

Prussian blue immobilization on various filter materials through Layer-by-Layer Assembly for effective cesium adsorption

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Abstract. Prussian blue (PB) is well known for its excellent Cs⁺ ions adsorption capacity. Due to the high dispersibility of PB in aqueous phase, composite materials imbedding PB in supporting materials have been introduced as a solution. However, building PB particles inside porous supporting materials is still difficult, as PB particles are not fully formed and elute out to water. In this study, we suggest layer-by-layer (LBL) assembly to provide better immobilization of PB on supporting materials of poly vinyl alcohol sponge (PVA) and cellulose filter (CF). Three different PB attachment methods, ex-situ/in-situ/LBL assembly, were evaluated using PB leaching test as well as Cs⁺ adsorption test. Changes of surface functionality and morphology during PB composite preparation protocols were monitored through Fourier transform infrared spectroscopy and scanning electron microscopy. The results indicate that LBL assembly led to better PB attachment on supporting materials, bringing less eluting PB particles in aqueous phase compared to other synthesis methodologies, such as ex-situ and in-situ synthesis. By enhancing the stability of the adsorbent, adsorption capacity of PVA-PB with LBL improved nine times and that of CF-PB improved over 20 times. Therefore, the results suggest that LBL assembly offers a better orientation for growing PB particles on porous supporting materials

Keywords: prussian blue; cesium; polyvinyl alcohol sponge; cellulose filter; layer by layer

1. Introduction

Prussian blue (PB) is well known for its excellent capacity to adsorb cesium ions (Cs⁺). The structure of Prussian blue is a simple lattice in which the cation of the hydrated Cs⁺ ion is bound via electrostatic force in a cage of the PB lattice (Ishizaki *et al.* 2012). Having this special structure, PB was used as adsorbent in the decontamination of radioactive cesium after the Fukushima nuclear plant disaster.

Because of its high Cs⁺ ion adsorption capacity, Prussian blue has been applied in the water treatment field in many studies. However, the attraction force between PB and water leads the particles to be dispersed in water, and this makes it difficult to recover or separate them from the treated water stream due to the few-tens of nanometer size of PB. In order to overcome this size issue, intensive studies have been carried out to immobilize PB in/on the supporting matrix. Especially, PB composites based on organic polymers having numerous pores have recently come to be preferred as supporting material in applications in the water treatment field. PB immobilization technologies using cellulose (Vipin *et al.* 2016), chitin (Vincent *et al.* 2015) and alginate (Vipin *et al.* 2016) as supporting materials have been introduced.

PB immobilization methods can be roughly classified

into ex-situ synthesis and in-situ synthesis. In ex-situ synthesis of PB, pre-synthesized PB is attached on supporting matrix by physical interaction, but it is difficult to deliver PB particles deeply inside the pores (Montazer and Maali Amiri 2014). In this sense, the in-situ synthesis method has been more actively studied in cases of porous supporting materials. PB particles were synthesized in the presence of supporting materials in in-situ synthesis, but this also caused a problem of residue inside pores when the concentrations of precursors were not carefully regulated, which occurs when growing unstable PB particles.

For the in-situ synthesis of PB, two precursor solutions, iron (III) solution and ferrocyanide solution, were used, as suggested in a previous study (Vincent *et al.* 2014, Jang *et al.* 2014, Yang *et al.* 2014). Typically, supporting materials were immersed in iron (III) solution; then, the supporting materials were immersed again in ferrocyanide solution prepared in a separated vessel. However, the amount of immobilized iron (III) was much lower than the initial iron (III) concentration in the solution; therefore, the stoichiometric ratio was not well maintained if the concentration was not well regulated. Due to the deficiency of iron(III) ion, PB prepared by in-situ synthesis would be unstable on the surface of supporting materials.

2. Materials and method

2.1 Materials

Poly vinyl alcohol sponge was obtained from

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that LBL assembly offers more stable growth of PB particles for immobilization on the surface of supporting materials having –OH groups, showing a clear peak in the region of C≡N groups.

- An additional step using iron(III) solution provided suitable stoichiometric condition to produce more PB and stable composition; this method prevented the eluting of PB during washing steps.
- Especially, L-PVA-PB and L-Cell.-PB had almost no leached-out PB particles during washing, because the LBL assembly contributed to the extraction of residues in pores of supporting materials, while at least 3 times of washing was required for other cases.
- The Cs⁺ adsorption capacity of L-PVA-PB improved from 0.910 mg/g to 0.8626 mg/g and the cesium adsorption capacity of L-Cell.-PB also improved from 0.9305 mg/g to 2.2510 mg/g; both improvements are due to the higher content of PB attained by LBL assembly.
- Therefore, LBL assembly will be a highly efficient process for growing PB particles on a porous supporting material.

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