Decorporation of Cesium

Prussian Blue Capsules for Decorporation of Cesium from Human Body

Prithwish Sinharoy[1]*, Sher Singh Meena[2], D. Banerjee[1], G. Sugilal[1] and C. P. Kaushik[1]

[1]*Nuclear Recycle Group, Bhabha Atomic Research Centre, Mumbai-400085, INDIA*
[2]*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, INDIA*

Prussian Blue capsules

ABSTRACT

This paper reports indigenous development of a process for synthesizing high purity, insoluble Prussian blue (PB) powder. The purity of the product has been established using techniques like Mossbauer spectroscopy, SEM-EDS and XRD. It is confirmed that the synthesized PB powder has very high cesium uptake (K_d = 5.2 x 10^4) performance from a wide range of simulated solutions generated from different parts of the human digestive system. A comparison with literature data shows that the synthesized PB capsule is a suitable drug for the decorporation of radioactive cesium from the human body.

KEYWORDS: *Prussian blue capsules, Cesium, Decorporation, Remediation, bio-hazard.*

Introduction

Insoluble Prussian blue (PB), having chemical formula $Fe_4^{III}[Fe^{II}(CN)_6]_3$, is a well-known agent for decorporation of Cesium and Thallium contamination from the human body[1-3]. This has been used as a counter-measure for treating internal cesium contamination in several nuclear accidents like the Chernobyl reactor accident, the Goiânia tragedy[4] and in the comparatively recent Fukushima disaster. Radioactive cesium released from nuclear accidents or radiological bombs (dirty bombs), can enter the human body through ingestion or the food chain. Within the human body, it follows the path of potassium, gets absorbed through the intestine wall and is distributed in all soft tissues via blood. PB capsule is administered as an immediate medical intervention. The insoluble PB binds cesium during its passage through the digestive system and excretes it from the body. The rapid decorporation of Cs by PB helps in reducing the detrimental effect of radiation on human health. It is to be noted that PB capsule is a USFDA approved drug for Cs decorporation from the human body and is available in the international market in the trade name of *"Radiogardase"*.

This article reports a novel approach towards indigenous development of PB capsules and its evaluation towards removing cesium from the human body under simulated conditions.

Experimental Section

PB powder was synthesized by two methods *viz.* i) reacting K_4FeCN_6 with $FeCl_3$ (Code: PB-10B) and ii) reacting H_4FeCN_6 and $FeCl_3$ (Code: PB-6) utilizing AR grade chemicals. The final precipitate obtained from both processes were washed thoroughly with 0.01 M HCl, water followed by Ethanol. After drying under a vacuum at room temperature, the product was filled in zero size empty gelatine capsules and stored in a well-capped glass bottle. Purity of the product was assessed using techniques like x-ray diffraction (XRD), Mössbauer and SEM-EDS. Cesium uptake performance was evaluated by conducting batch equilibration tests using 0.1 g powder (particle size: 175 to 250 micron) and 10 mL water spiked with ^{137}Cs radiotracer. Cesium activity in the solutions before and after equilibration was measured using a NaI/Tl scintillation detector, and the results were used to calculate Cs uptake performance.

Results and Discussion

The optimized procedure for the synthesis of PB (PB-6) is summarised in Fig.1. $H_4Fe(CN)_6$ was prepared from K_4FeCN_6 using a cation exchange column and reacted with $FeCl_3$. In addition, a batch of PB was prepared as per conventional procedure (PB-10). Several factors like pH, temperature, stirring speed, and mode of addition were optimized for better product quality.

XRD spectra of the synthesized PB products are shown in Fig.2. The compounds synthesized by two routes (PB 6 and PB 10B) have identical XRD patterns. The major peaks at ~18°, 24°, 35°, and 39° (2θ) can be assigned to (200), (220), (400), and (420) planes of the PB crystal lattices, respectively. These peaks confirm a face centred cubic lattice structure and space group Fm_3m [Space group No.: 225] of PB crystal lattice.

Fig.3 shows the room temperature Mössbauer spectra of the synthesized PB samples. Mössbauer spectra are fitted with three symmetric doublets (A, B and C)[5]. For PB-6, the doublet (B) with low isomer shift (IS_B = - 0.158 mm/s), quadrupole splitting (QS_B = 0.141 mm/s), and relative area

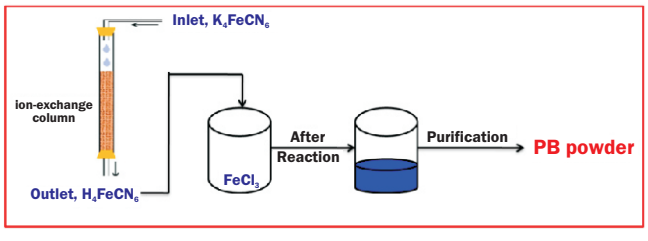

Fig.1: Procedure for synthesis of Insoluble PB powder.

*Author for correspondence: Prithwish Sinharoy
E-mail address: psroy@barc.gov.in

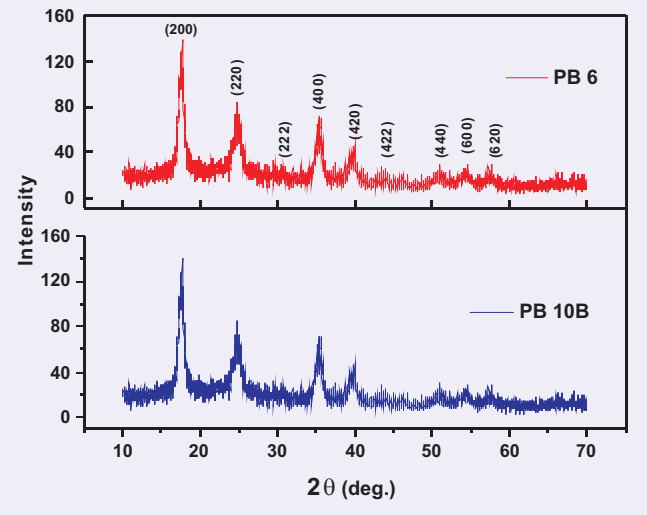

Fig.2: XRD spectra of synthesized Prussian Blue samples.

Table 1: Cs uptake performance of PB samples under in vitro conditions

Sr. No.	Initial pH	[K+] solution (ppm)	[Fe] solution (ppm)	Kd (mL/g) [^{137}Cs]
1	1.36	0.48	1.3	$4.2*10^3$
2	3.16	0.26	BDL#	$2.3*10^4$
3	5.36	0.15	BDL	$5.1*10^4$
4	6.57	0.39	BDL	$5.2*10^4$
5	8.56	0.26	BDL	$3.0*10^4$

 # MDA for iron analysis is 1 ppm (spectrophotometric method)

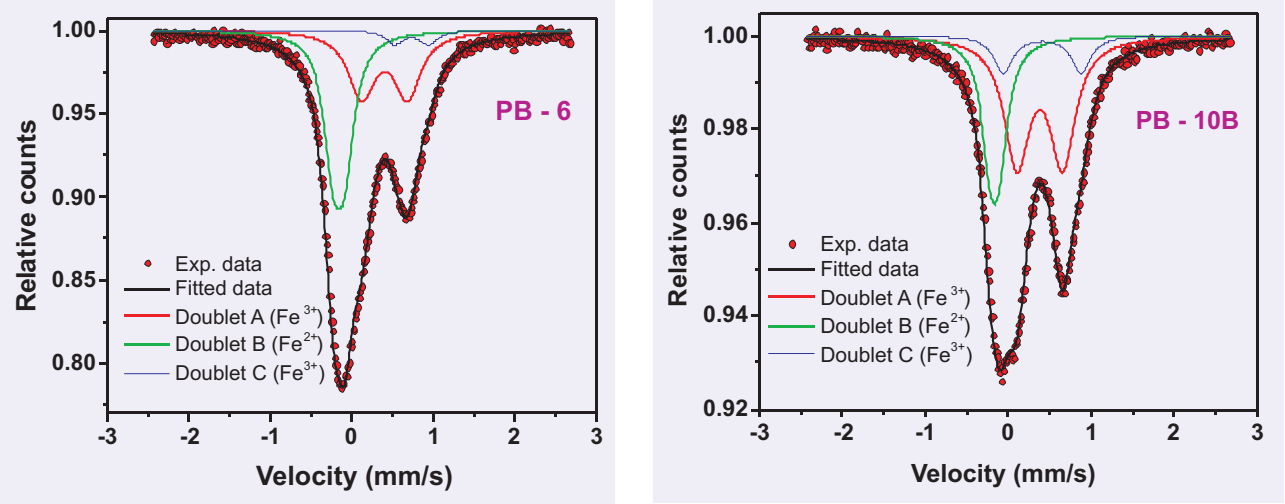

Fig.3: Mössbauer spectra of synthesized PB.

(RA_B = 44.7%) values corresponds to low spin (LS) Fe(II) ions. The remaining two doublets (A and C) with higher IS values (IS_A = 0.401 and IS_c = 0.732 mm/s, QS_A = 0.569 and QS_c = 0.416 mm/s, RA_A = 50.4 and 4.9%) are corresponding to Fe(III) ions in high spin (HS) state. Similarly, the PB-10 sample was also analyzed. It can be noted that the IS values are relative Fe-metal foil. Amount of Fe^{III} and Fe^{II} presented in these two samples were determined from the relative area of doublets. The calculated values of Fe^{3+}/Fe^{2+} ratio arrived at 1.45 and 1.51 for PB-6 and PB -10B, respectively, as against the theoretical value of 1.33 from molecular formula.

Identification of the trace impurities in the samples was done by EDX (energy dispersive X-ray) study. The absence of heavy elements and potassium ion peaks is confirmed from the EDX spectrum of the PB-6 sample. In contrast, a substantial amount of potassium contamination is noted in the PB-10B sample, as the product is made from $K_4Fe(CN)_6$.

Table 1 shows the results of Cs sorption performance of PB-6 powder at different pH. It can be seen that PB-6 samples have very high Cs uptake affinity, and it is same for the entire pH range investigated. Results of the study can be correlated with its Cs decorporation performance from the human body. As PB capsule is administered orally and is insoluble in nature, it will pass through the digestive system like non-digestible foods and finally excretes through faeces. While passing through the digestive system sample, it will mix with different types of food juices and body fluids of varying pH levels, such as 1.0 to 2.5 in the stomach, 4.9-6.4 in the duodenum, and 4.4 to 6.4 in the jejunum and ~7.5 in Colon. The high Cs sorption capability of PB indicates that it can effectively pick up Cs from all parts of our digestive system. The binding mechanism is ion exchange and physical adsorption (electrostatic or mechanical trapping) in the PB crystals, the former being predominant. The Cs pick up by PB can be depicted as follows:

$$\{Fe_4(FeCN_6)_3.H_3O^+_{[S]} + Cs^+_{[L]} = Fe_4(FeCN_6)_3.Cs^+_{[S]} + H_3O^+_{[L]}\}$$

The release of a higher concentration of K^+ during Cs decorporation will have a significant detrimental effect and lead to potassium imbalance in the body. With this consideration, it can be stated that the PB 6 is more suitable for decorporation of Cs from the human body.

As a final step, formulation for active decorporating agent has been constituted, and around 0.5 g product has been filled in each zero-size empty gelatine capsule. Afterwards, the tablets were packed in a glass bottle and sealed. A photograph of the capsules prepared in laboratory is presented in Fig.4. Efforts are being made to obtain regulatory clearance as applicable for medical administration.

Fig.4: Photographs of PB capsules.

Conclusions

A simple process has been developed for the synthesis of insoluble Prussian blue. The process is efficient for the synthesis of high purity materials. It is confirmed that the synthesized products have high cesium uptake ability from a wide variety of solutions similar to that produced at different regions of our digestive system. Development of the indigenous capability is the first step towards self-reliance for treatment of personnel having internal cesium contamination and ensuring the supply of the product at the need of the hour.

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