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ARTICLE

Potassium Zinc Hexacyanoferrate Encapsulated Hydro-Gel Beads for Removal of Radio-Cesium

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Asian Journal of Materials Chemistry

Volume: 1 Year: 2016
Issue: 1 Month: January-March
pp: 14-20
DOI: http://dx.doi.org/10.14233/ajmc.2016.AJMC-P3

Received: 18 February 2016
Accepted: 11 April 2016
Published: 6 May 2016

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ABSTRACT

Present investigation explores the sorption potential of the indigenously synthesized potassium zinc hexacyanoferrate (KZnHCF) encapsulated calcium alginate hydro-gel beads for the removal of radio-cesium ion (^{137}Cs) from radioactive solutions. The polyvinyl alcohol stabilized aqueous sol of KZnHCF crosslinked with alginate binding matrix yielded almost uniformly distributed fine particles of KZnHCF in the inter-penetrating network of polyvinyl alcohol and alginate polymeric chains. These hydro-gel beads were characterized by XRD, SEM, FTIR and TGA techniques. The ability of these beads for the removal of cesium ion has been studied by batch method as a function of equilibration time and pH. Even in the presence of usual interfering metal ions, like Na, Ca and Ba, the % removal of cesium ions from the solution by these beads is quite high, which establishes the potential of these beads for efficient removal of cesium ions from low level waste matrix.

KEYWORDS

Sorption, Hydro-gel beads, Radio-cesium, Remediation, Uptake capacity.

INTRODUCTION

The operations of nuclear installations (nuclear power reactors as well as nuclear fuel reprocessing and radio-isotopes production facilities) generate large amounts of low level radioactive wastes (LLW). The major contaminants of these wastes are the fission products especially cesium and strontium [1]. Cesium radioisotopes stand as the most concerned fission products because of their high fission yield, long half-life (^{137}Cs ($T_{1/2}$ ~ 30.17 year), ^{135}Cs ($T_{1/2}$~2.3 × 10^6 year), ^{134}Cs ($T_{1/2}$ ~2.06 year) and serious environmental impacts [2]. In fact, the cesium and strontium radionuclides are the main sources of decay heat for the first 50 to 100 years after discharge of the spent nuclear fuel from a reactor. Contamination of radio-cesium poses serious threat to human health and environment because it is a strong gamma emitter (^{137}Cs emits 0.66 MeV γ following its β-emission) and has high solubility that enhances its migration through groundwater to the biosphere [3-5]. Though large amounts of low level radioactive wastes contain very small concentrations of radioactive cesium, if it is not pretreated to follow the principle of zero disposal of radioactivity to the environment, over a long period it can cause accumulation of radioactivity in the water body. Later these may enter into the aquatic food chain and ultimately reach to the human environment. Because of the large volumes and the presence of significant quantities of non-radioactive constituents of these wastes, a pre-concentration step before fixation in a suitable matrix is required [6].

Selective separation of cesium ions from low level nuclear wastes is a challenging task as these monovalent cations, lacking unique chemical characteristics, can compete for reactive sites by other group I monovalent cations as well as group II divalent cations. The low content of radio-cesium in the presence of much higher concentration of sodium and calcium ions and the overall large volume of waste makes the sorption processes, using selective ion exchangers, as the most attractive approach for their treatment [7-9]. However, sorption technologies must be based on highly selective materials, which are difficult to decompose over a wide range of pH, remain stable at high temperatures and are resistant to ionizing radiation [10]. Considering this, solid phase extraction techniques employing inorganic ion exchangers have attracted a lot of attention due to high selectivity, rapid separation and high thermo-chemical and radiation stabilities [11-14]. The real challenge for solid phase separation is to select the most promising type of sorbent, mainly in terms of high capacity, sorption rate and selectivity and low cost. Transition metal hexacyanoferrates have been reported to be the promising sorbents for separation of radioactive cesium from nuclear wastes over a wide pH range even in the presence of high salt loadings [15-19]. Zinc hexacyanoferrates (ZnHCF) have been reported as hexagonal skeleton where Zn^{2+} ion is found tetrahedrally coordinated to four N atoms from CN ligands. Such coordination provides a relatively high thermal stability to these materials and also an interesting porous framework because both metal centers have saturated their coordination sphere with atoms from the bridge group (–Fe–CN–Zn–) [20,21]. However, these sorbents frequently exist only as powders and consequently are not readily adaptable to continuous processing such as column chromatography. Making these inorganic ion exchangers as microspheres or granular forms with the help of suitable polymeric materials improves the flow dynamics for column operations and expands their practical applications.

This study was aimed to synthesize spherical hydro-gel beads, encapsulated with inorganic sorbent potassium zinc hexacyanoferrate (KZnHCF) using calcium alginate as organic binding matrix, amenable for column operation for the decontamination of radionuclides. The methodology adapted for the preparation of these composite beads and their physico-chemical characterizations are evaluated in details. These beads are termed as 'KZnHCF-gel beads' and their feasibility for the removal of cesium ions from aqueous solutions were examined by determining the ^{137}Cs distribution coefficients (K_d value) as a function of pH and the equilibration time. The effect of the macro-component Na^+, Ca^{2+}, Ba^{2+} which is present in low level nuclear waste solutions and interferes with ^{137}Cs removal, was also studied.

EXPERIMENTAL

Sodium alginate and polyvinyl alcohol (molecular weight 1, 25,000) were purchased from SD Fine chemicals. Cesium nitrate of 99 % purity, potassium hexacyanoferrate (KHCF), zinc sulphate of 97 % purity and 25 % glutaraldehyde (AR grade) were obtained from Merck. All the other solvents and the chemicals used were of analytical grade and used as received. ^{137}Cs was procured from Board of Radiation and Isotope Technology (BRIT), India and used in the batch sorption experiments after checking its radiochemical purity. Milli-Q water (resistivity of 18.20 MΩ cm or more) was used in all experiments.

Optical microscope images of the beads were recorded in a digital Blue QX5 computer microscope. The X-ray diffraction pattern was recorded using a Bruker AXS D8SWAX diffractometer with CuK_α radiation ($\gamma = 1.54$ Å), employing a scanning rate of 0.5° s^{-1} in the 2θ range from 10° to 60°. A fine coating of powdered KZnHCF-gel beads, over the amorphous silicon sample holder, was used for XRD measurement. The morphologies of the samples were studied by a field emission scanning electron microscope (FESEM, JEOL, JSM 6700F). IR spectra (4000-500 cm^{-1}) were recorded using a diamond ATR probe, with an IR affinity-1 Fourier transform infrared (FT-IR) spectrophotometer. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/differential scanning calorimetry (DSC) analyzer. Brunauer-Emmett-Teller (BET) surface area of the synthesized beads was determined by N_2 sorption-desorption measurement using 'SORPTOMATIC 1990' analyzer from CE Instruments, Italy. Sample was out-gassed at 100 °C in vacuum before the measurement. The assay of ^{137}Cs was done using NaI(Tl) scintillation counter (ECIL, India). The γ-spectrum of the feed and raffinate solution was recorded using HPGe, 4K Multi Channel Analyser (MCA). For this purposes, 5 mL solution of feed and raffinate was sealed in a plastic vial and counted for 5 min in a MCA counting system. The pH of the test solution was measured using a Metrohome pH meter calibrated with standard buffers (4.00, 7.00 and 9.00 from Merck).

Synthesis of KZnHCF-gel beads: The KZnHCF-gel beads used in this study were prepared indigenously, using polyvinyl alcohol stabilized sodium alginate as a binding matrix. KZnHCF sol was prepared by the reaction of $ZnSO_4$ (0.1 M) and KHCF (0.1 M), in 5:3 volume ratio, in the presence of polyvinyl alcohol. The final concentration of polyvinyl alcohol in the solution was 4 %. The polyvinyl alcohol controls the size of the KZnHCF particles formed by acting as a stabilizer. To this polyvinyl alcohol stabilized KZnHCF sol, 8 g (w/w) of aqueous solution of 4 % sodium alginate was added. This mixture was used to prepare KZnHCF containing polymer composite beads, by dropping it into an aqueous bath containing 4 wt % $CaCl_2$, through a 0.8 mm diameter needle. Thus formed beads were kept in the same $CaCl_2$ solution, for about 4 h, for complete conversion of sodium alginate to calcium alginate. Then, the beads were separated from the solution and washed with water. A schematic diagram, representing the preparation method of the KZnHCF-gel beads, is given in Fig. 1.

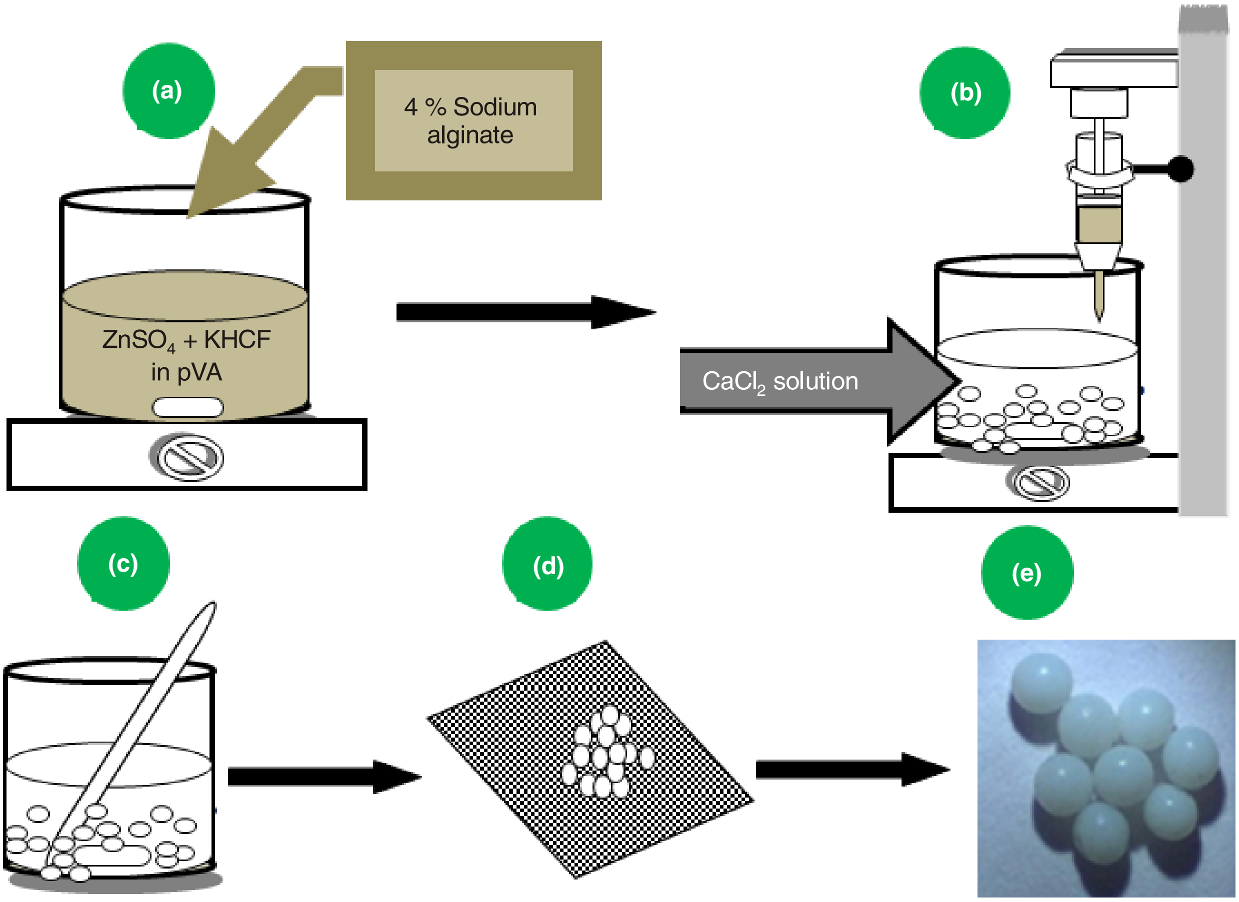

Fig. 1. (a) Schematic of the procedure for preparation of KZnHCF-gel beads (a) Preparation of a formulation of ZnSO$_4$ (0.1 M) and KHCF (0.1 M) in the presence of PVA (b) Drop wise addition of the formulation in CaCl$_2$ aqueous solution (c) Curing of the beads for 4 h (d) Separation and washing of the prepared beads (e) Optical microscope image of the swollen beads

Batch sorption studies: The sorption experiment were performed using 0.05 g of KZnHCF-gel beads, added to the 5 mL of CsNO$_3$ solutions having known quantity of radiotracer in a laxbro extraction tube at selected pH in the range of 1 to 12, followed by equilibration using Vortex shaker for the fixed interval of 3 h. Thereafter suitable aliquot was taken for the assay of ^{137}Cs in the aqueous solutions before and after equilibration. The batch distribution coefficient (K$_d$) of Cs ion per unit mass of the gel-beads was calculated using the eqn. 1.

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{W} \quad \text{mL/g} \tag{1}$$

where C$_0$ and C$_e$ are respectively the initial and equilibrium concentrations (mg/L) of Cs in the aqueous phase, V is the volume of the aqueous solution in mL and W is the weight of the surface dried swollen KZnHCF-gel beads in grams. Interference of sodium, barium and calcium ions on the cesium uptake, at the concentration range of 4 to 32 ppm, was studied employing 5 mL feed solution having 5 ppm of Cs concentration and 0.05g of KZnHCF-gel beads at neutral pH (6.95).

Kinetic studies: To optimize the time for maximum sorption, the beads were equilibrated with the test solution for different time intervals. A known aliquot of the solution was taken, for counting the initial and the final counts and the % sorption of Cs ions with respect to a particular equilibration time was calculated using the eqn. 2.

$$\text{Sorption}\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

All the experiments were carried out at 25 ± 0.5 °C, in duplicate and reproducibility of the result was found to be within ± 5 %.

RESULTS AND DISCUSSION

Characterization of KZnHCF-gel beads: The optical microscopic images clearly show the formation of spherical KZnHCF-gel beads (Fig. 1e). The rough diameter of the beads was found to be 0.5 cm. The XRD pattern of crushed KZnHCF-gel beads (Fig. 2) indicated the formation and incorporation of potassium zinc hexacyanoferrate(II) into the beads. The diffractogram indicates six characteristic peaks at 2θ° = 16.69, 19.96, 22.03, 24.89, 28.96 and 33.49 consistent with database in JCPDS file no. 28-0855 showing roughly 0.3° increase in the peak positions corresponding to the alginate binding matrix.

The SEM image (Fig. 3) shows morphology of the KZnHCF-gel beads. It reveals that the KZnHCF-gel beads had almost homogeneous distribution of agglomerated spherical KZnHCF particle of size about 100 nm in the inter-penetrating network (IPN) of polyvinyl alcohol and alginate polymeric chains. In between agglomerates irregular micron size pores

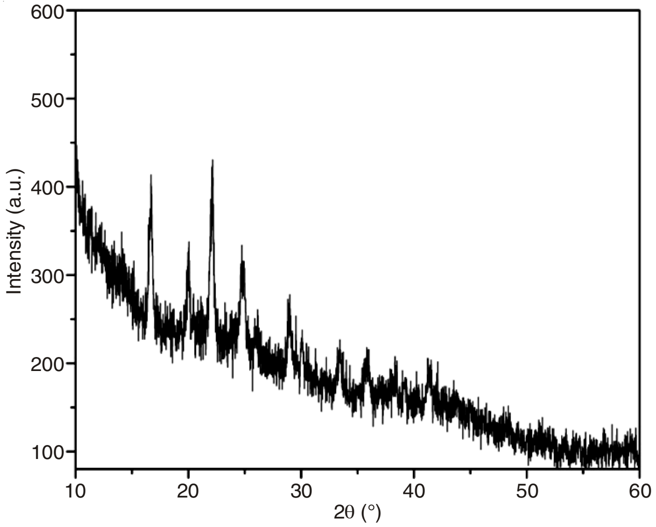

Fig. 2. XRD pattern of KZnHCF-gel beads

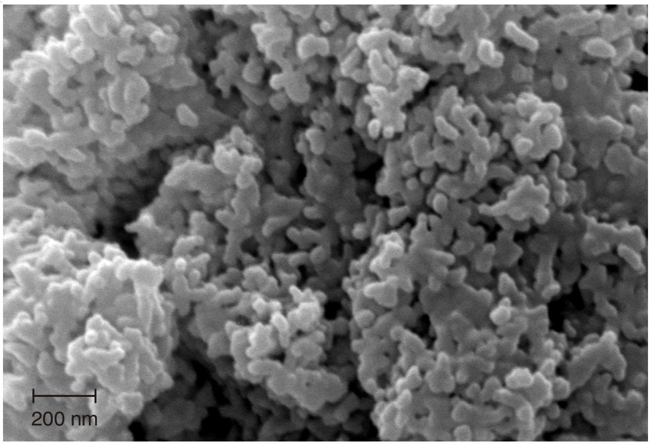

Fig. 3. SEM images of KZnHCF-gel beads

are there and the surface is quite rough. These pores, which have different diameters, clearly demonstrate the porous structure of the KZnHCF-gel beads and reduce the internal diffusion resistance of the sorbate ions and so increase the sorption potential and kinetics as well.

The surface area and the pore volume were found to be 342.67 m^2/g and 1.53 cc/g respectively. Surface area and pore volume are measured for the dried beads, but the actual experiments are carried out using swollen beads. Therefore, the effective surface area and the pore volume of the swollen beads are expected to be still higher.

The FTIR spectrum of KZnHCF-gel beads shown in Fig. 4 indicates that there is a chemical bonding between polyvinyl alcohol and alignate. The carboxylic groups are generally the most abundant acidic functional groups in the alginate polymer. From the IR spectra it is obvious that both polyvinyl alcohol and alginate show a broad peak at 3450 cm^{-1} for -OH group, two peaks at 1618 and 1440 cm^{-1} for the –COO group and one sharp peak at 1050 cm^{-1}, which is for the -CO group. The most characteristic band is the one around 2100-2050 cm^{-1}. It is a stretching vibration of the cyanide ligands (C≡N) in the cyanoferrate ion. The bands at 615 cm^{-1} and 850 cm^{-1} indicate the out of plane vibrations of OH and CH in polyvinyl alcohol.

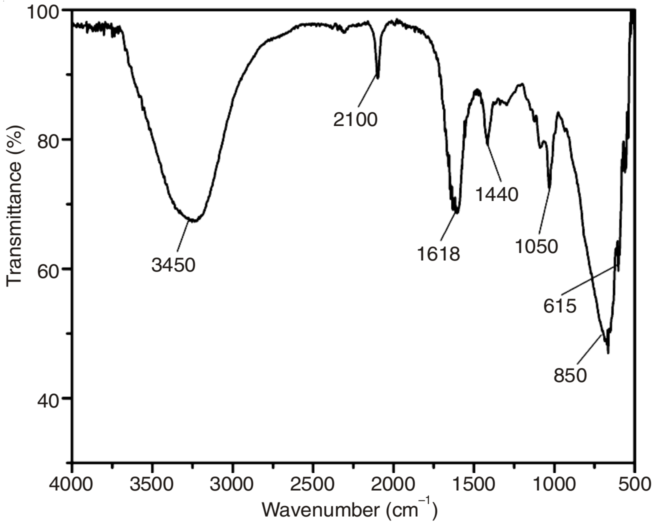

Fig. 4. FT-IR spectrum of the synthesized KZnHCF-gel beads

Thermo gravimetric analysis (TGA) of the synthesized beads was performed at a heating rate of 10 °C/min, in nitrogen atmosphere, from ambient temperature up to 900 °C for both swollen and dry beads. TGA of the synthesized swollen beads (Fig. 5) was carried out after just removing the surface water of the beads using a tissue paper. The thermal degradation profile of the swollen KZnHCF-gel beads consists of two main steps. The first step, from 25 to 130 °C, corresponds to a weight loss of about 90 % due to release of water from the beads. The second step, represents the degradation of KZnHCF-gel beads starting at 200 °C, indicate reasonably good thermal stability of the beads. The main degradation details of the KZnHCF-gel beads are masked due to the presence of high amount of water in the swollen beads. The high water content of these swollen beads is responsible for excellent exchange of metal ions from the aqueous medium.

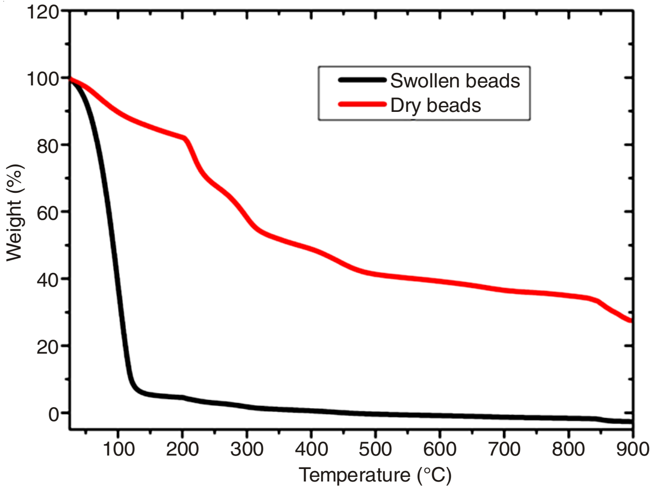

Fig. 5. TGA profile of swollen and dry KZnHCF-gel beads

The TGA profile of KZnHCF dry beads was recorded to ascertain the degradation characteristics of the individual components present in the non-swollen beads. For this purposes a known quantity of the swollen beads were dried by keeping under IR lamp, till no further weight loss was observed. The obtained TGA profile of the KZnHCF dry beads can be divided into three main stages (Fig. 5). The first stage is from 30 to 200 °C, over which a mass loss of about 20 % is observed due to release of moisture picked-up probably during the storage of the dry beads. The second stage, from 200 to 450 °C, contains more than one step, experiences an additional mass decrease of about 40 %. This is assigned to the dehydration of the zinc and calcium hydrates. There is no significant change observed on further heating up to 850 °C. The final residual mass of about 30 %, mainly due to inorganic components of the beads, is left at the studied temperature of 900 °C.

Effect of sorption time: To understand the effect of contact time, for optimum sorption of cesium ion onto the synthesized KZnHCF-gel beads, the experiments were conducted by equilibrating 5 mL of solution containing 10 mg/L of cesium along with tracer and 0.05 g of the KZnHCF-gel beads, in separate vials. The mixtures were equilibrated in a mechanical shaker, at a constant temperature (T = 25 °C) and were sampled at different times, ranging from 1 to 180 min, to estimate the sorption of cesium as a function of equilibration time. The results are shown in Fig. 6. The sorption is fast in the initial stage, followed by a slow process, leading to saturation sorption in about 120 min. Therefore, the time period of 120 min has been used in further sorption experiments, as the optimum contact time for the maximum sorption.

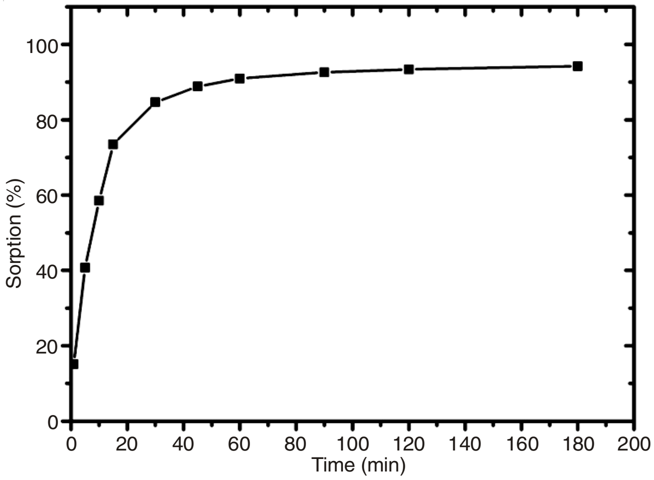

Fig. 6. Sorption of cesium ion onto the KZnHCF-gel beads as a function of equilibration time. Initial Cs concentration: 10 ppm; pH: 6.9; Weight of the beads: 0.05 g

Effect of pH: The pH of waste solutions plays an important role in sorption process. It influences the ionization of surface functional groups and the precipitation of metal ions. Sorption of cesium ion by the synthesized KZnHCF-gel beads has been studied in the pH range 1 to 12. The effect of initial pH on cesium ion sorption was studied at 20 mg/L initial cesium concentration (with tracer of ^{137}Cs) at 25 °C. It is known that transition metal hexacyanoferrates are able to effectively bind cesium in acidic as well as in alkaline pH [22]. As seen in Fig. 7, the sorption of cesium increases with an increase in pH of the solution from 1 to 4 and remains practically same up to pH 10, then drastically decreases at pH 12. At low pH, strong acidity results in replacing the sorbed Cs ions by the H$^+$, which will decrease the sorption capacity of Cs ions. The metal ion binding in hexacynoferrate sorbent could be attributed to either ion exchange process or fixing of the metal ions into the porous framework of the sorbent [23]. In both the cases, as pH increases, the number of protons on the surface of the sorbent moiety decreases and more electrostatically attractive surface to the cations occurs, allowing more Cs$^+$ to sorbed. A possible degradation of calcium alginate moiety of the KZnHCF-gel beads at high pH level and thus blocking the pores of the beads by forming hydroxide species is likely to reduce Cs$^+$ ions sorption significantly after pH 10. These results indicate that the synthesized beads can be efficiently utilized for sorption of cesium in the wide pH range of 3 to10. The cesium sorption is observed to be quite optimum in the near neutral pH region. Therefore, pH 6.9 was selected for further experiments.

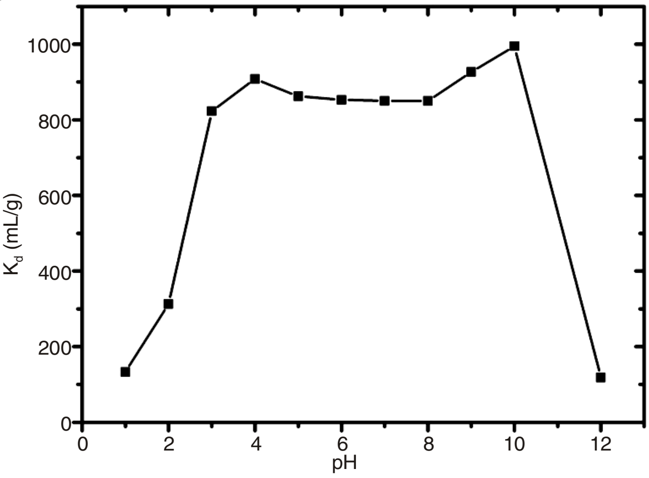

Fig. 7. Effects of pH on sorption of cesium ion onto the KZnHCF-gel beads; Initial Cs concentration: 20 ppm; Weight of the beads: 0.05g; Equilibration time: 3 h

Effect of interfering ions: The influence of interfering cations (Na$^+$, Ca^{2+} and Ba^{2+}) on the sorption of cesium ions onto the KZnHCF-gel beads was investigated by keeping the concentration of cesium ions constant (5 mg/L) and varying the concentration of the interfering ions, at neutral pH. Table-1 presents results of the study of effect of the interfering metal ions on % removal of cesium ions. No significant interference of Na$^+$ and Ca^{2+} ion was observed for Cs uptake but a relatively small decrease in Cs-uptake was observed for Ba^{2+} ions when present at higher concentrations. Only about 8 % decrease in the removal efficiency of the beads is observed at the highest studied concentration (32 mg/L) of the Ba^{2+} interfering ions.

The observed marginal decrease, in case of the alkali metal ions, could be due to the lower hydration energy of the cesium ions as compared to the interfering ions. The relatively higher effect of Ba^{2+} ions on the sorption of cesium ions could be due to the other processes involved, such as complexation, or nonspecific surface sorption. Moreover, Ba^{2+} ions may also replace Ca^{2+} ions present in the calcium alginate moiety of the beads, as reported by Mandal *et al.* [24]. Even in the presence of these usual interfering metal ions, the % removal of cesium ions from the solution is quite high (more than 85 %), which indicates that these beads can be used effectively for the removal of cesium ions from low level waste.

TABLE-1
EFFECT OF INTERFERING IONS (Na^+, Ca^{2+}, Ba^{2+}) ON SORPTION OF Cs^+ IONS BY KZnHCF-GEL BEADS

Interfering ions	Concentration in feed solution (ppm)	Sorption of Cs (%)	K_d value for Cs (mL/g)
	0	94.14	1605.77
Na^+	4	93.92	1544.15
	16	93.45	1425.89
	32	92.21	1183.63
Ca^{2+}	4	94.07	1586.20
	16	93.60	1463.11
	32	93.80	1512.46
Ba^{2+}	4	90.12	911.86
	16	89.78	878.54
	32	86.48	818.26

Experimental condition: pH 6.9, Weight of the beads: 0.05 g, Volume of solution: 5 mL, [Cs^+]: 5 ppm + tracer, Equilibration time: 2 h

A case study: Cesium removal from the spent fuel storage pond water: Basically, spent fuel removed from the reactor, after its productive utilization, is kept under demineralized water filled in a pond, known as spent fuel storage pond, to remove the decay heat generated by the short lived fission products. A major problem associated with the operation of fuel storage ponds is the leakage of radioactive cesium from defective irradiated fuels. Other fission products present in the pond water include ^{144}Ce, ^{106}Ru and ^{125}Sb along with the traces of elemental impurities. A typical composition of spent fuel storage pond is given in Table-2. Because cesium is highly soluble and has a long half-life, its presence in significant amounts results in high radiation field surrounding the pond, leading to radiation exposure to operators. The organic ion exchangers, which are generally used to maintain the permissible limit of activity and desirable pH level of the pond water exhibit certain drawbacks, especially non-selectivity for Cs ion. Generally, buffers containing Na^+ and K^+ ions are added to control the pH of the pond water. Most of the bulk capacity of these ion exchangers is used by the uptake of these sodium and potassium ion. Moreover, the thermal and radio-chemical decomposition of organic binding matrix, in the case of organic ion exchange resins, leads to release of radionuclides and causes problems for long term storage [25].

TABLE-2
A TYPICAL COMPOSITION OF THE SPENT FUEL STORAGE POND WATER

pH	6.5-6.8
Conductivity (µS/cm)	≤ 1
Total dissolved solid (TDS) ppm	30-40
Gross activity (Bq/mL) (mostly due to ^{137}Cs, ^{144}Ce, ^{106}Ru and ^{125}Sb)	350-450
Elemental impurities (ppm) [Al, Ca, Fe, Mg, Si, Na]	< 20

To overcome some of the above mentioned problems the synthesized KZnHCF-gel beads were tested for extraction of Cs from the spent fuel storage pond water. The Cs specific KZnHCF sorbent, encapsulated inside the porous polymeric matrix, which otherwise lacks the granularity for column operation, is expected to be effective in removing Cs from radioactive waste solutions. The results obtained from the batch sorption experiments demonstrated the feasibility of removal of cesium ion by the synthesized KZnHCF-gel beads. The 0.1 g of beads were equilibrated with 25 mL of pond water at constant agitation for 3 h. The solution was then filtered and the activity of ^{137}Cs was radiometrically determined before and after equilibration. The observed results indicate that the quantitative sorption of cesium from real pond water solution is achievable. The result is also supported by the γ-spectrum of the feed solution before equilibration (Fig. 8a) and that of the aqueous raffinate solution after equilibration (Fig. 8b). Thus the synthesized KZnHCF-gel beads are very promising for removal of cesium ion from spent fuel storage pond water as well as from other aqueous waste solutions in the pH range of 3 to 10.

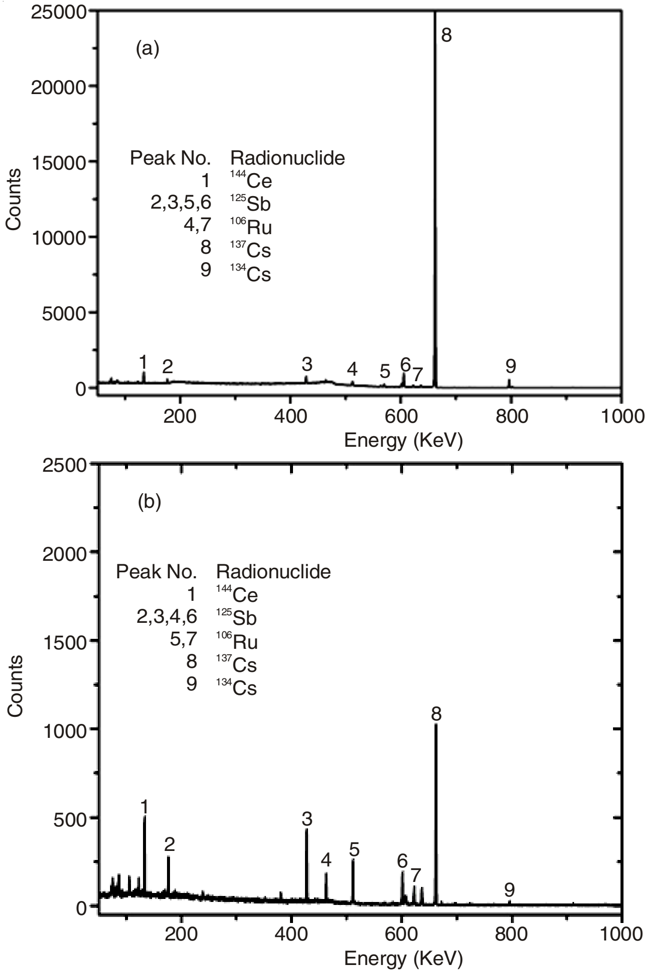

Fig. 8. γ-Spectrum of (a) the feed solution and (b) the raffinate solution after 2 h of equilibration with the synthesized KZnHCF-gel beads (Experimental conditions: Feed volume: 25 mL pond water at pH 6.9; Weight of the beads: 0.1 g; HPGe counting time: 5 min; Temperature = 25 °C)

Conclusion

The present study focuses on the preparation and characterization of inorganic sorbent KZnHCF encapsulated hydrogel beads for the recovery or removal of cesium from low level nuclear waste streams as well as neutral aquatic environments. The XRD pattern and FTIR spectra of the synthesized beads confirm the incorporation of sorbent in the bead, while the SEM examination reveals unevenness on the surface, resulting in higher surface area for efficient extraction of Cs ion. TGA profile shows that these beads have high water content and the dried beads are stable up to 200 °C. Absence of structural deformity and leaching out of the sorbent, observed during the course of the experiments confirmed the robustness of beads. The results suggest that the sorption process is quite efficient in the pH range of 3 to 10 and 2 h of equilibration time is optimally required to remove almost 95 % of the cesium from the solution. Under the optimum condition these synthesized beads were able to remove radio-cesium almost quantitatively from the real spent fuel storage pond water. The cesium uptake capacity of these beads at neutral pH was not found to be affected significantly by the interfering ions, like Na^+, Ca^{2+} and Ba^{2+}, implying practical application for remediation of cesium bearing aqueous nuclear wastes.

ACKNOWLEDGEMENTS

The authors acknowledge their sincere thanks to Dr. B.N. Jagtap, Director, Chemistry Group and Dr. D.K. Palit Head, Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Mumbai, India for their encouragement during the course of the present research and development work. Thanks are also due to Indian Association for the Cultivation of Science for providing XRD and SEM analysis.

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