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Enhanced surface decontamination of radioactive Cs by self-generated, strippable hydrogels based on reversible cross-linking

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ABSTRACT

A self-generated, strippable hydrogel containing adsorbents was developed to remove the radioactive cesium from surfaces by adsorption for wide-area surface decontamination. Two aqueous polymeric solutions of polyvinyl alcohol (PVA) and phenylboronic-acid-grafted alginate (PBA-Alg) were easily applied to surfaces and subsequently self-generated a hydrogel based on the PBA-diol ester bond. Compared to the strippable coating and chemical gels, the PBA-diol ester bond-based hydrogel was easily peeled off the surfaces without a drying step due to its high elasticity, which is more practical and time saving. The resulting hydrogel displayed high ^{137}Cs removal efficiencies of 91.61% for painted cement, 97.505% for aluminum, 94.05% for stainless steel, and 53.5% for cement, which was 2.3 times higher than that of Decongel due to the presence of the adsorbent in the hydrogel having an excellent Cs distribution coefficient (3.34×10^4 mL/g). Moreover, the volume of radioactive waste generated after the surface decontamination could be reduced by a simple magnetic separation of the adsorbent from the used hydrogel, which can reduce the waste disposal cost. Therefore, our hydrogel system has great potential as a new, cost-effective surface decontaminant in various nuclear industry fields including wide-area environmental remediation after a nuclear accident or terrorist attack.

1. Introduction

Due to increased energy demands and global warming concerns, cheap and carbon-free nuclear power has been proposed as an alternative to thermal power derived from fossil fuels [1]. However, nuclear power is perceived as a threat due to the potential for unexpected releases of radionuclides. For example, various surfaces, such as concrete, steel, and paint, in most nuclear facilities, including nuclear power plants, are contaminated with radioactive materials during nuclear facility operations [2]. Unfortunately, severe nuclear accidents, such as those at Chernobyl or Fukushima Daiichi, have also contaminated various urban structures, such as roofs, exterior building surfaces, and roads, in extremely large areas [3]. Recently, concerns about nuclear terrorism using a radionuclide dispersal device to contaminate an urban area have increased [4]. Thus, surface decontamination is an important technology for environmental remediation after a nuclear accident or terrorist attack and various nuclear industry applications, including nuclear facility decommissioning. Among the various radionuclides, radioactive Cs is one of the most problematic components of radioactive fallout due to its long half-life (30.2 y) and high water solubility, forming compounds/complexes with many other substances in urban and rural areas [3,5].

Although current surface decontamination methods, including physical and chemical methods, are well established in the nuclear industry [6], the decontamination of radioactive Cs from wide-area exterior surfaces after nuclear accidents or terrorist attacks is still challenging due to some drawbacks of the current surface decontamination techniques [7]. Physical decontamination methods such as the physical removal of contaminated surfaces using a grinder or blast and high-pressure water are the primary surface decontamination method used at nuclear accident sites [8]. However, the application of physical methods using a grinder or blast incurs the cost of specialized equipment and workers and damages the structure of urban objects. In addition, high-pressure water has a low removal performance and further requires an additional water treatment system to prevent secondary environmental contamination. Although strippable coatings that can be easily peeled from a surface after drying can avoid the damage to structures and additional radioactive water treatments [2,9], their use is only effective on nonporous surfaces [10]. Moreover, strippable coatings employed for wide-area surface decontamination become radioactive waste and result in high waste disposal costs.

Chemical decontamination methods using ionic washing, clay, physical gels, supergels, or foam, except for those containing aggressive chemicals (strong acids) due to the hazards, have been extensively

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studied to decontaminate various surfaces, including porous surfaces, because they can chemically promote the desorption of cesium from the surface without damage to the structure [7]. Ionic washing using an ammonium salt can promote the ion exchange of radioactive cesium present on surface [11–13]. However, this technique only resulted in a limited improvement in removal performance. Although electrokinetic treatment combined with ionic washing was recently suggested to enhance the removal performance [14], this method is not suitable for wide-area surface decontamination. Moreover, the other chemical agents composed of clay paste (a natural adsorbent for various metal cations, including ^{137}Cs) [15], physical gels formulated by suspending mineral colloids in a washing solution [16], supergels that can absorb the radioactivity [17], or foam (RadRelease®) [18] were effective against surface decontamination. However, such methods generate a large amount of secondary radioactive liquid waste during the rinsing step and necessitate a wet-vacuum machine to remove residues from the treated surfaces. Thus, costly water treatments and specialized equipment are required for wide-area surface decontamination after a nuclear accident or terrorist attack [19].

Our group recently reported magnetic adsorbent-suspended Ca^{2+}-alginate hydrogels, capable of absorbing water, as a new strippable coating for the removal of ^{137}Cs from surfaces by adsorption [20,21]. Based on a simulation study, the strippable coating does not exhibit an evaporation boundary condition, and thus, it is effective for the removal of ^{137}Cs from a porous surface [22]. The hydrogels can be easily removed from surfaces without leaving a residue like strippable coatings due to their excellent peeling-off property, and the radioactive waste generated after the surface decontamination can be easily reduced by magnetically separating the adsorbent with ^{137}Cs from the hydrogel. However, the decontamination procedure requires two steps to form a strippable Ca^{2+}-alginate-based hydrogel because Ca^{2+} ions must be added after the application of an alginate-based polymeric solution to a contaminated surface. In addition, decrosslinking agents, such as EDTA and Na_2CO_3, are needed for the Ca^{2+}-alginate complex to separate the magnetic adsorbent from the hydrogel and reduce the radioactive waste volume [21]. Although a temperature-sensitive hydrogel based on a PVA-monoborate ($B(OH)_4{}^{-}$) complex, which is a thermally reversible borate ester cross-linked with hydroxyl groups in PVA, was successfully developed for a one-step decontamination and magnetic separation without the use of harmful additives, the hydrogel exhibited a relatively low Cs removal performance of 83.5% from a contaminated surface [23]. This is attributed to the short transition time from a polymeric dispersion with a low elasticity at a high temperature (50 °C), which is suitable for the surface application, to a strippable hydrogel with a high elasticity at room temperature, resulting in the polymeric solution only being in contact with the ^{137}Cs on the contaminated surface for a short time. Moreover, the ^{137}Cs removal tests using a PVA-borate complex-based hydrogel were only carried out using a painted cement surface as the model surface.

To overcome the shortcomings of previous hydrogels, reversibly crosslinked PBA-Alg and PVA hydrogels based on PBA-diol ester bond interactions were investigated in the present study as a self-generated, strippable coating to increase the time the polymeric solution is in contact with ^{137}Cs to enhance the removal performance. The PVA and PBA-grafted polymer complex has a higher storage modulus and longer junction zone lifetime than the PVA-monoborate ($B(OH)_4{}^{-}$) complex due to the multipoint interactions of the PBA-grafted polymer with PVA [24,25], and a film composed of the PBA-grafted polymer and PVA can easily form on a surface by a simple layer-by-layer method [26,27]. Scheme 1 demonstrates the surface decontamination procedure using a PBA-grafted polymer and PVA-based hydrogel with a magnetic adsorbent. The solutions of the PBA-grafted polymer and PVA with adsorbent are simultaneously applied to a contaminated surface. Then, the hydrogel self-generates via the PBA-diol ester bond and can be removed due to its excellent strippable property. The magnetic adsorbent suspended in the hydrogel adsorbs the ^{137}Cs and is magnetically separated from the hydrogel to reduce the radioactive waste volume. Alginate was used as the backbone polymer for the PBA-grafted polymer because it has a good chemical affinity for Cs due to its carboxyl groups [28]. Furthermore, we conducted a Cs removal test on various porous and nonporous surfaces, including painted cement, aluminum, stainless steel, and cement, which are general components of building structures in the nuclear industry and urban areas.

2. Materials and methods

2.1. Synthesis of phenyl boronic acid (PBA) conjugated alginate (PBA-Alg)

Sodium alginate (2 g, 10 mml on monomer unit), 3-aminophenylboronic acid (0.78 g (5 mmol) or 0.39 g (2.5 mmol)), and 1-3(-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) were dissolved in deionized water (200 mL). The mixture was stirred at room temperature for 24 h, extensively dialyzed against distilled water for 1 week (MWCO = 3000 Da), and freeze-dried.

2.2. Synthesis of the Cs adsorbent

The Cs adsorbents were synthesized following a procedure previously reported by our group [29]. 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 was transferred to a Teflon-lined, stainless-steel autoclave. The autoclave was sealed and heated to 200 °C for 8 h. After washing the resultant mixture with excess ethanol and deionized water several times, the aqueous magnetic nanoparticles solution (0.5 mg/mL and pH = 2) was reacted with a 2.5 mM $K_4[Fe(CN)_6]$ solution. After stirring for 1 h, black particles were obtained and washed with deionized water several times. Finally, the product was dried under a vacuum at 60 °C overnight.

2.3. Preparation of the PBA-Alg/PVA/adsorbent hydrogel for the rheological experiments

A desired amount of PBA-Alg was dissolved in water with or without the Cs adsorbent. The total weight of the solution was 5 g, and the wt% of PBA-Alg ranged from 0.2 to 2 wt%. The wt% of the adsorbent was fixed at 0.5 wt%. Next, 5 g of a polyvinyl alcohol (99 + % hydrolyzed, avg M_w 146,000–186,000, 8 wt%) solution was added to the mixture. Then, a NaOH solution was added to increase the pH of the mixture to 9, and the hydrogel formed immediately after vortexing the solution. Oscillatory shear measurements were performed using 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 determined by a dynamic strain sweep. The storage and loss shear moduli, G'(w) and G" (w), of the samples were measured over a frequency range of 0.05–100 rad/s at 25 °C A controlled humidity chamber was used to prevent solvent evaporation.

2.4. Surface decontamination procedure

To prepare the various contaminated surfaces, stainless steel or aluminum was deposited onto the surface of a planchet (diameter = 4 cm). In addition, cement and painted cement were also prepared as model surfaces by depositing cement onto a planchet, and the cement was coated with paint (Ilshin Co. Ltd., South Korea) for the painted cement. The surface morphologies of the cement before and after the paint coating are shown in Fig. S1. The model surfaces were contaminated with ^{137}Cs by dropping and evaporating a known amount of a ^{137}Cs solution on the surface [23], and then, the samples were stored at 50 °C for 1 week. For the surface decontamination, the PBA-Alg solution (1.5 mL) and PVA solution (1.5 mL) were simultaneously applied in the presence of NH_4Cl or the adsorbent on the various ^{137}Cs-contaminated surfaces. After 3 h, the hydrogels that formed were peeled off