontamination. After this surface decontamination, the adsorbents capturing the ^{137}Cs are magnetically separated for the volume reduction of radioactive waste and the reuse of the PVA-borate hydrogel (Yang et al., 2016a).

As the component used for both ^{137}Cs capture and the volume reduction of the used surface decontaminant, the magnetic adsorbent was synthesized by coating magnetic nanoclusters with Prussian blue (PB), which is an iron-ferrocyanide complex that has a strong selectivity for binding Cs, via a reaction with potassium hexacyanoferrate and Fe^{3+} and was created on the surface of magnetic nanocluster under acidic conditions (Yang et al., 2016b). Transmittance electron microscopy images (Fig. 1(a)) show that the dark magnetic nanocluster, which consists of a large number of individual magnetic nanoparticles with a size of approximately 5–10 nm, was successfully coated with gray cubic shapes of PB. The X-ray diffraction (XRD) pattern reveals the characteristic peaks of both magnetite (Yang et al., 2013) and PB (Yang et al., 2016b), thus indicating the successful coating of the MNC surface by PB (Fig. 1(b)). The magnetic sensitivity of the magnetic adsorbent was examined using a vibrating sample magnetometer at 300 K (Fig. 1(c)). It exhibited superparamagnetic behavior, and the saturation magnetization (Ms. values) of the magnetic nanoadsorbent at 1.5 T was 27.8 emu g^{-1}, which is sufficiently high to collect the adsorbent in water by using an external magnet (Yang et al., 2015; Yang et al., 2016c). The Cs removal performance of the magnetic adsorbent was evaluated in terms of the removal efficiency (R), as defined by the following equation:

$$R = (C_0 - C_f)/C_f \times 100\%$$

where C_0 and C_f are the initial and equilibrium concentration of Cs in water, as determined by inductively coupled plasma-mass spectrometry (ICP-MS). The magnetic adsorbent (25 mg/mL) was added into the water, 0.01 M or 0.1 M NH_4Cl solution containing 5 ppm Cs. Although the R value decreased in the presence of NH_4Cl (Fig. 1(d)), the adsorbent displayed a good removal efficiency that exceeded 96.3%, indicating that our adsorbent has excellent selectivity for Cs even in the presence of NH_4Cl.