

Surface decontamination of radioactive cesium by reversibly cross-linkable hydrogel/adsorbent based coating

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1. Introduction

The high pressure water and physical removal of contaminated surfaces using grinder or blast, is widely used as the primary surface decontamination method at nuclear accident sites [1]. However, they generate the large amount of secondary radioactive waste and have risk of spread of radioactive contamination. Alternately, various coating materials such as strippable coating, clay, physical gel, supergel, and foam (RadRelease®) have been developed for the enhanced surface decontamination with preventing the spread of secondary radioactive contamination. However they are not still suitable for wide area surfaces decontamination after a nuclear accident or terrorist attack because they become radioactive waste themselves after use, resulting in high waste disposal costs [2]. Moreover, their coatings were not removed well from the treated surfaces and leave some residues when applied on the porous surfaces [3].

In the present study, hence, a new reversibly cross-linkable hydrogel composed of poly(vinyl alcohol)(PVA) and phenyl boronic acid (PBA)-grafted polymer having the high content of PBA was developed for the improved surface decontaminant from porous surface.

2. Methods and Results

2.1 Synthesis of phenyl boronic acid (PBA) grafted poly(methyl vinyl ether-alt-mono-sodium maleate)(PMVE-SM)

PBA-g-PMVE-SM/PVA was synthesized by grafting 3-aminophenylboronic acid (PBA) onto poly(methyl vinyl ether-alt-maleic anhydride) (PVM-MA) (Fig 1). At first, Poly(methyl vinyl ether-alt-maleic anhydride) (PVM-MA) and 3-aminophenylboronic acid were dissolved in deionized water, and stirred for 24 h, extensively dialyzed against distilled water for several days. Next, the sodium hydroxide aqueous solution were added into upper solution. After the mixture was stirred at room temperature for 24 h, and then extensively dialyzed against distilled water for several days, and freeze-dried. The FT-IR analysis of PBA-g-PMVE-SM also confirmed the successful attachment of the PBA group to PMVE-SM, and this was indicated by the appearance of a new peak at 1351 cm^{-1} , which can be assigned to B-O stretching after grafting PBA onto the PMVE-SM

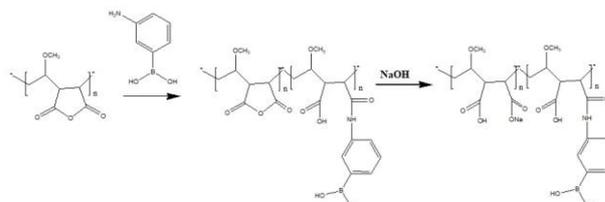


Fig. 1. The synthetic route of phenyl boronic acid (PBA) conjugated poly(methyl vinyl ether-alt-mono-sodium maleate) (PMVE-SM)

2.2 Synthesis of sulfur encapsulated chabazite (S-CHA)

The sulfur encapsulated chabazite having an excellent selectivity for ^{137}Cs were synthesized following a procedure previously reported by our group [4]. Briefly, after mixing of CHA and with elemental sulfur in glass tube, the mixtures were degassed, sealed using a torch under vacuum, and then heated at $310\text{ }^\circ\text{C}$ for 10 h. After cooling to room temperature, the product of S-CHA was obtained. As shown Fig 2. TEM images and energy-dispersive X-ray spectroscopy (EDS) elemental mapping of S-CHA shows that elemental sulfur (shown in pink) is uniformly distributed over the entire crystallites, indicating the successful encapsulation of sulfur in the micropores of CHA.

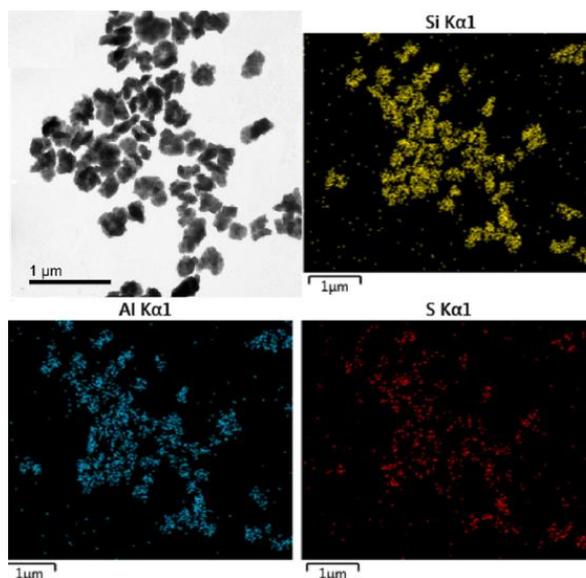


Fig. 2. TEM images and EDS elemental mappings (Si is shown in yellow Al is shown in blue and S is shown in red) of S-CHA.

3 Surface decontamination using PBA-g-PMVE-SM/PVA hydrogel containing S-CHA

To evaluate the decontamination ability of the PBA-g-PMVE-SM/PVA hydrogel containing S-CHA, ¹³⁷Cs-contaminated paint and cement were used as representative of model nonporous and porous surfaces, respectively. The cement and paint surface were prepared as porous and nonporous model surfaces, respectively, by depositing cement or paint onto a planchet (diameter = 4 cm). At first, the model surfaces were contaminated with ¹³⁷Cs by dropping and evaporating a known amount of a ¹³⁷Cs solution on the surface. Then, hydrogel composed of PVA and PBA-g-PMVE-SM/PVA without or with S-CHA were applied on the ¹³⁷Cs-contaminated surfaces. After 3 h, the hydrogel was soaked with 20 g of water to remove itself from the surface. The radioactivity (counts per minute, cpm) of the model surfaces before and after decontamination was measured using an automatic, low-background alpha/beta counting system (Tennelec series 5-XLB, Canberra, USA). The ¹³⁷Cs removal performance of our surface decontaminant was evaluated in terms of the removal efficiency (R) and decontamination factor (DF), as defined by the following equations:

$$R = (A_0 - A_f)/A_0 \times 100 \%, \quad (1)$$

$$DF = A_0/A_f \quad (2)$$

where A_0 and A_f are the ¹³⁷Cs activity of the initial surface and the ¹³⁷Cs activity of the final surface, respectively, after the treatment with our surface decontaminant. As shown in Table 1, all R values for cement surface are lower than those for paint surface because the silicate in cement has the strong chemisorption for Cs, whereas the paint surface has weak sorption property with Cs due to the hydrophobic surface.

Table 1. Removal performance of PBA-g-PMVE-SM/PVA hydrogel with and without S-CHA on ¹³⁷Cs-contaminated surfaces of painted cement and cement

		Water (soaking)	Hydrogel without S- CHA	Hydrogel containing S- CHA
Paint	A_0	4485.7	4506.0	4095.3
	A_f	1322.7	752.0	255.3
	R	70.513%	81.461%	93.766%
Cement	A_0	3309.0	3216.7	3259.0
	A_f	2468.0	2244.6	2045.3
	R	25.416%	30.220%	37.241%

In addition, the hydrogel containing S-CHA showed the much higher R values exceeding 93.7% for paint surface, and 37.2% for cement, compared with hydrogel without S-CHA. This is entirely attributed to additional

decontamination effect of S-CHA having the excellent Cs⁺ adsorption property [4]. This result demonstrated that the S-CHA suspended in the hydrogel can efficiently remove ¹³⁷Cs from surfaces because the hydrogel provides wet conditions for ¹³⁷Cs to bind to the adsorbent, which is consistent with previously reports [5,6].

3. Conclusions

In this study, a PBA-g-PMVE-SM/PVA hydrogel containing S-CHA was successfully developed for the enhanced surface decontamination of ¹³⁷Cs. Moreover, our hydrogel shows higher ¹³⁷Cs removal % (R value) on cement surface due to presence of S-CHA having high K_d value for Cs⁺ and their increased loading amount in hydrogel, respectively. From the above results, our hydrogel containing S-CHA has excellent potential for surface decontamination in various nuclear fields including nuclear facilities during operation and decommissioning or emergence situation in nuclear accident or terrorist attack.

REFERENCES

- [1] International Atomic Energy Agency, Report of the International Mission on Remediation of Large Contaminated Areas Off-Site the Fukushima Dai-ichi NPP, (2011)
- [2] M. D. Kaminski, S. D. Lee, M. Magnuson, Wide-area decontamination in an urban environment after radiological dispersion: a review and perspectives, J. Hazard. Mater., Vol. 305 p. 67, 2016.
- [3] US Environmental Protection Agency, Technical Report for the Demonstration of Wide Area Radiological Decontamination and Mitigation Technologies for Building Structures and Vehicles, EPA/600/R-19/019, Technical Report, U. S. Environmental Protection Agency, Washington, DC, 2016.
- [4] H.-M. Yang, C. W. Park, I. Kim, I.-H. Yoon, Y. Sihn, Sulfur-modified chabazite as a low-cost ion exchanger for the highly selective and simultaneous removal of cesium and strontium, Applied Surface Science, Vol 536, 147776, 2021.
- [5] H.-M. Yang, C. W. Park, K.-W. Lee, Enhanced surface decontamination of radioactive Cs by self-generated, strippable hydrogels based on reversible cross-linking, J. Hazard. Mater., Vol. 362 p. 72, 2019.
- [6] H.-M. Yang, I.-H. Yoon, Y. Lee, Poly(vinyl alcohol)-borax complex-based spray coating for the decontamination of radioactive Cs from wide-area surfaces, Chem. Eng. J. Vol 402, 126299, 2020.