

Synthesis of Potassium Nickel Hexacyanoferrate Encapsulated Polymeric Beads for Extraction of Cesium

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ABSTRACT: A novel potassium nickel hexacyanoferrate (KNiHCF) sorbent-encapsulated polymeric beads (SEPBs) were synthesized by phase inversion method, characterized by various techniques viz. FTIR, optical microscopy, SEM and TGA, and used for extraction of cesium. Polyether sulfone was used to encapsulate the KNiHCF sorbent. The batch extraction method was used, to study the effect of different physical parameters on the extraction process. The kinetics measurement suggests about 200 min equilibration time was sufficient to extract maximum amount of cesium from solution. Various kinetic and isotherm models were used for analysis of the extraction data, which is found to fit well in the pseudo-second-order model and the Langmuir isotherm model. The experimental maximum sorption capacity was found to be ~22.5 mg/g which is very close to the theoretical monolayer capacity ~ 23.1 mg/g for the dry SEPBs.

KEYWORDS: Cesium, Sorption, Radioactive acidic waste, KNiHCF, SEPBs.

I. INTRODUCTION

Cesium radioisotopes ¹³⁴Cs and ¹³⁷Cs are often located in aqueous radioactive wastes generated from nuclear reactors and some research institutes, mostly at levels beyond the standards. The radiochemical laboratories produce large volumes of radiotoxic liquid wastes. ¹³⁷Cs is an important nuclear fission products present in the radioactive waste sewage resulting from the reprocessing of nuclear fuels. In this context, the separation and recovery of ¹³⁷Cs present in aqueous wastes is a major challenge and a great environmental concern [1]. Cesium is chemically analogous with sodium and ingestion of its radioisotopes results in accumulation in the soft tissues of the body, consequently affecting the reproductive system. Therefore, cesium-containing radioactive wastes have to be adequately treated before discharging into the environment. Researchers have been taking effort on developing prominent solutions towards the removal of radioactive cesium from various nuclear streams. Techniques, such as precipitation, solvent extraction, volatilization and adsorption using inorganic ion exchange have been extensively used for tackling this problem [2-5]. Among these ion exchange methods, particularly employing aluminosilicates, phosphates, hydrous oxides of multivalent cations, pillared clays and ferrocyanides, have been evaluated for removal of cesium [5-7]. Adsorption is a feasible technique to eliminate radioactive species from water contaminated through radioisotopes. Zeolites and insoluble metal ferrocyanides [8] are well known adsorbents for capturing ¹³⁷Cs ions specifically. The incorporation of Cs into hexacyanoferrates (HCFs) of divalent transition metal cations is one of the most practical methods of cesium removal. HCFs have a first preference over other materials due to their selectivity and high capacity [9, 10]. Hence, large amount of these compounds have been used as precipitants for all alkali metal cations, particularly cesium, to strip off those from aqueous radioactive wastes [11-15]. Inorganic ion exchangers are well known for their good thermal and radiation stabilities in addition to compatibility with the matrices generally used for final encapsulation. It

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, January 2016

is easy to prepare transition metal hexacyanoferrates by incorporating a solution of alkali metal hexacyanoferrate (II) with soluble transition metal salts [16] for in-situ co-precipitation of cesium ions or by initially making the slurry of the metal hexacyanoferrate, and then its addition to the aqueous waste solution for elimination of cesium. It is difficult to separate the co-precipitates from the waste solution, in both these procedures, due to its fine morphology.

Keeping these in mind, here we describe a simple method to produce spherical potassium nickel hexacyanoferrate-PES, beads by phase inversion technique and study of these for batch extraction of cesium from aqueous waste.

II. MATERIALS AND METHODS

A. MATERIALS

Potassium hexacyanoferrate (KHCF), nickel sulphate, and cesium nitrate were procured from Merck. Polyvinyl alcohol (molecular weight 125 000) was purchased from SD Fine Chemicals, India. All the chemicals used were of analytical grade. Water obtained from a Millipore-Q water purification system, with conductivity $<0.06 \mu\text{S cm}^{-1}$, was used in all the experiments.

B. SYNTHESIS OF KNiHCF -PES BEADS

The KNiHCF-PES beads utilized in the study were prepared using polyether sulphone (PES) as a binding matrix. PES is a well known polymeric material used in the preparation of beads. The PES based beads show outstanding oxidative, thermal as well as acid stability in wide pH range. Initially, we prepared KNiHCF by the reaction of KHCF (0.1 M) with NiSO_4 (0.1 M) in 3:5 volume ratio, in the presence of 10% PVA solution. PVA is used as a stabilizer which controls the size of the KNiHCF particles. The synthesized KNiHCF was separated from the solution by high speed centrifuge.

In the present work, KNiHCF-encapsulated porous PES beads were prepared by the phase inversion technique. PES powder was dissolved in appropriate amount of 1-methyl -2- pyrrolidone (NMP), to get the PES solution of required viscosity. An appropriate amount of KNiHCF was mixed into the PES solution and the almost homogeneous mixture was added drop wise into an aqueous bath, through a syringe needle (0.8 mm diameter), using a syringe pump. After stirring, soft beads were obtained which were incubated in water for overnight, for complete curing. Now, these beads are commonly called as sorbent encapsulated polymeric beads (SEPBS). These beads were used in the water-swollen state, for the optical microscopy, TGA and extraction experiments, while for SEM and EDX analysis, the dried beads were used.

C. CESIUM FEED SOLUTION

A stock solution of 1000 ppm was prepared by dissolving appropriate amount of cesium nitrate in water. The aliquots were taken from this stock solution and properly adjusted for the required Cs (I) concentrations, for different sorption experiments.

D. CHARACTERIZATION OF THE SEPBS

The synthesized SEPBS were characterized by FT-IR analysis using diamond ATR holder, employing IR Affinity-1 FT-IR spectrophotometer, in the range $500\text{-}3600 \text{ cm}^{-1}$. The thermogram was measured by STARE System METLER TOLEDO instrument using a small amount (4-8 mg) of the sample beads in an alumina sample holder, and thermo gravimetric curves were recorded at the heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, from 25 to $900 \text{ }^\circ\text{C}$, in nitrogen atmospheres (50 ml min^{-1}). Composition and thermal stability of the beads were determined from the thermo gravimetric data. Morphology of the beads was established by simple microscopy, using QX5 DIGITAL BLUE computer microscope, and scanning electron microscopy, using TESCAN VEGA MV 2300 T/A microscope. Also, the composition analysis of the beads were done by Energy Dispersive X-ray (EDX) using oxford instrumentation UK (model No. INCAE350).

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, January 2016

E. SORPTION PROCEDURES

The batch method was used for metal extraction, and the experiments were carried out at room temperature. Approximately, 0.04 g of the encapsulated polymeric beads were treated with 2 ml aqueous solution of metal ions for different time periods, for kinetics study, and approximately 200 min were required in order to reach equilibrium. The metal concentration in the aqueous phase was measured by AAS after separating the beads. For equilibrium sorption studies, the mixtures were equilibrated at room temperature by using a controlled rotospin rotor for a desired time period. Then, the raffinate was filtered and the filtrate was examined by the AAS. The % sorption (%A) and the amount of cesium sorbed per gram of the SEPBs (q_e) were calculated using the following equation.

$$\%A = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = (v/w) \times (C_0 - C_e) \quad (2)$$

Where, C_0 and C_e are respectively the initial and the equilibrium concentrations of Cs(I) ion, in ppm, V is the volume of the Cs(I) ion solution (ml) and 'w' is the weight of the swollen SEPBs in gram.

III. RESULTS AND DISCUSSION

A. IDENTIFICATION AND CHARACTERIZATION OF THE SYNTHESIZED BEADS

Morphology of the beads was determined by optical and scanning electron microscopy. The optical image of the beads is given in Fig.1.A and the SEM image of surface of the bead is shown in Fig.1.B. It clearly indicates that size of the bead is around 1-2 mm, the bead surface is quite rough, and has enough porosity, which enhances the surface area for metal ion sorption.

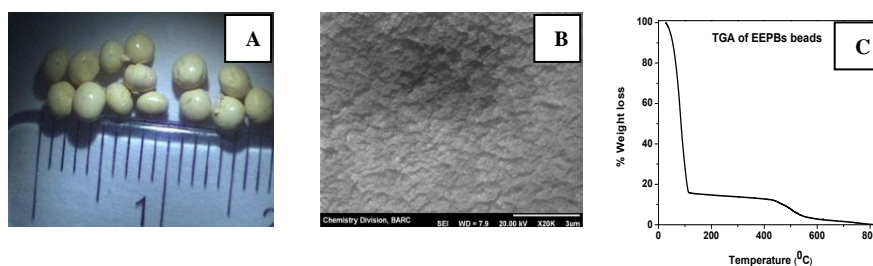


Fig.1 A) The optical photograph, B) SEM image of outer surface and C) TGA curve of the synthesized SEPBs

The water content and the thermal stability of the beads were studied by thermo gravimetric analysis. TGA profile of the KNiHCF-PES beads is shown in Fig.1.C. It shows, a huge weight loss at 110 °C, indicating ~84% water content in the beads, followed by small change in weight mostly due to degradation of the organic polymer.

The IR spectra of KNiHCF powder, blank KNiHCF-PES beads and KNiHCF-PES beads loaded with cesium, are given in Fig.2.A, B and C respectively. The IR spectra of KNiHCF are characterized by the C≡N stretching band in the region 2000-2100 cm^{-1} as shown in Fig.2.A. Also the absorption peaks at 1101 cm^{-1} were characteristic of the vibrations of the sulfone group (R_2SO_2). A strong ether band at around 1240 cm^{-1} was also observed which is shown in Fig.2.C. Changes in the IR spectra were observed on loading of cesium onto the beads. The band at 2095 cm^{-1} , attributed to C≡N stretching, shifts to lower wave number at 1721 cm^{-1} with increase in intensity, on loading of cesium. In addition a decrease in the intensity of the band at 1100 cm^{-1} along with appearance of a new band at 1380 cm^{-1} is observed, indicating the presence of C-N bond.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, January 2016

The presence of cesium in the beads after sorption was confirmed from the EDX pattern as shown in Fig.3.A and B. The EDX mapping of the un-doped beads shows the presence of carbon, oxygen and a small amount of sulphur. While the EDX mapping of the doped beads also shows the presence of cesium. The elemental composition at different location of the bead shows similar atomic wt. % of the detected elements, indicating homogeneity of the sample. Thus the EDX study reveals almost uniform loading of Cs metal on the synthesized beads.

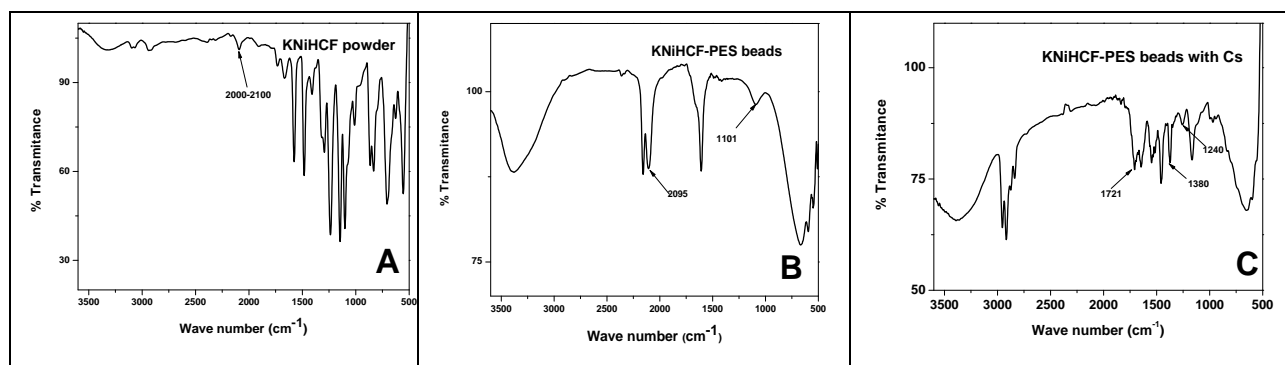


Fig.2 FTIR spectra of A) KNiHCF powder, B) Blank KNiHCF-PES beads and C) KNiHCF-PES beads loaded with cesium.

B. EFFECT OF pH ON SORPTION OF CESIUM IONS

Fig.3.C shows the effect of pH of the sample solution on the sorption behaviour of the synthesized beads. From this figure we can conclude that over the entire studied pH range q_e value varies from 2.71 mg g^{-1} to 2.79 mg g^{-1} of the swollen beads, the obtained change in the equilibrium capacity value is not much. These results clearly indicate that the sorption efficiency of the synthesized beads is quite good in almost the entire studied pH range from 2–12 and the beads can be used efficiently for separation of cesium over the wide pH range.

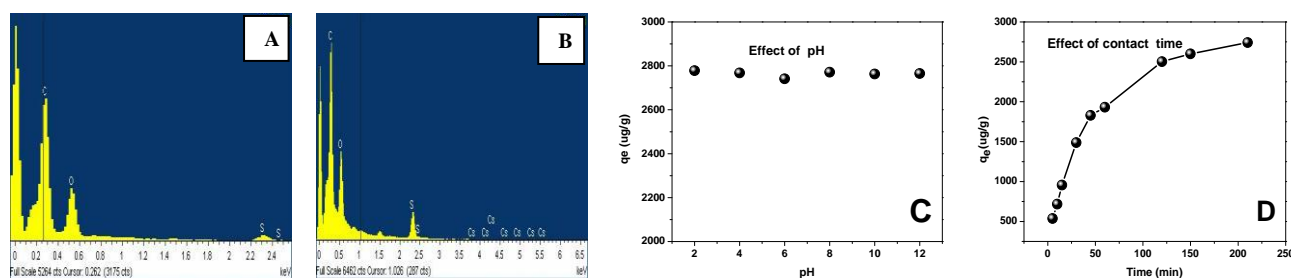


Fig. 3 EDX mapping of A) Blank and B) Cs doped synthesized SEPBs. The effect of C) pH and D) Equilibrium time on the sorption of Cs^+ ions onto the SEPBs.

C. EFFECT OF SORPTION TIME

Sorption kinetics is very important, as it assists in measuring the equilibration time required for most favourable sorption. The result of different contact time on the sorption of cesium ions on the SEPBs, at 100 ppm of Cs, is represented in Fig.3.D. For this study, the sorption experiments were carried out for different contact times, varying from 5 to 240 min., at constant temperature ($300 \text{ }^\circ\text{K}$). It is monitored that the amount of cesium ions sorbed onto the beads increases with the contact time, gradually becomes slower and then there is no additional increase in the sorption

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, January 2016

and the saturation is achieved. Almost saturation sorption is attained approximately in 200 min for 100 ppm cesium solutions, at the studied temperature, which can be replicated for practical usefulness of the synthesized beads. Hence, the 200 min contact time period have been used for all the sorption experiments requiring complete sorption.

D. SORPTION KINETICS MODELS

The kinetic sorption data were examined using different kinetic models, such as pseudo-first order model, pseudo-second order model, intraparticle diffusion model, and the Boyd's plot to explore the rate law for sorption of cesium onto the beads. Table 1 corresponds to the outcomes attained by fitting the experimental data onto these models.

E. PSEUDO-FIRST ORDER MODEL:

The Lagergren pseudo-first-order equation [17] can be written as

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{3}$$

where q_e (mg g^{-1}) is the sorption capacity at equilibrium, q_t (mg g^{-1}) is the amount of metal ion sorbed at time t (min), and k_f (min^{-1}) is the rate constant for pseudo-first-order model. On integrating equation (3), we get;

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_f t}{2.303} \right) \tag{4}$$

Table 1. Pseudo-first Order and pseudo-second order parameters, R^2 values and the experimental q_e value for the sorption of cesium onto SEPBs.

Cesium conc. (ppm) 100	Pseudo first-order Model			Pseudo second-order Model			Experimental q_e (mg/g) 2.80
	k_f	R_1^2	q_e (mg/g)	k_s	R_2^2	q_e (mg/g)	
	18.88×10^{-3}	0.9973	2.33	9.655×10^{-8}	0.9971	3.21	

F. PSEUDO-SECOND ORDER MODEL:

The pseudo-second-order model can be specified by the equation [18].

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{5}$$

where k_s ($\text{in g mg}^{-1} \text{min}^{-1}$) is the rate constant for pseudo-second order model. Integrated form of Eq. (5), can be written as:

$$\frac{t}{q_t} = \frac{1}{(k_s q_e^2)} + \left(\frac{1}{q_e} \right) t \tag{6}$$

The data were found to fit properly and almost equally into both the pseudo first order and the pseudo second order models. The linear pseudo first order plot of $\log(q_e - q_t)$ vs t , gave straight line as shown in fig.4.A and the pseudo second order plot of t/q_t vs. t also provided a straight line, as shown in fig.4.B. The correlation coefficient values and the calculated q_e and rate constants values obtained from the observed intercept and the slopes are shown in the Table.1. The correlation coefficient values for both the graphs are almost same. The experimental capacity value (2.80 mg/g), at the studied initial concentration of 100 ppm, is almost average of the two calculated capacity values, but the one obtained from the pseudo second order model is marginally closer to the experimental q_e . Thus, we can conclude from the above results that kinetics of the Cs sorption onto the SEPBs can be explained somewhat better by the pseudo second order model.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, January 2016

Hence, for further understanding the kinetics mechanism, the intraparticle diffusion model was also employed. The fractional methodology were applied for equilibrium change as a function of $(Dt/r^2)^{1/2}$, where r is the radius of particle and D is the diffusivity inside the particle [19]. The initial rate of intraparticle diffusion was attained from the linear equation as shown below;

$$q_t = k_{id}t^{1/2} + I \tag{7}$$

where k_{id} is the rate constant for intraparticle diffusion. The value of intercept I indicates the outline concerning the thickness of boundary layer. The sorption data was fitted into intraparticle diffusion model. The plot of q_t vs $t^{1/2}$ is shown in Fig.4.C. There were three linear portions which indicate the three sorption stages: initial external mass transfer followed by intraparticle diffusion of cesium onto the SEPBs. Larger is the intercept I, greater is the boundary layer effect. The variation of straight line from origin appears to be due to differentiation within initial and final steps of the sorption. The multi-linearity plots point out the involvement of two or more steps [20]. The initial sharper portion was due to the instant sorption stage or outside surface sorption. The second portion was steady sorption stage, where the intraparticle diffusion was rate controlling step. The third portion was last equilibrium phase where the intraparticle diffusion starts to reduce due to very small solute concentration in the solution. This model shows a good correlation with rate data that justifies the sorption mechanisms.

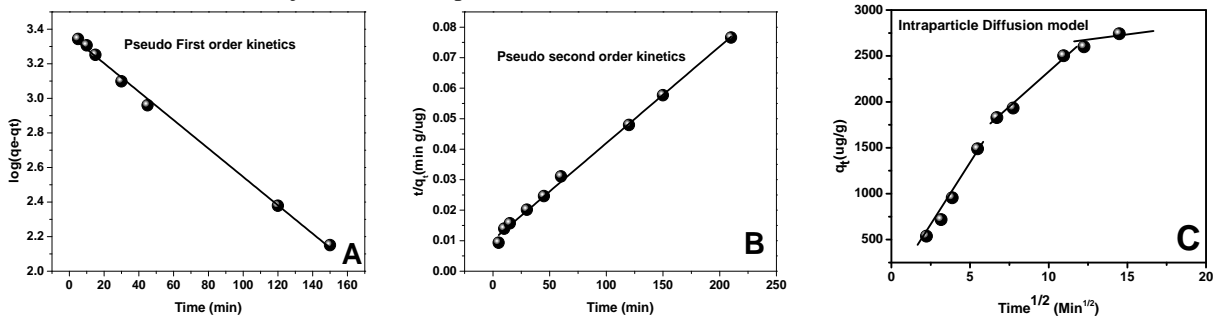


Fig.4 A) Pseudo-first order, B) Pseudo-second order and C) Intraparticle diffusion plots for cesium ion sorption onto the SEPBs.

In order to further confirm whether the sorption mechanism is through intra-particle diffusion or film diffusion, the kinetic information can be examined, employing the kinetic expression set by Boyd et al. [21]

$$F = 1 - \frac{6}{\pi^2} \exp\left(-\pi^2 Bt\right) \tag{8}$$

where F is the part of solute sorbed on various time, and Bt is a mathematical function of F.

$$F = \frac{q_t}{q_e} \tag{9}$$

where, q_t and q_e represents the amount sorbed (mg/g) at any time t, and at infinite time (in the current study 200 min.) respectively. Solutions to the equation (8), depending on the value of F, are as follows.

$$Bt = 2\pi - \frac{\pi^2 F}{3} - 2\pi\left(1 - \frac{\pi F}{3}\right)^{1/2} \tag{10}$$

$$Bt = -0.4977 - \ln\left(\frac{1}{3}(1 - F)\right) \tag{11}$$

The value of Bt can be calculated for each value of F, using equation (10) for F values up to 0.85 and, equation (11) for higher F values.

The linear plot of Bt vs. time provides important information to distinguish between the film diffusion and the intraparticle diffusion mechanism of sorption. A straight line passing through the origin will indicate that the sorption process is regulated only by intraparticle-diffusion mechanisms; or else, it is regulated by film diffusion. The observed linear Boyd plot does not pass through the origin, which clearly suggests that the sorption process also follows the

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, January 2016

external mass transfer, and intra-particle diffusion may not be the only rate controlling step in the removal of the sorbate.

G. SORPTION ISOTHERMS

The sorption isotherm models are important for explaining interaction of the solute with the sorbent. The data shown in Fig.5.A clearly indicate that, with increasing initial cesium ions concentration, the amount of sorbed cesium increases significantly. The sorption increases linearly in the initial stages, indicating that the sorption sites on the SEPBs are sufficient. On the other hand at higher metal ions concentration the sorption was comparatively slower, which indicates that amount of sorbed cesium ions on the surface of SEPBs is limited due to decrease in the number of sorption sites on the SEPBs. The maximum experimental sorption capacity was found to be ~3.5 mg/g for the swollen beads.

To know the mechanism of sorption, we have fitted the sorption data into the different sorption isotherm models such as Langmuir, Freundlich and Tempkin. These models show characteristic sorption mechanisms, with characteristic interactions between sorbate and the sorbent. The Freundlich isotherm assumes a heterogeneous surface with an unequal distribution of heat of sorption over the surface. While, the Langmuir isotherm presumes that the sorption is attained at specific homogeneous site within the sorbent. The Tempkin isotherm gives the explanation of sorbent-sorbate interactions. This isotherm assumes that (i) the heat of sorption of every part of the molecules in the layer decaying linearly with coverage due to sorbent-sorbate interactions, and that (ii) the sorption is differentiated by an identical distribution of binding energies, up to some highest binding energy.

H. THE FREUNDLICH ISOTHERM

Freundlich isotherm is suitable for multilayer sorption in addition to non-ideal sorption on heterogeneous surface. The model can be represented by the following equation [22]

$$q_e = k_f c_e^{1/n} \quad (12)$$

Rearranging the above equation in to the linear form, to verify the applicability of the model with the experimental results, gives:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad (13)$$

where, n and k_f are Freundlich constants representing the intensity and sorption capacity, respectively. Freundlich model suggests the multi-layer sorption pattern by assuming that the sorbent have energetically heterogeneous surfaces with variation in affinity for the sorbate. Correlation coefficient along with Freundlich constants are shown in Table 2. The linear plot of Freundlich isotherm is shown in Fig.5.B. The poor correlation coefficient (R^2) value of 0.964 indicates that the experimental results cannot be represented well by the Freundlich isotherm model.

I. THE TEMPKIN ISOTHERM

The Tempkin isotherm [23] is an important isotherm applicable in various sorption processes. The linear form of this model can be represented as:

$$q_e = \left(2.303 \frac{RT}{b}\right) \log A + \left(2.303 \frac{RT}{b}\right) \log C_e \quad (14)$$

This can be simplified to the equation (15), by replacing $2.303RT/b$ with B .

$$q_e = B \log A + B \log C_e \quad (15)$$

The sorption data can be tested by a linear Tempkin plot of q_e vs $\log C_e$. The values of constants A and B can be determined from the intercept and slope of the linear plot respectively. The values of Tempkin constants A and B and the correlation coefficient are shown in Table.2. The R^2 value of 0.986 clearly shows that this model may not be perfectly explaining the sorption results.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, January 2016

Table 2. Different isotherm constants and corresponding R² values for the adsorption of Cs⁺ onto the SEPBs.

Metal ion	Langmuir parameters			Freundlich parameters			Tempkin parameters		
Cs ⁺ ion	B (lmg ⁻¹)	q _{max} (mgg ⁻¹)	R ²	k _f (mgg ⁻¹)	n	R ²	B	A (lg ⁻¹)	R ²
	0.0822	3.7	0.9968	434.23	2.0682	0.9646	1247.9	2.5962	0.9862

J. THE LANGMUIR ISOTHERM

The Langmuir theoretical model is useful for monolayer sorption onto the surface with limited amount of identical sites. The general Langmuir equation can be shown as below [24].

$$q_e = q_{max} \left(\frac{bc_e}{1+bc_e} \right) \tag{16}$$

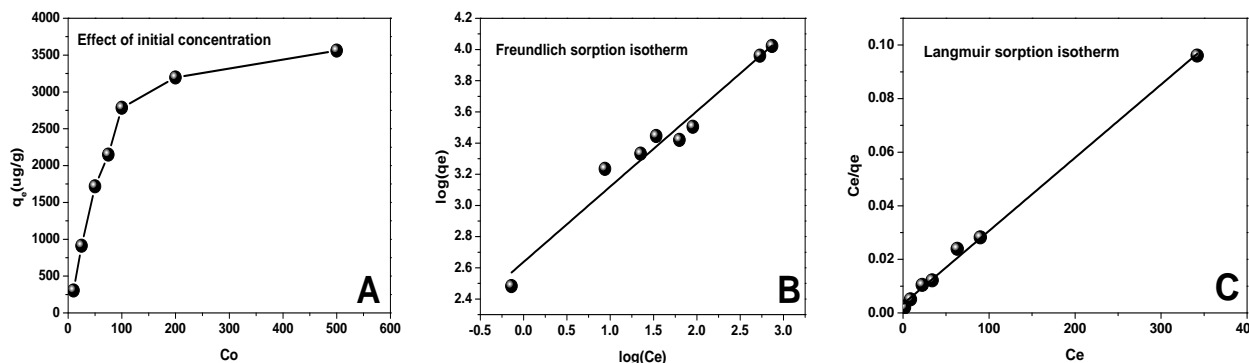


Fig.5 A) Effect of initial concentration on the uptake of metal ion, B) Freundlich isotherm plot, C) Langmuir isotherm plot for sorption of Cs⁺ on to the synthesized SEPBs.

Here, b (l/mg) is the Langmuir equilibrium constant, and the q_{max} (mg/g) is the maximum sorption capacity (theoretical monolayer saturation capacity). The main importance of the Langmuir equation is that the constants q_{max} and b can be found out by using the linear form of Langmuir equation, as shown below:

$$\frac{C_e}{q_e} = \frac{1}{(q_{max} b)} + \frac{C_e}{q_{max}} \tag{17}$$

The Langmuir plot of C_e/q_e vs C_e is as shown in Fig.5.C. The binding sites possess similarity for sorption of a single molecular layer. In this case the nature of binding can be physical or chemical but is relatively strong enough to stop displacement of the sorbed molecules. The correlation coefficients and the Langmuir constants q_m, and b are listed in Table.2. The comparison of correlation coefficients values of the different isotherm plots show highest value of 0.99689 for Langmuir isotherm, indicating the best fit for the sorption process.

IV. CONCLUSION

The KNiHCF-PES beads were synthesized by phase inversion method, and characterization of the synthesized beads was carried out by various methods such as optical microscope, EDX, FE-SEM, FT-IR, and TGA. The capability of the synthesized KNiHCF-PES beads to remove radioactive cesium ion from aqueous waste solution was explored by the batch studies. These beads were tested for separation of cesium by evaluating effect of various experimental parameters, such as pH, contact time, initial metal ion concentration, etc. The results were analysed by applying different kinetic models and sorption isotherms. From TGA study, it can be concluded that the beads have high water content of 84%, and have good thermal stability up to about 400°C. The cesium sorption capacity of the beads increases with increase in the initial cesium ion concentration while it is nearly independent of pH in the studied range of 2–12. Kinetics of

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, January 2016

sorption was fast, and equilibrium recovery of cesium was reached in ~200 min. The kinetic data have been found to fit well in the pseudo second-order kinetic model. The mechanism of sorption has been evaluated by various sorption

models and it was found to fit well into the Langmuir isotherm model. The maximum experimental sorption capacity of the swollen beads was calculated to be ~3.5 mg/g which corresponds to ~22.5 mg/g of the dry beads. The mechanism of the sorption of cesium ions onto the synthesized SEPBs is found to be complex; it is regulated by film diffusion as well as the external mass transfer. These results suggest that the synthesized SEPBs can be effectively used for removal of cesium ions from aqueous radioactive waste.

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