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Polymeric coatings for surface decontamination and ecofriendly volume reduction of radioactive waste after use

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ABSTRACT

A magnet-sensitive and strippable polymeric coating that consists of a magnetic adsorbent with ^{137}Cs adsorption properties using a polyacrylamide (PAAm)/alginate(Alg)-based hydrogel with highly elastic properties was developed for surface decontamination. The aqueous polymeric solution of PAAm and Alg containing adsorbent could be easily applied to ^{137}Cs-contaminated surfaces via the brush method. The simple addition of calcium ions on the surface induced the formation of an adsorbent/PAAm-Alg hydrogel film that could easily peel away from decontaminated surfaces due to its high elasticity. This polymeric coating displayed a good removal efficiency of 96.53% and a decontamination factor (DF) of 28.85 for ^{137}Cs-contaminated surfaces due to the presence of the adsorbent, which had a large distribution coefficient for Cs (3.34×10^4 mL/g), and the large amount of Cs chelating groups in the Alg and PAAm, such as carboxyl and amine groups. The generated volume of the radioactive wastes after surface decontamination was simply reduced due to the magnetic separation of the adsorbent from the used polymeric coating. Furthermore, this new ecofriendly volume reduction method for radioactive waste demonstrated the reusability of PAAm and Alg for further surface decontamination because almost all of the ^{137}Cs (99.838%) captured in the used polymeric coating was removed by magnetic separation of the adsorbent. Therefore, the adsorbent/PAAm-Alg-based polymeric coating system has excellent potential as a new cost-effective surface decontaminant.

1. Introduction

Radioactive materials have been extensively used in various industrial and research fields, particularly for nuclear research and industry. During their utilization, various surfaces, such as concrete, steel, and paint, in most nuclear facilities become contaminated with radioactive materials. Thus, surface decontamination is a very important technology for radioactive material utilization and even for decommissioning nuclear facilities because surface contamination can be transferred to workers by contact, and it may become airborne if not treated (Raio et al., 2004). Meanwhile, the nuclear accident at the Fukushima Daiichi nuclear power station in 2011 unfortunately released large amounts of radioactive cesium into the environment, which also affected various urban structures, such as roofs, building exterior surfaces, and roads in a wide area (Kinoshita et al., 2011). Although current surface decontamination methods, including physical or chemical methods, in nuclear facilities are well established, surface decontamination for wide-area remediation after nuclear accidents is still challenging due to some drawbacks of the current surface decontamination techniques (Tripp et al., 2001; Kaminski et al., 2016).

High-pressure water jet-based washing has been widely used as a primary surface decontamination method in nuclear accident sites, such as Chernobyl and Fukushima. However, this method exhibits a low removal performance and requires an additional radioactive water treatment due to the generation of large amounts of radioactively contaminated water (Report of the internation, 2011). Although chemical methods using strippable coatings (such as DeconGel), foams (such as RadRelease®) and Argonne supergel developed by Argonne National lab. have proven to be effective for the surface decontamination of nuclear facilities during operation or decommissioning, the commercialized strippable coatings incur great costs for waste disposal after being used for wide-area surface decontamination because they become radioactive waste themselves after use (Gray et al., 2001). In addition, the foam-based decontaminants and Argonne supergel generate large

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amounts of radioactive secondary liquid waste during the rinsing step that require costly water treatments (Technical report of Unite, 2015).

Our group recently developed a magnetic adsorbent embedded in Ca-Alg hydrogel beads as a new surface decontaminant that easily reduces the volume of radioactive waste generated after surface decontamination via magnetic separation of the adsorbent-captured ^{137}Cs from the beads (Yang et al., 2016a). Although these beads exhibited an effective Cs removal performance of 90.51% from contaminated surfaces, it is difficult to fully cover the contaminated surface during the application of the dried adsorbent/hydrogel beads. Moreover, the procedure requires a harmful chelating agent, such as EDTA, to break the Ca^{2+}-alginate crosslinks to magnetically separate the adsorbent (Yang et al., 2016a). Consequently, new surface decontaminants are still desired to easily apply a surface decontaminant to fully cover the contaminated surface, and an ecofriendly volume reduction method for radioactive waste is desired that does not use toxic additives, such as EDTA.

In this paper, we present a new convenient surface decontaminant composed of a polymeric coating that contains Alg, a magnetic Cs adsorbent, and PAAm, which can form a hydrogel film by the simple reaction of Alg with Ca^{2+}. The PAAm was selected as an additive because it, and its modification such as crosslinked PAAm, exhibits good decontamination properties for the treatment of ^{137}Cs-contaminated soils and surfaces after nuclear accidents (Arnaud et al., 1995). Moreover, it has been recently discovered that Ca-Alg/PAAm hydrogel films have excellent elasticity, higher than that of pure Alg or polyacrylamide (PAAm) hydrogels (Sun et al., 2012; Yang et al., 2013a), which allows them to be easily peeled from a surface after surface decontamination. It is also well known that Ca-Alg/PAAm hydrogels are ecofriendly due to their excellent biocompatibility (Darnell et al., 2013). Additionally, the applicability of Na_2CO_3 solutions, which can extract Ca^{2+} from the PAAm/Ca-Alg hydrogels due to CO_3^{2-}, as an alternative for harmful EDTA solutions was investigated for the enhanced ecofriendly volume reduction method for radioactive wastes generated after surface decontamination.

2. Materials and methods

2.1. Synthesis of the magnetic adsorbent for radioactive cesium (^{137}Cs) capture

Magnetic adsorbents were synthesized by following the procedure, previously reported by our group (Yang et al., 2016b). Briefly, 2.7 g of $FeCl_3 \bullet 6H_2O$ 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 being cooled to room temperature, the resultant was collected with the help of a magnet, washed with excess deionized water and then dried in vacuum at 60 °C overnight. The obtained magnetic nanoparticles (0.5 mg/mL) were reacted with a 2.5 mM $K_4[Fe(CN)_6]$ solution at pH 2. 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.

2.2. Polyacrylamide (PAAm)-alginate(Alg)-adsorbent-based surface decontaminants

First, Alg and acrylamide (Sigma-Aldrich) were dissolved in deionized water where the amounts of Alg and acrylamide were 4 and 7 wt%, respectively. Then, N,N′-methylenebisacrylamide, ammonium persulfate, and N,N,N′,N′-tetramethylethylenediamine at molar ratios of 0.03 mol%, 0.031 mol% and 0.152 mol%, respectively, relative to the acrylamide monomer, were added to the solution. After stirring for 1 h, the solution was transferred into a glass mold, which was placed in an oven at 50 °C for 3 h. This step produced a polymeric solution containing Alg and crosslinked PAAm. For the fabrication of the surface decontaminant, magnetic adsorbents were then added to the polymeric solution with or without NH_4Cl.

2.3. Surface decontamination procedure

Cement was deposited on the surface of a planchet (diameter = 4 cm, thickness = 3 mm) and then coated with paint (400 g/m^2, white color and main composition is alkyd resine, Ilshin Co. Ltd., South Korea) to serve as a model surface. The painted cements were dried for 1 week and the surface morphologies of cement before and after coating with paint are shown in Fig. S1 (please see the supplementary data). The painted cements were next contaminated with ^{137}Cs by dropping and evaporating a known amount of ^{137}Cs solution on the surface (Yang et al., 2016a). After storing the model surface at 50 °C (or higher) for 1 week, 1.0 g or 1.5 g of the polymeric solution was deposited onto the contaminated surface. After 3 h, 0.6 mL of a 0.2 M $CaCl_2$ solution was added to the surface. Within a few minutes, an adsorbent/hydrogel composite film was generated and then peeled off the surface. The radioactivity (kBq/m^2) 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). All experiments were carried out in triplicate. After surface decontamination, the adsorbent/hydrogel films were added to a sodium carbonate (Na_2CO_3) solution, 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). As a control experiment, the contaminated painted cement was treated with distilled water, a 0.1 M NH_4Cl solution, a polymeric coating without adsorbent or an aqueous solution of 0.5 wt% adsorbent for 3 h.

3. Results and discussion

Fig. 1 demonstrates the surface decontamination procedure using our PAAm-Alg-adsorbent-based polymeric coating. As shown in Fig. 1, the polymeric solution, containing the adsorbent, Alg, and PAAm, was applied to the contaminated surface to capture the ^{137}Cs. Then, the strippable polymeric coating film was formed due to crosslinking of the Alg with Ca^{2+} for easy removal. Finally, the removed polymeric coating film was transferred to a Na_2CO_3 solution to degrade the Ca-Alg crosslinks and enable magnetic separation of the adsorbent from the mixture solution to achieve ecofriendly volume reduction of the radioactive waste without using harmful EDTA solutions (Yang et al., 2016a).

The magnetic adsorbent for ^{137}Cs capture was synthesized using magnetic particles coated with Prussian blue (PB), which has a strong selectivity for binding Cs, via a simple reaction with potassium hexacyanoferrate under acidic conditions (Yang et al., 2016b). The X-ray diffraction pattern of the adsorbents revealed the characteristic peaks of the magnetite (Yang et al., 2013b) and PB (Yang et al., 2016b), indicating the successful formation of magnetite and PB (Fig. 2(a)). The transmittance electron microscopy image (Fig. 2(b)) shows core-shell structure of the magnetic adsorbent, which consisted of magnetic particles with sizes of approximately 200–250 nm in the core part and cubic shapes of PB in the shell part. This result indicated that the magnetic particles were successfully coated with PB. In the FTIR spectrum (Fig. 2(c)), a strong