Removal of americium from aqueous nitrate solutions by sorption onto PC88A—Impregnated macroporous polymeric beads

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HIGHLIGHTS

- The PC88A EIMPBs were synthesized and characterized by FTIR, TGA and SEM.
- The physiochemical strength of these beads was found to be excellent.
- The synthesized beads show a great potential for effective removal of Am (III).
- The sorption kinetics and sorption isotherms explain the mechanism of extraction.
- The synthesized EIMPBs have good reusability up to 10 successive cycles.

GRAPHICAL ABSTRACT

Schematic of the procedure for preparation of extractant impregnated polymeric beads.
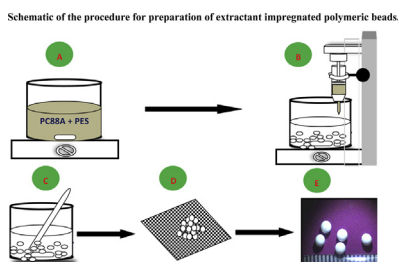
Schematic of the procedure for preparation of extractant impregnated polymeric beads.

ABSTRACT

The removal of Am (III) ions from aqueous solutions was studied by solid–liquid extraction using indigenously synthesized Extractant Impregnated Macroporous Polymeric Beads (EIMPBs). These beads were prepared by an *in situ* phase inversion method using polyethersulfone (PES) as base polymer and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) as an extractant. The synthesized EIMPBs were characterized by FTIR, TGA and SEM techniques. The batch equilibration study using these beads for the uptake of Am (III) was carried out as a function of parameters, like pH, equilibration time, Am (III) concentration, *etc*. The blank polymeric beads, without PC88A, have shown negligible sorption of Am (III) under the experimental conditions. The experimental data on the sorption behavior of Am (III) on the polymeric beads fitted well in the pseudo-second-order kinetics model. The synthesized polymeric beads exhibited very good sorption capacity for Am (III) at pH 3. The reusability of the beads was also ascertained by repetitive sorption/desorption of Am (III) up to 10 cycles of operation, without any significant change in their sorption characteristics.

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1. Introduction

Aqueous radiochemical separations employed in nuclear industry are aimed at recovery of useful isotopes and actinides thereby generate a variety of waste streams. Most of these waste streams are acidic in nature, containing varying amount of radioactive elements, which must be removed owing to their extremely hazardous characteristics. The principal aim of radioactive waste treatment in nuclear industry is to minimize the volume of the secondary waste via optimized treatment processes, leading to generation of effluents, free from radioactive contaminants, for their final disposal [1,2]. Therefore, such stream needs to be efficiently treated

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to bring down the radiotoxicity to permissible levels or to level of zero discharge. 241Am, is formed in nuclear reactor from 241Pu on emission of beta particle, with a half life of 13.6 years. The risk of radiation exposure associated with 241Am, due to emission of 60 keV gamma photons, can be minimized after its removal from the waste streams. It is a good source of alpha and neutron radiation and is also used as a target material for production of transuranium elements. 241Am also has intrinsic value, especially when used in smoke detector. Thus, the separation of americium from nuclear waste is essential not only to prevent its radiation hazards but also to utilize it for the important radiological applications mentioned above. The currently available technologies for separation and recovery of metal ions are solvent extraction, ion-exchange, chemical precipitation, membrane based technologies and sorption on solid matrix using natural and synthetic adsorbents [3–8]. Inspite of being popular and fairly efficient for bulk separations, these methods do have marked limitations that force the separation scientists to look for more efficient and technically feasible alternatives. In case of solvent extraction, yielding high throughput, efficiency and ease of operation suffers from practical problems of aqueous solubility of the extractants, solvent entrainment in aqueous streams, phase disengagement, curd formation as well as requirement of huge amount of organic diluents [9]. It results in generation of a large volume of contaminated secondary radioactive waste, after its productive utilization [10,11]. The use of membrane based technologies, such as supported liquid membranes (SLM), emulsion liquid membranes (ELM) and bulk liquid membranes (BLM), for removal of radionuclides from low level nuclear waste streams, have shown some distinct advantages over the solvent extraction [12–15]. But, inherent drawbacks, like bleeding out of the solvent from the SLM and the instability of emulsion globules in ELM, limit their practical applicability. The ion exchange purification process is quite a suitable method to achieve high degree of selectivity yet has low throughput. However, their extensive application in the field of separation science gained less significance due to limitations that include, slow kinetics, resin fouling and additional treatment during regeneration step. Hence, it is always advisable to choose an extraction process, which generates minimum secondary waste, and has a long-term multi-cycle applicability.

The development of macroporous polymeric beads, impregnated with metal-specific extractants, show extraction capability under column operation, and hence bridge the gap between solvent extraction and ion exchange techniques [16–18]. The extractant impregnated polymeric beads (EIMPBs), are completely free from organic diluents, and can overcome the typical problems of liquid-liquid extraction process [19–22]. These polymeric beads represent second generation of extraction system and offer distinct advantages due to possibility of high extractant loading, resulting in large metal uptake capacity. In this connection, polyethersulphone (PES) is well known for its application in preparation of polymer supported extraction systems, like membranes, beads, etc. The PES shows outstanding oxidative, thermal and hydrolytic stabilities, as well as good mechanical and film-forming properties. The PES based EIMPBs assisted radio-chemical separations have been therefore investigated for removal of radionuclides from low level nuclear waste. In the present work, PC88A impregnated PES beads are prepared and the sorption of Am (III) from aqueous waste solutions is investigated.

2. Materials and methods

2.1. Reagents and solutions

2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester, $C_{16}H_{35}O_3P$ (commercially known as PC88A) obtained from Daihachi Chemical Industry Co. Japan, was used without further purification for preparation of the beads. Laboratory reagent (LR) grade 1-methyl 2-pyrrolidone, C_5H_9NO (NMP), polyethersulfone, $[C_{12}H_8O_3S]_n$ (PES) and poly vinyl alcohol, $[C_2H_4O]_n$ (PVA) were procured from local market. Dowex 1×4 anion exchange purified Americium (major isotope 241Am) solution in its nitrate form, used in this study, was obtained from research reactor Fuel Reprocessing Facility, Trombay. The pH of the Am containing solutions was adjusted by adding appropriate quantity of dilute HNO_3 or NaOH solutions and measured with a pH electrode. De-ionized (DI) water (conductivity < 0.06 μS/cm), obtained from MilliQ water purification system, was used for the preparation of aqueous solutions.

2.2. Preparation of EIMPBs

The PC88A encapsulated PES beads were prepared, using phase inversion technique. The detailed procedure, used for the preparation of different extractant-encapsulated macroporous beads have been described in a number of papers [23–25]. Typically a formulation, of required viscosity, containing appropriate amounts of PES, NMP, and PC88A was prepared. The mixture was filled in a 20 ml syringe having needle of appropriate diameter. A dilute aqueous PVA solution (~0.1%), under continuous stirring by a mechanical stirrer was used as a suitable phase inversion medium. The organic mixture from the syringe was then added drop-wise into the phase inversion medium with the help of a syringe pump. The soft beads are formed almost instantaneously which were filtered and repeatedly washed with DI water. The resulting EIMPBs were then incubated in excess water, for 24 h, for complete curing. A schematic diagram, representing the preparation method of the EIMPBs, is given in Fig. 1.

2.3. Characterization

The synthesized beads were characterized by different techniques. The presence of different functional groups was established by recording its IR spectra in diamond ATR holder, using IR Affinity-1 FTIR spectrophotometer. Morphology of the beads was studied by simple microscopy, using QX5 DIGITAL BLUE computer microscope, and scanning electron microscopy, using TESCAN VEGA MV 2300T/A microscope. Pore volume and thermal stability of the beads were determined by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) using STAR^e System METLER TOLEDO instrument. A few mg of the sample was taken in an alumina sample holder, and TGA/DSC curves were recorded at the heating rate of $15\,^{\circ}C\,min^{-1}$, from 30 to $900\,^{\circ}C$, under dynamic condition, and in N_2 atmospheres ($50\,ml\,min^{-1}$).

2.4. Extraction and stripping studies

The extraction of Am (III) by the synthesized swollen EIMPBs was tested, in batch experiments, from very dilute nitric acid solutions. Typically about 0.10 g of the beads were equilibrated with a given volume (2 ml) of Am (III) solution of known concentration, for 60 min, at different pH range. The concentration of Am in the aqueous solutions, before and after equilibration, was estimated by gamma spectrometry in a well type NaI(Tl) scintillation counter, using 60 keV γ line of 241Am. The distribution ratio (K_d) of Am (III) was calculated using Eq. (1).

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{W} \tag{1}$$

where C_0 and C_e are, respectively, the initial and equilibrium concentrations (mg/l) of Am (III) in the aqueous phase, V the volume
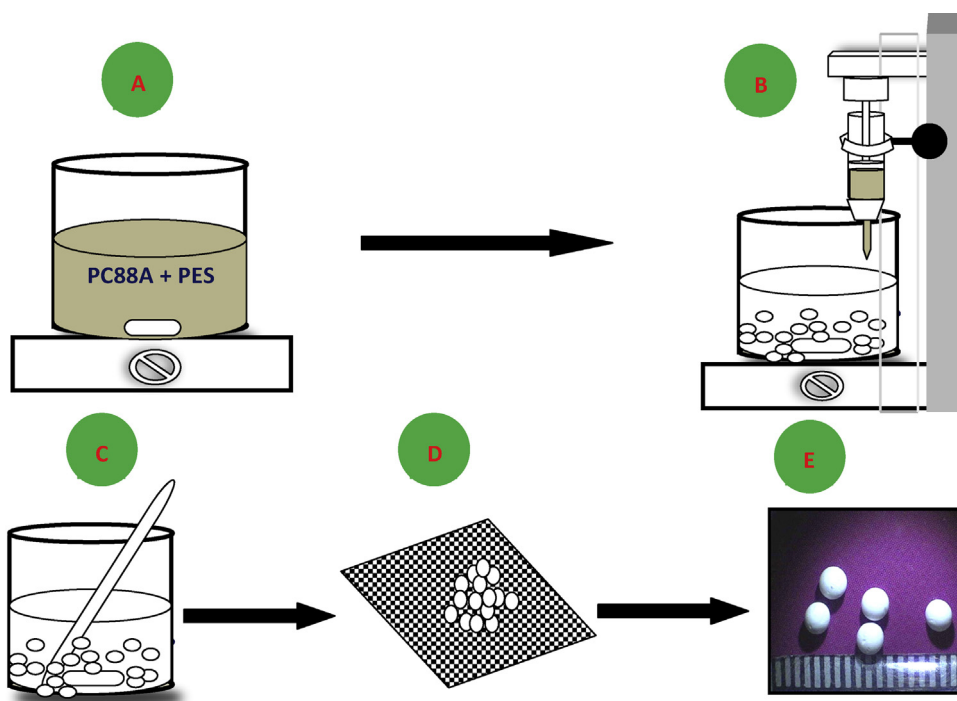
Fig. 1. Schematic of the procedure for preparation of PC88A impregnated polymeric beads. (A) Preparation of a formulation of PES powder and PC88A in 1-methyl-2 pyrollidone (NMP). (B) Drop-wise addition of the formulation in aqueous bath (phase inversion medium). (C) Curing for 24 h. (D) Separation and washing of the prepared beads. (E) Optical microscope image of the synthesized beads (10× zoom).

of the aqueous solution in ml and W is the weight of the beads in grams.

Stripping study of the Am loaded beads was carried out by using various stripping agents, viz., 0.1 M oxalic acid, 0.1 M ascorbic acid, 0.1 M EDTA and mixture of 0.5 M nitric acid and 0.1 M oxalic acid. The percentage stripping was calculated using Eq. (2).

$$\%\text{Stripping} = \left(\frac{A_{\text{strippant}}}{A_{\text{beads}}} \right) \times 100 \qquad (2)$$

where $A_{\text{strippant}}$ and A_{beads} are the amount (mg) of Am in stripping solution and the amount of Am retain on the EIMPBs, respectively.

The equilibrium capacity of the beads (q_e) is calculated using Eq. (3).

$$q_e = (C_0 - C_e) \times \frac{V}{W} \qquad (3)$$

2.5. Kinetic studies

To optimize the time for maximum sorption of Am (III) by the EIMPBs, 0.1 g of the beads were equilibrated with 2 ml of 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 percentage uptake (%E) was calculated, using the following equation.

$$\%E = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (4)$$

The experimentally observed kinetic data was fitted into different kinetic models, like pseudo-first-order, pseudo-second-order and Weber–Morris intraparticle diffusion model, to explain the kinetic of sorption of Am (III) on the synthesized beads.

3. Results and discussion

3.1. Characterization of the EIMPBs

The scanning electron microscope (SEM) images of the beads, as shown in Fig. 2(A) and (B), depict morphology and porosity of the beads. A porous skin layer is found on the outer surface of the beads, while many bigger pores, filled with the extractant, are visible inside the beads, as evident from the cross-sectional image. The diameter of the synthesized beads was found to be ~2 mm as evident from the optical microscope image of the beads shown in Fig. 1(E). The average size of the beads, though can be controlled by selecting the diameter of the syringe needle used to prepare the beads, was much larger than the syringe needle diameter. The surface tension and viscoelasticity nature of the polymeric formulation also play an important role in deciding the size of the beads.

The FTIR spectra of blank PES beads and the PC88A encapsulated beads are shown in Fig. 3(A) and (B), respectively. The evidence for the presence of PES comes from the observation of a strong band at 1578 cm^{-1} which can be assigned to the C–C bond stretching vibration of the aromatic benzene ring (Fig. 3(A)). The absorption peak at around 1483 cm^{-1} was attributed to the symmetrical bending motion in the aromatic rings of C–H in the plane. Absorption peaks at 1150 and 1296 cm^{-1} were attributed to the vibrations of the sulfone group (R$_2$SO$_2$). A strong aromatic ether band at around 1240 cm^{-1} was also observed. Peak at 3434 cm^{-1}, indicating the presence of hydroxyl group, is quite broad because of the presence of hydrogen bonding in the swollen beads. Fig. 3(B) shows the presence of PC-88A in the synthesized beads, as evident from the bands at 2930 cm^{-1} (C–H stretching of methyl) and 1128 cm^{-1} (P=O stretching).

Fig. 4 shows the TGA/DSC profiles of neat PC88A liquid, polyethersulphone powder and the synthesized swollen beads. The TGA thermogram of the PC88A liquid, used in the synthesis of beads, shows main weight loss in the temperature range of 200–500 °C,
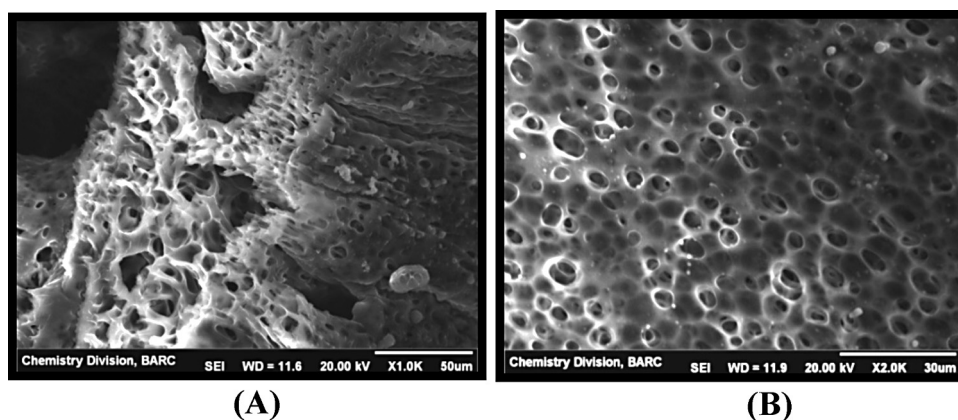
Fig. 2. The scanning electron microscope (SEM) images of the synthesized EIMPBs (A) outer surface and (B) cross-sectional view.
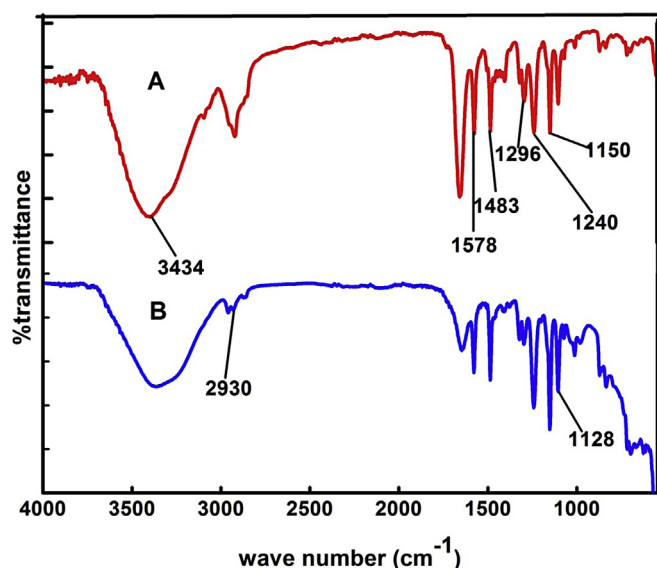

Fig. 3. The FTIR spectra of synthesized (A) Blank PES beads and (B) PC88A encapsulated beads.

and a total of about 93% of the starting weight is lost in the two steps, up to the studied temperature of 900 °C (Fig. 4(A)). The DSC profile shows that both the steps are endothermic. Degradation of polymer backbone begins at around 500 °C, and the weight loss of almost around 64% of the starting weight is observed up to the studied temperature (Fig. 4(B)). Thermo gravimetric analysis of the synthesized swollen beads shows the presence of high water content. A weight loss of 69.6% is observed during the heating of the beads up to the temperature of 150 °C, mainly due to evaporation of water, as shown in Fig. 4(C). The corresponding two endothermic peaks in the DSC profile indicate the presence of two types of water, probably free and bound water, in the swollen beads. Further a weight loss of ~18%, observed around 200–500 °C, is attributed to the decomposition of PC88A extractant. The weight loss above 500 °C represent the decomposition of PES. These results suggest that the swollen beads contain 69.6% of water, 17.5% of PC88A and the remaining (~13%) base polymer (PES). These beads, in the swollen form, are used for the Am (III) extraction experiments.

3.2. Extraction and stripping of Am (III)

The extractant PC88A, loaded in the EIMPBs, is a cationic type of extractant, and is known for the intensive extraction of actinide and lanthanide elements from their dilute solutions [26–28].

Table 1
Distribution coefficient (K_d) and percentage extraction (%E) of Am (III) by the EIMPBs as a function of nitric acid strength.

HNO$_3$ (M)	Distribution coefficient and percentage extraction of Am (III)	
	K_d (ml/g)	% E
0.001 (pH 3)	360.8	94.8
0.01 (pH 2)	69.9	77.8
0.1 (pH 1)	1.1	5.3
0.5	0.6	3.0
1.0	0.3	1.5
2.0	0.2	0.7
4.0	0.1	0.5

Experimental conditions: Concentration of Am (III) in the feed solution = 2.94 ppm; weight of the beads = 0.1 g; volume of test solution = 2 ml; equilibration time = 60 min; temperature = 294 K.

Solid–liquid extraction, using EIMPBs, differs from liquid–liquid extraction, since the former process involves diffusion across the porous beads. The experiments carried out, using the blank beads, without the extractant PC88A, showed negligible extraction of Am (III) at all the studied HNO$_3$ concentrations. Thus the principal functional group responsible for Am (III) extraction by the EIMPBs is the phosphate group of the extractant PC88A impregnated in the beads, and not due to any other functional group present in the polymeric skeleton of the beads. On the basis of studies reported in the literature [29,30], the following reaction mechanism can be given for the extraction of Am (III) by the EIMPBs from nitric acid medium.

$$Am^{3+} + 3NO_3^- + \overline{H_2A_{2B}} \leftrightarrow \overline{Am(NO_3)_2HA_{2B}} + H^+ + NO_3^- \qquad (5)$$
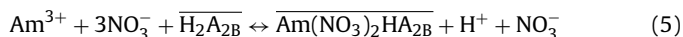
Molecular species under line bar with subscript B represents the species present in the beads. H$_2$A$_2$ denotes the dimer of the extractant PC88A.

Extraction of Am (III) by the EIMPBs has been carried out from solutions with different nitric acid concentrations. The extraction of Am (III) is particularly negligible when pH of the solution is <1, whereas it increases at and above pH 2. Almost a quantitative recovery of Am (III) (~95%), could easily be accomplished at low HNO$_3$ concentration of 0.001 M (pH 3). The higher K_d values of Am (III) obtained at lower strength of nitric acid can be attributed to cation-exchange behavior of the extractant PC88A present in the synthesized beads. Greater dissociation of cationic extractant H$_2$A$_2$ at higher pH favours its higher complexation with Am (III). The observed highest K_d value was 360.8 ml/g at the studied acid strength of 0.001 M (pH 3). The distribution coefficient (K_d) and percentage extraction (% E) values for Am (III), from the different nitric acid solutions, are given in Table 1.
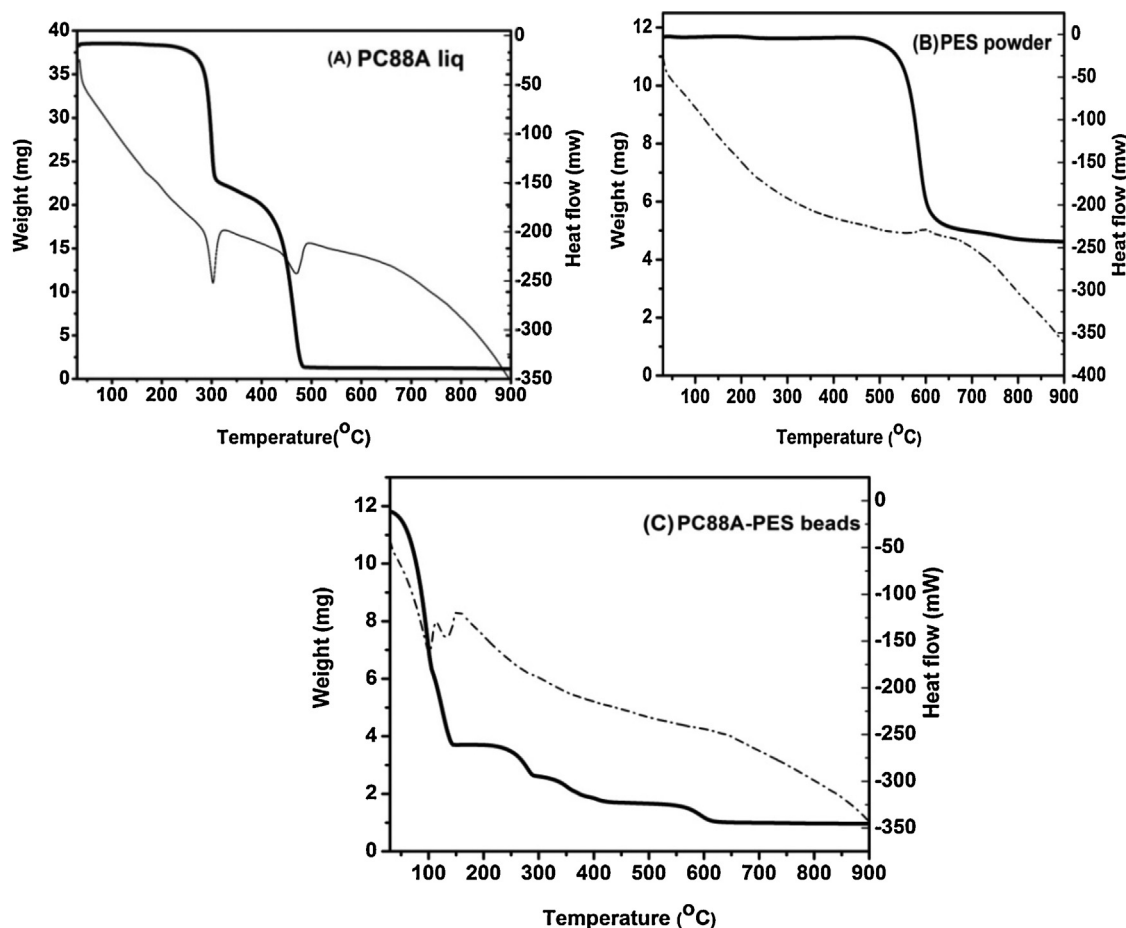
Fig. 4. TGA (—) and DSC (—) curves of the (A) PC88A liquid, (B) PES powder and (C) synthesized EIMPBs.

Various stripping agents, such as 0.1 M oxalic acid, 0.1 M Ascorbic acid, 0.1 M EDTA and mixture of 0.1 M oxalic acid and 0.5 M HNO₃, were used for carrying out the back extraction of Am (III) from the loaded EIMPBs. Stripping data are presented in Fig. 5. Though a solution of 0.5 M HNO₃ is good enough for quantitative back extraction of Am (III), loaded onto the EIMPBs, to minimize the number of washing steps during the regeneration of the EIMPBs, a

solution of 0.1 M oxalic acid was found to be the most suitable, for stripping of the loaded Am (III). The mechanism of stripping with oxalic acid can be expressed by the reaction given below.
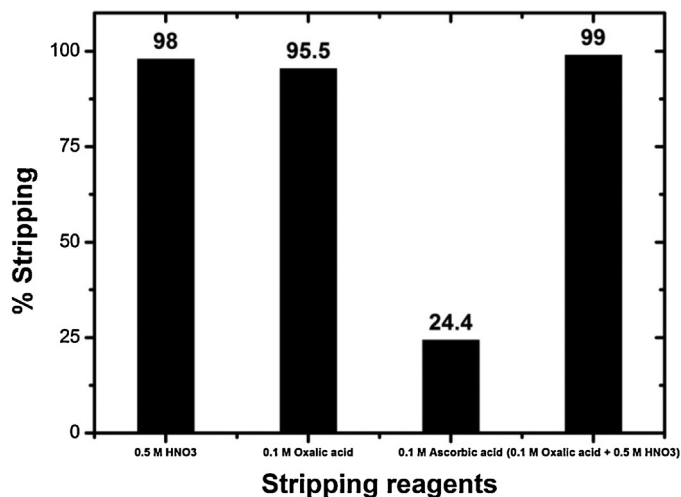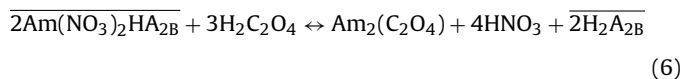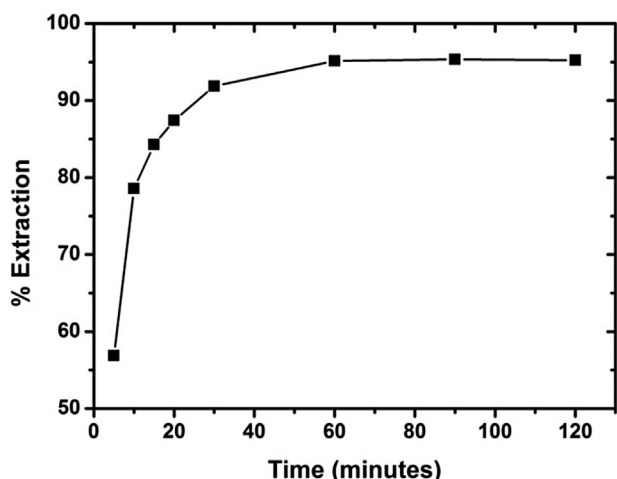
$$\overline{2Am(NO_3)_2HA_{2B}} + 3H_2C_2O_4 \leftrightarrow Am_2(C_2O_4) + 4HNO_3 + \overline{2H_2A_{2B}}$$

$$(6)$$

It was observed that a single contact was not enough for quantitative stripping of Am (III). Hence two contacts were given to ensure the complete back extraction. The kinetics of the back extraction was also found to be very fast. The saturation stripping was achieved in less than 10 min of equilibration.

3.3. Kinetics of sorption

3.3.1. Effect of sorption time

Kinetics play an important role in the sorption process, since it helps in determining the most appropriate contact time needed, which depends on the nature of the system used. To understand the effect of contact time, for optimum sorption of Am (III) onto the synthesized beads, the experiments were conducted by equilibrating 2 ml of 2.94 ppm Am (III) solution and 0.1 g of the sorbent beads, in separate vials. The mixtures were equilibrated in a mechanical shaker, at a constant temperature (T = 294 K), and were sampled at different times, ranging from 5 to 120 min, to estimate the concentration of Am (III) sorbed as a function of equilibration time. The results are shown in Fig. 6. A rapid sorption is observed at the initial stage, followed by a slow process, leading to saturation sorption in about 60 min. Therefore, the time period of 60 min has been used

Fig. 5. Performance of various stripping agents for back extraction of Am (III) loaded onto the EIMPBs. Experimental conditions: Volume of stripping solution = 2 ml each; equilibration time = 10 min; temperature 294 K

Fig. 6. % Extraction of Am (III) by the synthesized EIMPBs as a function of equilibration time. Experimental conditions: pH 3; volume of the solution = 2 ml; weight of the beads = 0.1 g; temperature = 294 K.

in further sorption experiments, as the optimum contact time for the maximum sorption.

3.3.2. Sorption kinetics models

The uptake of Am (III) by the EIMPBs, involves diffusion of the sorbate to the surface of the beads, intra-bead diffusion and complexation with the extractant, sequentially. Therefore, the sorption isotherms and kinetic models applicable to sorption on sorbent particles, pure as well as composites, can be applied to these beads also. In order to investigate the mechanism of sorption, both pseudo-first-order and pseudo-second-order kinetics models were applied to analyse the experimentally observed kinetic data.

(i) Lagergren pseudo-first-order kinetics model

For a batch equilibration process, in a solid–liquid system, the rate of sorption of a solute onto the sorbent is governed by either film diffusion or intraparticle diffusion. The Lagergren pseudo-first-order kinetic model for the sorption process can be expressed as [31,32]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{7}$$

where q_e and q_t are the amount of Am (III) sorbed onto EIMPBs (mg/g) at equilibrium and at time t, respectively, and k_1 is the rate constant (min^{-1}), of the pseudo-first-order sorption process.

The model parameters k_1 and q_e can be obtained respectively from the slope and the intercept of the linear plot of $\log(q_e - q_t)$ versus t. However, the data plotted do not fit well in the whole range of contact time ($R^2 = 0.3639$), indicating that this model is not appropriate for explanation of the studied sorption process.

(ii) Pseudo-second-order kinetics model

To describe the sorption process, a linear form of the pseudo-second-order kinetics model equation was used, which can be expressed as follows [33,34].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant for the pseudo-second-order sorption process. The plot of t/q_t versus t gives a straight line, as shown in Fig. 7(A), with a correlation coefficient (R^2) value of 0.9997, indicating that the sorption data fit well in the pseudo-second-order kinetics model. Therefore, the Lagergren pseudo-second-order kinetics model is more relevant to explain the sorption of Am (III) onto the EIMPBs. The pseudo-second-order model assumes that chemisorptions is the rate controlling step. The

value of q_e and k_2, can be obtained from the slope and the intercept of the linear plot, respectively, and are found to be 0.0574 mg/g and 7.072 g mg^{-1} min^{-1}. These values, along with that of R^2, are listed in Table 2.

(iii) Weber–Morris intraparticle diffusion model

Sorption of the metal ions to the active sites of the sorbent is usually controlled by diffusion mechanism, including the rapid boundary layer diffusion which causes surface sorption, a gradual sorption stage due to intraparticle diffusion, and plateau to equilibrium [35]. A graphical method was introduced by Wever and Morris to establish the intraparticle diffusion mechanism and to determine if it was a rate determining step [36]. The equation of this model is expressed as follows:

$$q_t = K_{id}\left(t^{1/2}\right) + I \tag{9}$$

where K_{id} is the intra-particle diffusion rate constant (mg/g min$^{-1/2}$) and I is a constant that gives an idea about the thickness of the boundary layer, i.e., the larger the value the greater is the boundary layer effect. If the sorption process follows the intraparticle diffusion model, a plot of q_t as a function of $t^{1/2}$ should be a straight line and pass through the origin if the intraparticle diffusion would be the rate controlling parameter [37].

To see whether the sorption kinetics of Am (III) on the PC88A beads is following intraparticle diffusion mechanism, a graph of q_t versus $t^{1/2}$ was plotted as shown in Fig. 7(B). The experimental curve gives three straight lines with three different slopes (all with $R^2 > 0.995$). The observed multi-linearity in the plot suggests that an intraparticle diffusion mechanism is involved. However, intraparticle diffusion is not applicable to the entire time scale of the sorption process. The first straight line, which corresponds to the fast sorption, represents the external surface sorption or instantaneous sorption where intraparticle diffusion has no significant contribution. The second stage is the gradual sorption, corresponding to intra-particle diffusion, followed by a final equilibrium stage where intra-particle diffusion starts to slow down due to extremely low sorbate concentration in the solution. As shown in Fig. 7(B), the external surface sorption, stage 1, is completed before 15 min, and then, the stage of intra-particle diffusion (stage 2) is attained, and continues from 15 to 30 min. Finally, the last straight line is representing the chemical equilibration of Am (III) in the swollen PC88A beads. In general, the slope of the line in stage 2 gives intra-particle diffusion rate constant, K_{id}. From these results, it can be concluded that the intra-particle diffusion inside the beads have significant influence in sorption of Am (III) ions onto the PC88A beads. Since the straight line does not pass through the origin, the intra-particle diffusion is not the sole rate determining parameter controlling the sorption of Am (III) onto the PC88A beads. The intra-particle diffusion rate constant (K_{id}) and the value of I corresponding to the intermediate time scale (stage 2) is given in Table 2.

3.4. Effect of initial metal ion concentration

The relationship between the amounts of metal ion sorbed per unit mass of sorbent and the equilibrium concentration in the aqueous phase plays an important role in optimizing the sorption behavior. The highly radioactive nature of americium restricted us to perform sorption isotherm experiments with actual americium solution at higher concentration range. Hence, Eu (NO$_3$)$_3$ was taken as counter metal ion, assuming that Eu (III) will show physicochemical behavior similar to Am (III). The sorption curve was obtained by equilibrating 0.018 g of beads with 2 ml of working solution, having Eu(NO$_3$) concentration in the range of 1–200 ppm along with tracer of ^{241}Am, at pH 3, for 60 min (Fig. 8(A)). The amount of metal uptake was found to increase significantly with increase in initial metal concentration in the studied concentration range. As expected, at lower initial metal
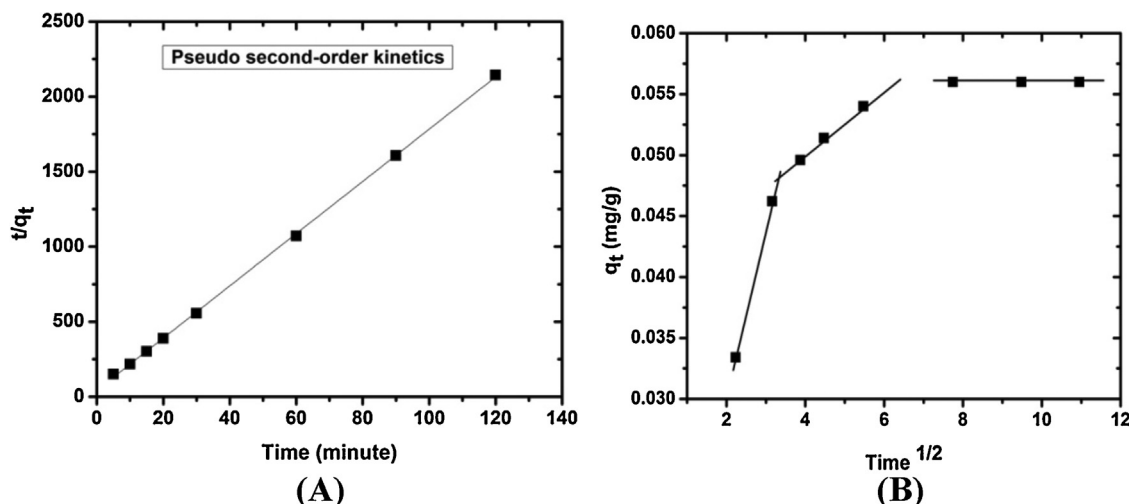
Fig. 7. Kinetics models for the sorption of Am (III) on the synthesized EIMPBs: (A) pseudo-second-order kinetics and (B) intraparticle diffusion kinetics.

Table 2
Kinetics parameters of Am (III) sorption by PC88A EIMPBs.

Kinetic model					
Pseudo-second order			Intra-particle diffusion model		
q_e (mg/g)	k_2 (mg^{-1} min^{-1})	R^2	K_{id} (mg/g min$^{-1/2}$)	I	R^2
0.0574	7.072	0.9997	0.0027	0.0391	0.996

ions concentration, the sorption increases linearly suggesting that the adsorption sites on the EIMPBs are sufficient, and in this case, the amount sorbed is dependent on the number of the metal ions transported from the bulk solution to the surfaces of the beads. While at higher metal ion concentrations, the sorption no longer increases proportionally with the initial metal ions concentration, indicating that the number of adsorption sites on the surfaces of the EIMPBs actually limits the amount of Am (III) sorbed. The steep slope at lower concentrations is a desirable feature of the sorption system and the results indicate that the synthesized PC88A containing composite in the form of beads, is an efficient sorbent for Am (III) from very dilute nitric acid solutions.

3.4.1. Sorption isotherms

Sorption isotherms describe fundamental understanding of distribution of sorbates on the surface of the sorbents at equilibrium, and are important in optimizing the use of the sorbents. Various sorption isotherms, viz. Langmuir, Freundlich, Temkin, Dubinin-Radushkevich are widely employed to investigate the amount of the metal ions sorbed per unit weight of the sorbent, i.e. q_e, as a function of the concentration of metal ions in the aqueous phase. The sorption data have been subjected to different isotherm models and their detailed description is given below.

(i) The Langmuir model

The simplest sorption model is Langmuir isotherm which assumes a monolayer sorption, with a homogenous distribution of the sorption sites and the sorption energies, without interactions between the sorbed molecules, or ions. Though the Langmuir isotherm was developed originally for the sorption of the gases on the solid surface, it is also applied for the solid–liquid systems. The linear form of the Langmuir isotherm can be expressed as: [38].

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{(Qb)C_e} \tag{10}$$

where q_e (mg/g) is the amount of metal ions sorbed on the solid phase, C_e the equilibrium concentration of metal ions in the

aqueous phase, Q (mg/g) the maximum sorption capacity (theoretical monolayer saturation capacity) and b (ml/mg) is the Langmuir constant, which is related to the affinity of the binding sites. The Langmuir constants b and Q, can be obtained from the linear plot of $1/q_e$ against $1/C_e$.

The plot of $(1/q_e)$ versus $1/C_e$ gave straight line, indicating that the sorption behaviour follows the Langmuir isotherm, as shown in Fig. 8(B). The values of Q and b were found to be 2.498 mg/g and 0.512 ml/mg, from the intercept and the slope, respectively.

The characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor, R_L, which is defined by the following equation.

$$R_L = \frac{1}{1 + bC_0} \tag{11}$$

where C_0 is the initial metal ion concentration. The value of R_L, for the entire studied concentration range lies between 0 and 1, indicating favourable sorption, as reported by McKay et al. [39].
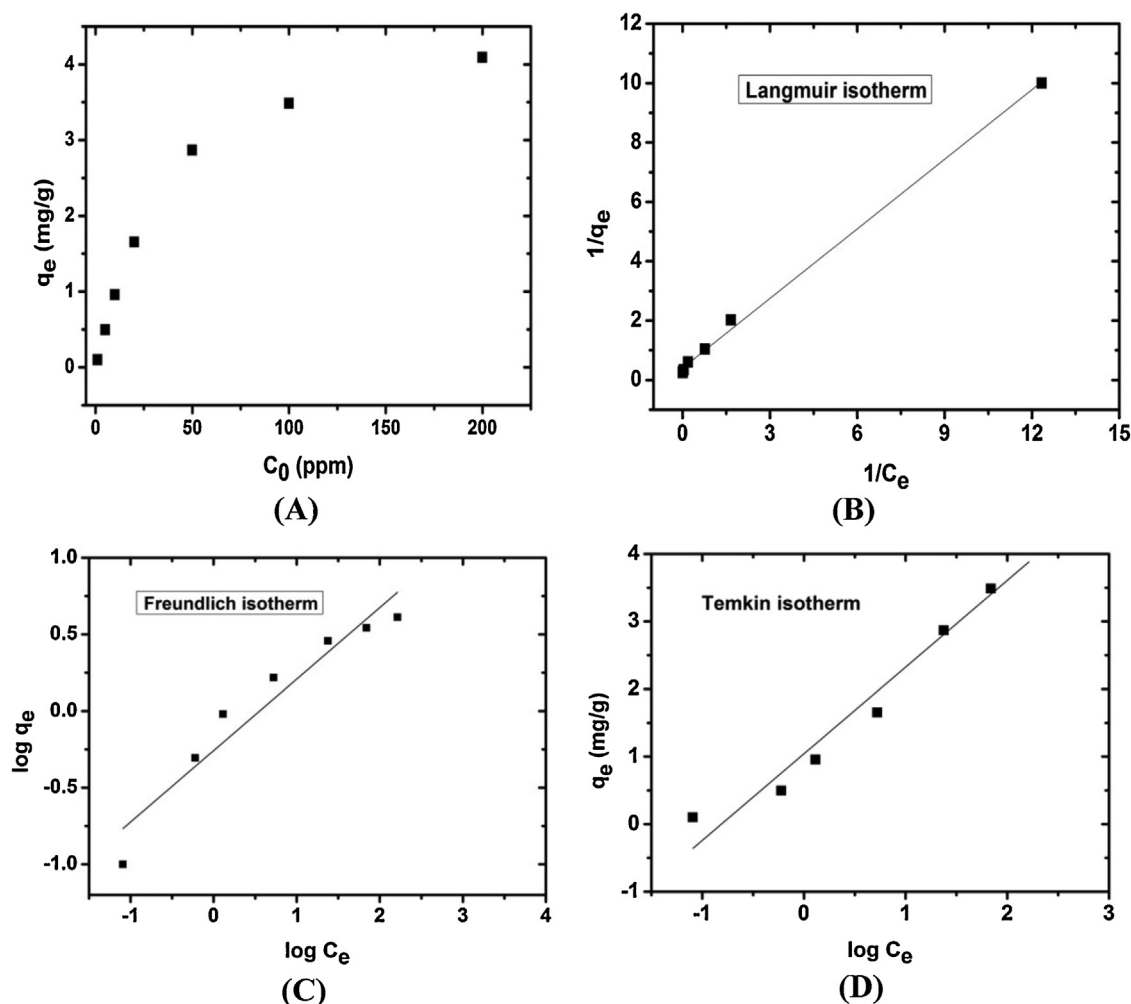
(ii) The Freundlich isotherm

In the case of the Freundlich model, the energetic distribution of the sites is heterogeneous, due to diversity of the sorption sites, or diverse nature of the metal ions sorbed, free or hydrolyzed species. The sorption data were also tested on the following linearized form of the Freundlich sorption isotherm [40].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{12}$$

where K_f (mg/g) and n are Freundlich constants related to sorption capacity and the sorption intensity, respectively and can be obtained from the linear plot of $\log q_e$ versus $\log C_e$. The plot of Freundlich isotherm is shown in Fig. 8(C). From the slope and intercept of the plot the values of Freundlich parameter, i.e. $1/n$ and K_f are computed and given in Table 3.

(iii) The Temkin isotherm

The Temkin sorption isotherm model was chosen to evaluate the sorption potential of the sorbent (PC88A beads) for the sorbate (Am (III)). The Temkin isotherm model assumes that the heat of

Fig. 8. (A) Effect of initial concentration of metal ion on q_e, (B) Langmuir isotherm plot, (C) Freundlich isotherm plot and (D) Temkin isotherm plot for the sorption of Am (III) by the PC88A composite beads. Experimental conditions: Feed volume = 2 ml containing 1–200 ppm Eu (III) and [241]Am tracer at pH 3; weight of the beads = 0.018 g; equilibration time = 60 min; temperature = 294 K)

Table 3
Isotherm model parameters for sorption of Am (III) by the PC88A beads.

Langmuir parameters			Freundlich parameters			Temkin parameters		
Q (mg/g)	b (ml/mg)	R^2	k_f (mg/g)	n	R^2	A_T (l g^{-1})	B (J mol^{-1})	R^2
2.498	0.512	0.9974	0.552	2.145	0.9115	0.631	1.283	0.9590

sorption of all the molecules in layer decreases linearly with coverage due to sorbent–sorbate interactions [41]. The model is given by the following equation:

$$q_e = \left(2.303 \frac{RT}{b}\right) \log A_T + \left(2.303 \frac{RT}{b}\right) \log C_e \quad (13)$$

It can be simplified to Eq. (15) by taking a constant B for $2.303RT/b$.

$$q_e = B \log A_T + B \log C_e \quad (14)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T the absolute temperature (K), b the Temkin isotherm constant, A_T the Temkin isotherm equilibrium binding constant (l g^{-1}) and B is constant related to the heat of sorption (J mol^{-1}).

A linear plot is obtained when q_e was plotted against $\log C_e$ over the concentration range investigated (Fig. 8(D)). The values of B and A_T, respectively, are computed from the slope and intercept of the plot, and are given in Table 3.

On the basis of the R^2 values given in Table 3, it can be concluded that the monolayer Langmuir sorption isotherm is more suitable to explain the sorption of Am (III) on the PC88A beads.

4. Reusability of the beads

In order to find out practical applicability of the EIMPBs for extraction of Am (III), repeated extraction (at pH 3) and stripping (with 0.1 M oxalic acid) experiments were carried out with the same set of beads. The extraction was carried out for 60 min of equilibration, followed by washing with DI water, and two contacts of the stripping solution, to ensure quantitative recovery of the loaded Am (III). The beads were also washed thoroughly with DI water after stripping, to remove oxalic acid from the beads, before repeating the extraction cycle. The results shown in Fig. 9 indicate that, even after 10 operation cycles of extraction and stripping, there is no significant change in extraction efficiency of the beads.
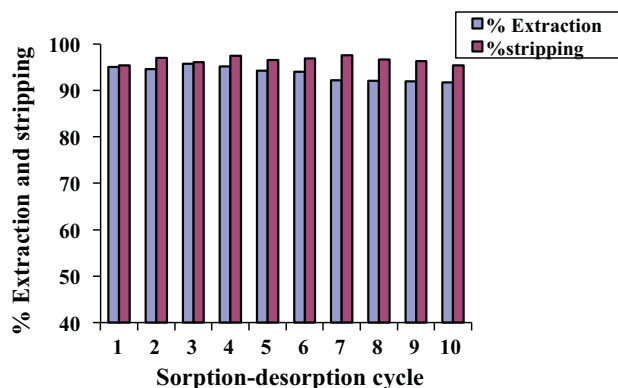
Fig. 9. Reusability cycles of the synthesized EIMPBs with respect to Am (III) extraction/stripping process. Feed pH 3; stripping agent = 0.1 M oxalic acid.

5. Conclusions

The EIMPBs containing PC88A as extractant were prepared by *in situ* phase inversion method. The synthesized polymeric beads show a great potential for effective removal of Am (III) from low level nuclear waste streams. The FTIR spectra of the EIMPBs confirm the presence of PC88A in the bead, while the SEM examination reveals unevenness on the surface, arising from the phase inversion, during the synthesis of the beads. TGA profile shows that loading of the solvent in swollen beads is 17.54%. Absence of structural deformity and leaching out of the extractant, observed during the course of the experiments, confirmed the robustness of beads. The results suggest that the sorption process is more efficient at pH 3 and 60 min of equilibration time is optimally required to remove almost 95% of the Am (III) from the solution. The sorption kinetics data fits well in the pseudo-second-order model, indicating that the sorption is dominated by chemisorption. The sorption of Am (III) on the EIMPBs of PC88A is observed to follow Langmuir isotherm and the monolayer capacity was calculated as 2.498 mg/g. The quantitative stripping of the extracted Am (III) can be achieved by using 0.1 M oxalic acid. The extraction performance of EIMPBs remains unchanged for 10 successive cycles of extraction/stripping experiments, reflecting on its desirable recyclability for remediation of radioactive effluents. Solvent encapsulated polymeric beads, with suitable porosity and hydrophilicity, have been demonstrated as promising material for the extraction of metal ions from aqueous media. Use of solid–liquid extraction using such composite materials make the use of diluent completely redundant hence avoid typical problems of aqueous solubility of solvents and their degradation behaviour in liquid–liquid extraction process.

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