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# Porous hydrogel containing Prussian blue nanoparticles for effective cesium ion adsorption in aqueous media

Youngjin Kim[a], Inhye Kim[b], Taek Seung Lee[c], Eunji Lee[b,*], Kyung Jin Lee[a,*]

[a] Department of Chemical Engineering and Applied Chemistry, College of Engineering, Chungnam National University, 99 Daehak-ro (st), Yuseong-gu, Daejeon 34134, Republic of Korea
[b] Graduate School of Analytical Science and Technology, Chungnam National University, 99 Daehak-ro (st), Yuseong-gu, Daejeon 34134, Republic of Korea
[c] Department of Organic Materials Engineering, College of Engineering, Chungnam National University, 99 Daehak-ro (st), Yuseong-gu, Daejeon 34134, Republic of Korea

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ABSTRACT

Cesium adsorbent was fabricated by synthesizing Prussian blue (PB) via redox reaction between $K_3[Fe(CN)_6]$ and $FeCl_3$ in inverse-high-internal-phase-emulsion (i-HIPE) hydrogel. The PB nanoparticles are successfully generated via novel pathway, in-situ redox reaction in hydrogel. Maximum cesium ion uptake capacity of composite is 0.1047 mmol/g (per composite amount) which is 3-times higher than that of purchased PB, even though very small amount of PB have been inserted. Adsorption kinetics and isotherm of PB/i-HIPE hydrogel was followed to pseudo-first-order and Langmuir model respectively. These results can provide excellent pathway to design effective absorbent for removal of radio-active, aqueous cesium ion in environments.



## Introduction

Concerns about radioactive species from nuclear power plants are steadily increasing owing to the recent accidents at Fukushima and the ageing of power plants worldwide [1]. Removal of radioactive species should be considered from two points of views: (1) decontamination and decommissioning of old power plants and (2) removal of radioactive species from the environment [2,3]. In particular, in March 2011, the Fukushima Daiichi nuclear power plant was damaged by a strong earthquake, which led to a huge explosion in the reactor. As a result, an enormous amount of radioisotopes, including $^{136}Cs$ and $^{137}Cs$, was spilled into the Pacific Ocean, soil, etc. [4–7]. This accident triggered many studies on radioisotope removal from environment [8–12].

According to several previous investigations, Prussian blue (PB) is capable of selectively adsorbing alkali cations, especially cesium ions [13–15]. Therefore, PB has been highlighted as a remarkable adsorbent to address radioactive cesium leaks. However, collection of PB nanoparticles after use in purification applications is expected to be difficult. Hence, to achieve easy collection after use, a number of studies have examined complexes between PB and matrix materials as efficient adsorbents for radioactive cesium [16,17]. Typical supporting materials include inverse opal-shaped carbon, graphene, particles, hydrogels, and nano/microfibers [16–22]. In comparison with the other materials, hydrogels have an obvious ability to interact with water, and hydrogels that support PB could be applied in many situations that require contact with water, such water pollution purification [17,23]. Moreover, when use the hydrogel as a supporting material for PB, volume of secondary pollutant containing radioactive materials can be much reduced by de-swelling.

Unfortunately, bulk type of hydrogels hinder the adsorption of cesium by PB because the rate of water flow within the hydrogel is limited [23]. In contrast, it is well-known that the porous hydrogels have high swelling rates because the swelling process is affected not only by diffusion but also by capillary phenomena in the pores. However, there are limited information considering porous hydrogel as a PB supporter, mainly because of difficulties in synthesis. There are various fabrication methods for porous hydrogel, such as the gas injection method and the inverse-template method [24–26]. Fabrication of adsorbent systems using an inverse high internal phase emulsion (i-HIPE) hydrogel is convenient and the obtained products have smaller channels between the pores than gas injection products [27].

Herein, we immobilized PB nanoparticles using a porous hydrogel as a structural support to fabricate a practical cesium

* Corresponding authors.
*E-mail address:* kjlee@cnu.ac.kr (K.J. Lee).

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ion adsorbent for applications under water. The porous hydrogel was fabricated using a i-HIPE system, and PB nanoparticles were synthesized in the porous hydrogel by a redox reaction between $FeCl_3$ and $K_3[Fe(CN)_6]$ [16,28]. The content of PB in the hydrogel was controlled by the concentration of the $K_3[Fe(CN)_6]$ aqueous solution. The cesium adsorption abilities of the PB-containing i-HIPE hydrogel using aqueous CsCl (simulant, non-radioactive ion) solutions, depended on various factors, such as pH and contact time with the solution.

## Experimental

### *Materials*

Acrylamide, *N*,*N*′-methylenebisacrylamide (BIS), paraffin oil, Triton™ X-305 (70% solution), ammonium persulfate (APS), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED), iron(III) chloride ($FeCl_3$), potassium hexacyanoferrate ($K_3[Fe(CN)_6]$), PB, cesium chloride (CsCl) and seawater were purchased from Sigma Aldrich Chemical Co. Hydrochloric acid (HCl) and ammonia solutions were purchased from Samchun Chemical. All chemicals were used as received without further purification.

### *Fabrication of i-HIPE hydrogel*

The 70% solution of Triton™ X-305 was diluted to 20% with deionized water. Then, the monomer (acrylamide, 10 w/v%), crosslinker (BIS, 10 mol% of monomer), and initiator (APS, 1 mol% of monomer) were dissolved in Triton™ X-305 20% solution. Paraffin oil (4 mL) was dropped into 1 mL of the aqueous mixture over 10 min with vortexing at 1500 rpm. Subsequently, TEMED was added to the mixture as a polymerization promoter with vortexing at 2000 rpm. To realize polymerization of the continuous phase, the reactor containing the stabilized HIPE was closed and maintained at 30 °C in an oven for 4 h. After polymerization, the paraffin oil was removed from the HIPE by washing wit THF and acetone alternately 3–4 times. Finally, the i-HIPE hydrogel was dried at 40 °C in an oven for 17 h to obtain white sponge-like hydrogels.

### *Fabrication of PB-containing i-HIPE hydrogel*

The dried i-HIPE hydrogel was soaked in 0.1 M $K_3[Fe(CN)_6]$ solution for 30 min. After removing the i-HIPE hydrogel from the $K_3[Fe(CN)_6]$ solution, excess solution was removed using filter

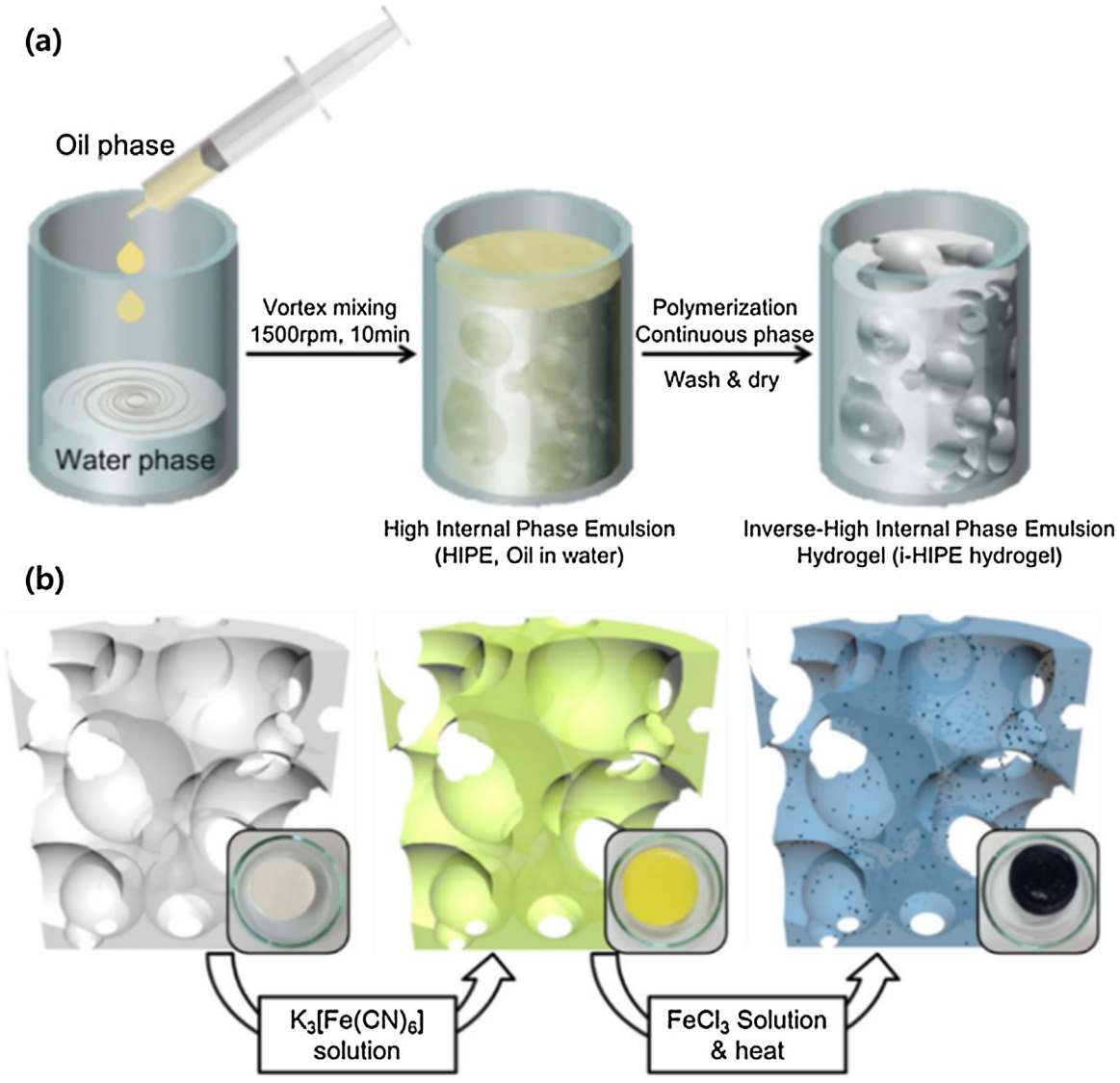


**Fig. 1.** Schematic diagrams of (a) preparation of i-HIPE hydrogels and (b) synthesis of PB nanoparticles in i-HIPE hydrogel.

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