Prussian Blue Nanoparticles for the Enrichment of Radioactive Cesium in Solutions – 13275

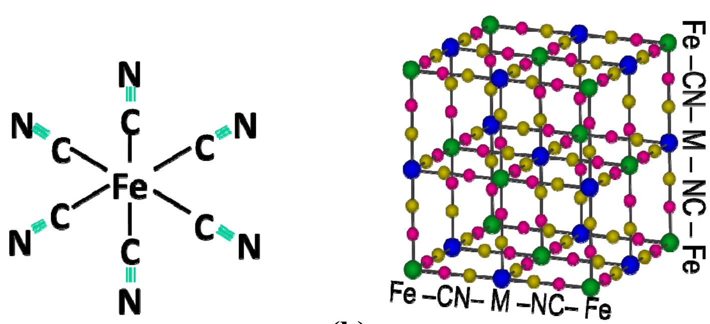
Durga Parajuli, Akiko Kitajima, Hisashi Tanaka, and Tohru Kawamoto
Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, 305-8565, Tsukuba, Japan

ABSTRACT

Prussian blue (PB) nanoparticles in different form were studied for the adsorptive enrichment of Cs in solutions. Water dispersible nano-PB was found to be highly effective on removing trace level Cs in stagnant waters. The nano-PB loaded filters were effective on collecting Cs in flow systems like river water, thus provides a big relief on controlling the environmental mobility of Cs and its entry to the productive lands via water. Water insoluble nano-PB adsorbent possesses high Cs loading capacity and selectivity and it is found to be the ultimate option for the systems containing high concentration Cs.

INTRODUTION

Prussian blue (PB), ferric hexacyanoferrate, is an inorganic complex, mostly known in the history for its peculiar Cesium (Cs) selectivity [1]. In reference to the PB parent molecule, a number of transition metal hexacyanoferrate are synthesized and named as PB-analogues. The PB forms an open cage structure, Figure 1, that possesses a typical zeolytic characteristic, an adjective typically given to any molecule capable of trapping other ions within its lattice cavities [2]. However, PB, different from the common zeolytic materials, possesses unique selectivity for the Cs-ion. Due to this structural coincidence, PB has become the ultimate Cs-trapper.



(a) (b) M = Fe, Co, Ni, Cu, Zn, etc.

Figure 1. Hexacyanoferrate (a) complexes with transition metal ions to form Prussian Blue, $Fe[Fe(CN)_6]_x$, type inorganic complex molecules, the vacancy of the hexacyanoferrate is neglected for simplicity (b), best known for peculiar Cs selectively.

A wide area of east Japan centering Fukushima prefecture is contaminated by radioisotopes released from destructed Fukushima Daiichi Nuclear Power Plant. Months after the accident, the major sources of environmental radioactivity are long living radioisotopes of Cesium, Cs-134 and Cs-137. Naturally existing clays with zeolytic or layer structure are well known for their ability to adsorb Cesium (Cs). But, when the issue is adsorption of Cs radioisotopes for the purpose of enrichment to the minimum possible extent, selectivity of the adsorption material is crucial. To the date, Prussian Blue (PB) and its analogues are the quite effective materials known for possessing peculiar selectivity for Cs. Along with the selectivity, the adsorption kinetic is also very important for trapping Cs from flowing systems, river waters, etc. Increasing the effective surface area of the material enhances its adsorption speed. Therefore we studied the Cs adsorption properties of Prussian blue nanoparticles, nano-PB, and their application on Cs-removal from various environmental waters and solutions generated during the decontamination of soil, ash, etc.

EXPERIMENTAL

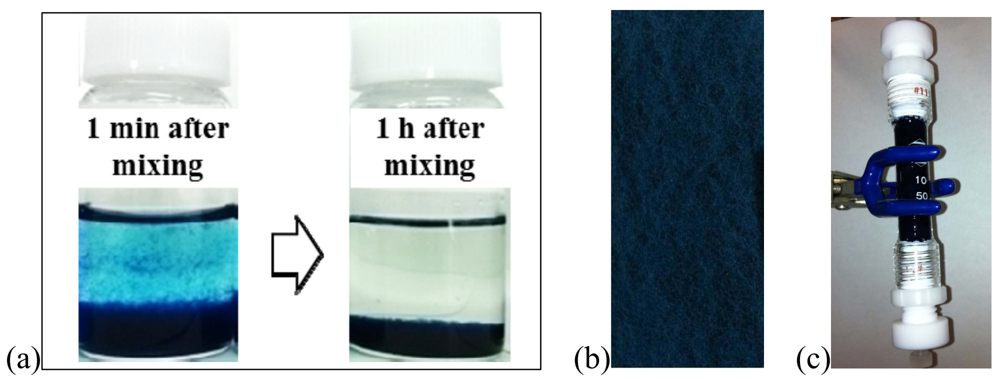


Figure 2. Methods for the removal of Cs from waters in various forms: (a) Coagulation of water dispersible nano-PB using coagulant for the stagnant water decontamination. (b) Nano-PB loaded filter for the removal of Cs from mobile waters. (c) Water insoluble nano-PB packed in a column for the Cs-washed solution decontamination.

Water soluble and water insoluble type of nano-PB were used in this study. The representative forms of nano-PB used for three different systems are given in Figure 2. The water dispersible nano-PB was used for the removal of Cs from stagnant waters by coagulation method. For this, certain concentration of Cs was mixed with pure water and river water containing some 0.1 ppb Cs-133. Then 0.1 wt% nano-PB solution was mixed and then a coagulating reagent, for example, polyaluminum chloride, was added to the mixture. After the complete coagulation of nano-PB, the supernatant solution was tested for the remaining Cs using Perkin Elmer Model NEXION 300D Inductively Coupled Plasma Mass Spectrometer (ICP-MS). In order to trap Cs in river or stream waters, the nano-PB filters were prepared by loading it to the non-woven fibers. Then the filters were either packed to tube-filter or were used as flow-bed. For the removal of Cs extracted to water or acid solutions while decontamination of soil, ash, etc, water insoluble nano-PB was used by packing it in a column.

RESULTS AND DISCUSSION

Coagulation Method for the Removal of Traces of Cs in Stagnant Waters.

It is well know that the radioisotopes of Cs even in trace level (ppt) emit gamma rays in higher scales. However, removal of any element in trace level is a difficult task. For the purpose of removing low concentration Cs using nano-PB, river water collected from Fukushima Prefecture was used as the solvent and added 0.05 to 1.0 ppb Cs-133. Then 0.1 ml of 0.1 wt% nano-PB solution was added to 10 ml of Cs solution. After mixing well, coagulating reagent was added in order to separate the nano-PB. The amount of Cs loaded to nano-PB was evaluated by the difference in the initial Cs concentration and the remaining Cs in the supernatant solution. The observed results are given in Figure 3.

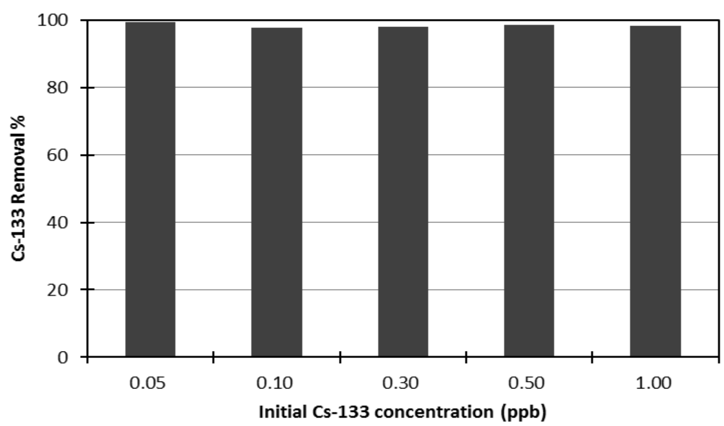


Figure 3. Demonstration of the feasibility of using water dispersible nano-PB for the removal of traces of Cs from environmental fresh waters.

The task of removal of contaminants in traces level needs material with very high selectivity otherwise the higher concentration species occupy the adsorption sites. For this reason, zeolites are good for overall purification, but are weaker options for trace level removal like Cs in environmental waters. Under such requirement, nano-PB can be the best option as demonstrated by the results in Figure 3. In addition, because the issue is volume reduction of the Cs radioisotopes contaminated waters/solutions, nano-PB possessing the best selectivity for Cs and capability for recovering Cs from trace levels is the ultimate choice.

Preparation of Nano-PB filters for the Removal of Traces of Cs in flowing waters

River or stream waters are mostly responsible for the mobility of Cs in the environment. Cs once come to contact with soil clay minerals, is usually get fixed. But, the Cs from nuclear fallout absorbed on plant parts are continuously carried to fields or drinking water systems via the flowing waters. Though the dispersion of nano-PB followed by its removal by coagulation method is found to be highly effective on removing Cs in traces levels, the method is not applicable for flowing waters. Therefore, nano-PB filters were prepared by loading it onto non-woven fibers, etc. The filters are found to be highly effective on removing traces of (as low as 10 Bq/l) Cs radioisotopes along with Cs-133. Because, loading optimum mass of nano-PB is important for making the filter compatible to use in the flowing system, this method is preferred for low Cs concentration systems so that a large volume of water can be treated using least possible filter.

Insoluble nano-PB for the Decontamination of high Cs Concentration Solutions

Selective Cs removal using nano-PB from trace levels is already explained. However, in the high concentration systems, dispersion followed by coagulation generated larger mass of flocculate. Therefore, in higher concentration systems using 100% nano-PB packed column is preferred. Cs selectivity and capacity of water insoluble nano-PB powder was tested by passing a wood-ash washed water (pH 7) with added 100 ppm Cs-133. The nano-PB successfully loaded as high as 10 wt% Cs at the breakthrough point. Because the solution contained excess of potassium along with other alkali metal and other metal ions possessing similar valence and hydration, both the selectivity and Cs-loading capacity of nano-PB are outstanding

Once nano-PB was proved to hold strong selectivity for Cs, adsorption of radioisotopes was also studied. For this, wood ash showing 36 kBq/kg radiocesium activities was washed with water to yield solution containing about 3.0 kBq/kg of Cs. Complete removal of overall Cs was observed by mixing for a minute only.

CONCLUSION

Prussian blue is known for its Cs trapping characteristic. By its conversion to water dispersible nano-PB, removal of traces of Cs in large volume of stagnant water system has become possible. Loading the dispersible nano-PB to a non-woven filter expands its application for the decontamination of flowing waters. In addition, the insoluble nano-PB offers high capacity and faster adsorption of Cs from very high to low Cs concentration solutions. By selecting the nano-PB adsorbents according to the system type and Cs concentration level, the enrichment and safe-storage of Cs radioisotopes can be smoothly conducted.

REFERENCES

1. M.T. GANZERLI VALENTINI, S. MELONI, V. MAXIA, J Inorg. Nucl. Chem., 34, 1427, 1972.

2. M. WARE, J Chem. Edu., 8,612, 2008