

## Study of Uranium Sorption Using D2EHPA-Impregnated Polymeric Beads

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**ABSTRACT:** The extractant-impregnated polymeric beads (EIPBs), containing Di(2-ethylhexyl) phosphonic acid (D2EHPA) as an extractant and polyethersulfone as base polymer, were prepared by phase-inversion method. These beads were characterized by fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscope (SEM) analysis to gain insight into the composition and morphology of beads. The beads exhibited good acid stability as no significant structural deformation or leaching out of the extractant was observed in 6M HNO<sub>3</sub> solution, up to the studied equilibration time of 15 days. The synthesized EIPBs were evaluated, for their ability to absorb uranium from aqueous solution, at different concentration and pH values. The kinetics measurement showed that about 90 min of equilibration time was enough to remove saturation amount of uranium from the solution. Kinetic modeling analysis of the extraction results was carried out using pseudo-first-order, pseudo-second-order, and intraparticle diffusion equations and the corresponding rate constants were determined. The equilibrium data were fitted into different isotherm models and were found to be represented well by the Freundlich isotherm equation. Reusability of the beads was also established by multiple sorption–desorption experiments. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3355–3364, 2013

**KEYWORDS:** adsorption; kinetics; separation techniques; thermogravimetric analysis (TGA)

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### INTRODUCTION

Uranium is found in the environment, in very small concentrations, mainly in rocks, soil, and water. Uranium is an important element having applications in several fields, such as nuclear fuel in nuclear power reactors, material of high density in the aeronautics industry, make isotopes for peaceful purposes, as radiation shielding, as an additive for catalysts or steels, in glass and ceramic industries, for making explosives, and so on. Uranium is the main source of atomic power, which is used to generate a large quantity of economical electricity to fulfill the increasing energy demands. Uranium metal is also used in X-ray targets, for generation of high energy X-rays. However, uranium and its compounds are highly toxic, from the chemical, biological, and the radiological standpoints.<sup>1,2</sup> Therefore, pre-concentration and separation of uranium from environmental, biological, and radioactive waste samples is extremely important.

Generally, uranium concentration in waste streams is either too low for a classical treatment or too high for its direct discharge into the environment.<sup>3</sup> It has been suggested that sorbents could be used to decontaminate these wastes and to concentrate metals. There are many reports on the selective removal of uranium

from different radioactive waste streams and from seawater.<sup>4–8</sup> Among the different methods for separation of uranium, liquid–liquid extraction (LLE) is widely used for bulk separation in the nuclear industry. Some of the main problems associated with solvent extraction techniques are third phase formation, large organic waste generation, and difficulty in handling. Solid–liquid mode of separation can solve some of these problems and can work in more efficient and environment friendly manner, and also makes it possible to tune the selectivity and capacity, by the development of new materials. Many organic and inorganic adsorbents, containing different functional groups, which show selectivity towards uranyl ions, have been synthesized and used for the separation of uranium. For example, neutral polymer—amberlite polystyrene divinylbenzene (amberlite XAD) series,<sup>9</sup> silica,<sup>10</sup> octadecyl silica membrane discs,<sup>11</sup> activated silica gel,<sup>12</sup> controlled-pore glass,<sup>13</sup> polyurethane foam,<sup>14</sup> and other polymeric resins<sup>15</sup>—have been appropriately functionalized and used for both pre-concentration of uranium (VI) from dilute solutions, prior to determination by a variety of analytical techniques and separation. Liquid extractant-impregnated polymeric materials, in the form of resins, beads, gels, membranes, and so on, are one of the important

ones for selective separation of target metal ions from multicomponent aqueous feed solutions, such as radioactive waste and seawater. The use of supported liquid membranes (SLMs) for removal of radionuclides from low-level nuclear waste streams<sup>16–18</sup> is the most common. However, bleeding out of the extractant from the SLM limits its repetitive usability. Hence, it is always advisable to choose a solid–liquid extraction process, which gives minimum secondary waste, and has a long-term multicycle applicability. A promising development in this direction has led to the design of porous polymeric beads by encapsulating extractants that permits exchange of metal ions without leaching out of the encapsulated extractant under column operation and hence expands their practical applications. These composites have been termed as extractant-impregnated polymeric beads (EIPBs). These beads, with suitable porosity and hydrophilicity have been demonstrated as promising materials for the extraction of metal ions from aqueous medium. Present investigation deals with the preparation of new EIPBs, containing di(2-ethylhexyl) phosphonic acid (D2EHPA) as an organic extractant to provide desired functionality and specificity, coupled with large capacity for uranium uptake. The D2EHPA extractant has been widely used for efficient separation of actinides, transition metals, rare earths, and base metals, employing solvent extraction technique.<sup>24,25</sup>

The aim of this study was to prepare a novel DEHPA containing polymeric sorbent, in the form of spherical beads, for uranium removal from dilute aqueous waste of radioactive laboratory, before final disposal, to prevent environmental pollution because of both toxic and radioactive nature of uranium. So, in this study, DEHPA impregnated beads have been synthesized and tested for separation of uranium from acidic and near-neutral aqueous waste. The effect of various experimental parameters, such as acid concentration, pH of the solution, uranium concentration, and time of equilibration, on the sorption of uranium has been studied. The kinetics of sorption has been investigated, and also the data have been fitted to different known isotherms, to understand the sorption process. These indigenously synthesized beads offer distinct advantage over other polymeric extractants because their metal uptake capacity can be augmented by increasing the amount of extractant per unit weight of the composite material. The extraction feasibility of U(VI) was evaluated using these synthesized EIPBs, with the highest possible efficiency, selectivity and with minimum feed adjustment.

## EXPERIMENTAL

### Materials

D2EHPA extractant, obtained from Daihachi Chemical Industry, Japan, was used for the preparation of the beads. Laboratory reagent (LR)-grade polyethersulfone (PES) and polyvinylalcohol (PVA) was procured from the local market. Aqueous solutions were prepared, using water purified by Millipore-Q water purification system, having conductivity of 0.6  $\mu\text{S cm}^{-1}$  or lower. A standard stock solution of uranium [1000 ppm (w/v)] was prepared, and diluted, as required, for different sorption experiments.

### Preparation of EIPBs

PES is a well-known polymeric material used in the preparation of membranes. The PES-based membranes show outstanding

oxidative, thermal, and hydrolytic stabilities, as well as good mechanical strength. In this article, D2EHPA extractant-encapsulated porous PES beads were prepared using phase-inversion technique.<sup>36</sup> Briefly, PES powder was dissolved in 1-methyl-2-pyrrolidone (NMP) to obtain the PES solution of required viscosity. A known amount of D2EHPA was added to the PES solution and the mixture was added dropwise into a suitable aqueous bath using a syringe with needle of appropriate diameter. Within a few minutes of stirring, soft beads were obtained. The beads were then incubated in water, for 24 h, for complete curing.

### Characterization of the Synthesized EIPBs

**FTIR Analysis.** The fourier transform infrared spectroscopy (FTIR) spectra of the synthesized bead samples were recorded using diamond ATR holder, employing IR Affinity-1 FTIR spectrophotometer, in the range 500–4000  $\text{cm}^{-1}$ .

**Thermal Analysis.** The thermogravimetric analysis (TGA) was carried out using STAR<sup>c</sup> System METTLER TOLEDO instrument. A few milligram of the sample was taken in an alumina sample holder, and the thermogravimetric curves were recorded at heating rate of 15°C  $\text{min}^{-1}$ , from 30°C to 900°C, under dynamic condition and in  $\text{N}_2$  atmospheres (50 mL  $\text{min}^{-1}$ ). Composition and thermal stability of the beads were determined from the thermogravimetric data.

**SEM and Optical Microscopy.** Morphology of the beads was determined by simple microscopy, using QX5 DIGITAL BLUE computer microscope, and scanning electron microscopy (SEM), using TESCAN VEGA MV 2300 T/A microscope. For cross-sectional view, the dried bead was cut with a single-edged razor blade attached to the sample support and then vacuum sputtered with a thin layer of Au prior to the analysis.

### Sorption of $\text{UO}_2^{2+}$ Ions by the Beads

A known weight (0.05 g) of swollen beads was added to 5 mL of uranyl ion solution of known concentration. After suitable equilibration time, the beads were separated from the solution and the raffinate solution was filtered. The concentration of U in the aqueous solution, before and after equilibration, was estimated by radiometry technique, using ZnS (Ag) scintillation counter. The amount of uranium sorbed per unit weight of the synthesized beads, at equilibrium, that is,  $q_e$ , and the percent sorption (%A) were determined, using the following equations:

$$q_e = (v/w) \times (C_o - C_e), \quad (1)$$

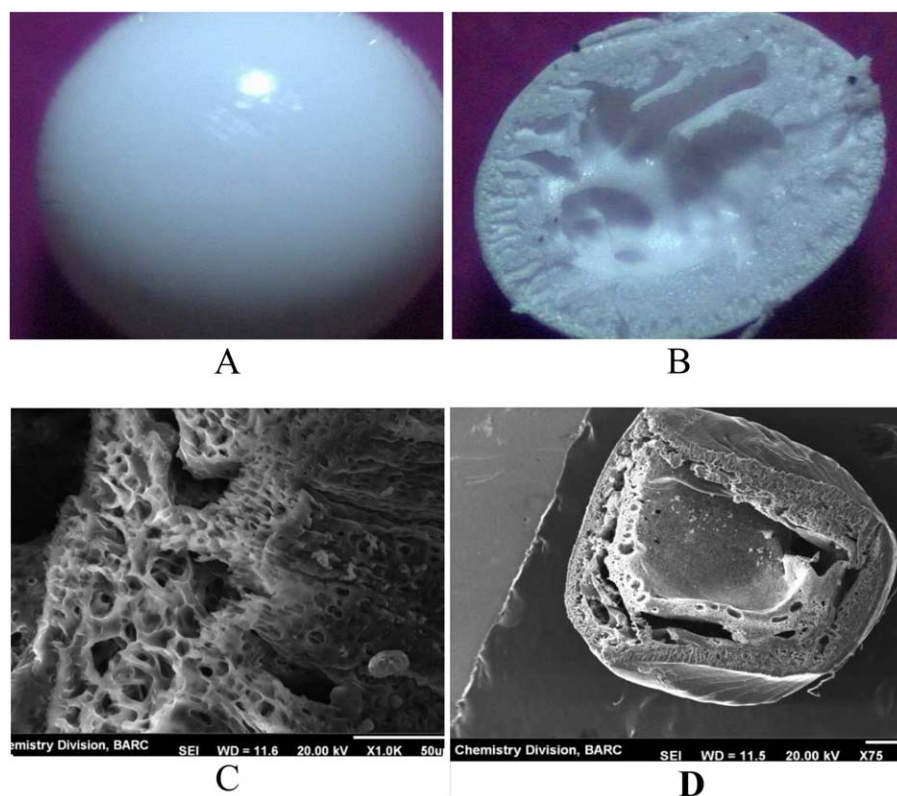
$$\%A = \frac{C_o - C_e}{C_o} \times 100, \quad (2)$$

where  $v$  is the volume of the solution containing uranium, in litres,  $w$  is the weight of the swollen sorbent beads at equilibrium, in grams,  $C_o$  and  $C_e$  are, respectively, the initial and the equilibrium concentrations of uranium, in ppm.

## RESULTS AND DISCUSSION

### Characterization of the Synthesized Beads

Morphology of the beads was determined by optical and SEM. The images of the surface and the cross section of a bead are given in Figure 1. These pictures clearly show that the bead



**Figure 1.** The optical photographs of (a) surface at 60 $\times$  magnification, (b) cross section at 60 $\times$  magnifying, (c) SEM image of outer surface, and (d) cross-sectional of the synthesized EIPBs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

surface is quite rough, and has enough porosity, which enhances the surface area for metal ion sorption.

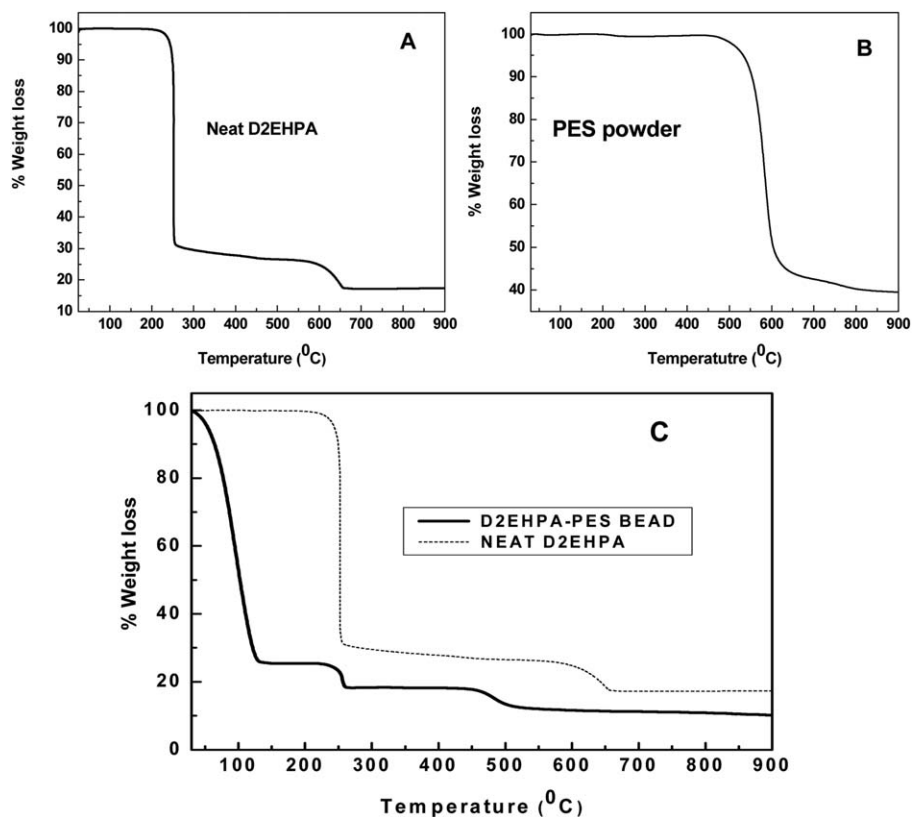
Results of the TGA, as shown in Figure 3, indicated that the beads have high water content. Figure 2(A and B) show the TGA profiles of neat D2EHPA liquid and PES powder, respectively. The TGA thermogram of the D2EHPA liquid, used in the synthesis of the composites beads, shows main weight loss in the temperature range of 200 $^{\circ}$ C to 650 $^{\circ}$ C and a total of  $\sim$ 88% of the starting weight is lost up to the studied temperature of 900 $^{\circ}$ C. While in the case of PES, degradation begins at around 500 $^{\circ}$ C and the weight loss of almost around 60% of the starting weight is observed up to the studied temperature [Figure 3(B)]. A weight loss of  $\sim$ 75%, observed during the heating of the beads up to the temperature of 120 $^{\circ}$ C, is because of evaporation of water present in the beads, as shown in Figure 2(C). Further weight loss of  $\sim$ 7.1%, observed around 200 $^{\circ}$ C–300 $^{\circ}$ C, is attributed to the decomposition of D2EHPA extractant present in the beads. It can be concluded from these results that the swollen beads contain  $\sim$ 75% of water,  $\sim$ 10% D2EHPA, and the remaining ( $\sim$ 15%) base polymer (PES). These swollen beads are used for the uranium-extraction experiments. Assuming that the volume of the water present in the swollen beads corresponds to the volume of the pores and the pore volume per unit weight of the beads was found to be 3 cc/gm. It shows high porosity of the synthesized beads.

The FTIR spectra of the D2EHPA pure liquid and D2EHPA-encapsulated beads are shown in Figure 3(A and B), respec-

tively. The absorption peak at around 1483  $\text{cm}^{-1}$  was attributed to the in-plane symmetrical bending motion of C–H in the aromatic rings. Absorption peaks at 1146 and 1296  $\text{cm}^{-1}$  were attributed to the vibrations of the sulfone group ( $\text{R}_2\text{SO}_2$ ). A strong aromatic ether band at around 1240  $\text{cm}^{-1}$  was also observed. The hydroxyl group stretching, observed at around at 3375  $\text{cm}^{-1}$ , is quite broad because of the presence of hydrogen bonding in the swollen beads. Figure 3(B) confirms the presence of D2EHPA, as evident from the bands at 2957 (C–H stretching of methyl) and 1222  $\text{cm}^{-1}$  (P=O stretching). The IR spectrum of pure D2EHPA liquid, Figure 3(A), shows the characteristic peaks because of the extractant.

#### Effect of pH and HNO<sub>3</sub> Concentration on Sorption of Uranyl Ions

Metal ion sorption onto specific sorbents is pH dependent. In the absence of a complexing agent, the hydrolysis and precipitation of the metal ions are affected by the concentration and form of soluble metal species. The effect of pH on the sorption of uranyl ions by the synthesized beads was studied and the results are shown in Figure 4. The extractant DEHPA, an active component of the synthesized composite beads, can form a strong complex with  $\text{UO}_2^{2+}$  ions. Sorption of uranyl ions is found to increase with pH, from 2 to 4, and remain almost constant up to pH 5, before decreasing, on further increase in pH up to 11. The decrease in the sorption is very sharp, when the pH changes from 5 to 6, while that above pH 6 is very

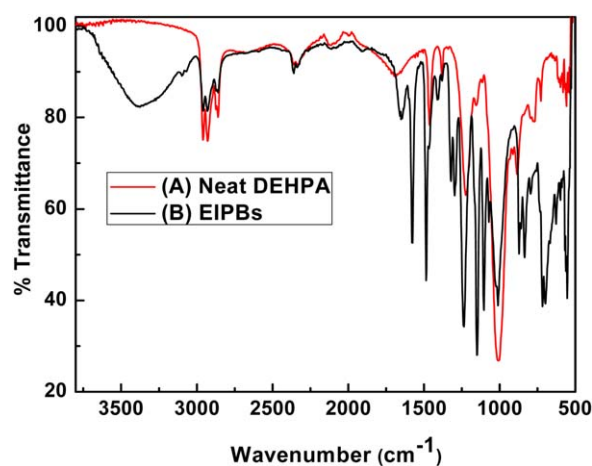


**Figure 2.** TGA curves of the (a) D2EHPA pure liquid, (b) PES powder, and (c) synthesized EIPBs.

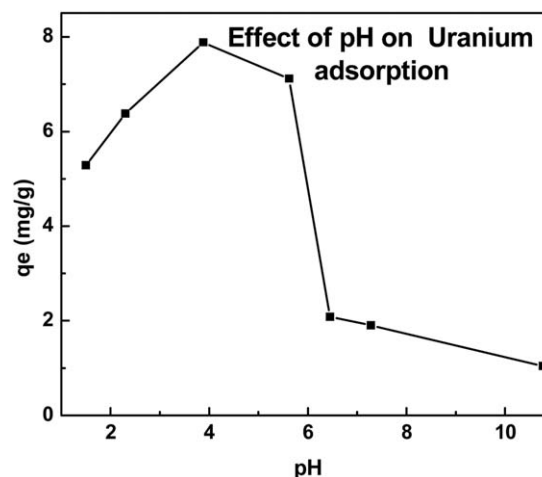
small. The lower-observed sorption of uranyl ions, in the acidic pH range, is because of the competition of  $\text{H}_3\text{O}^+$  ions, present in the solution, with the  $\text{UO}_2^{2+}$  ions, for complexation with the extractant in the sorbent beads. On the other hand, at higher values of pH, the uranyl ion may hydrolyze to form species such as  $\text{UO}_2(\text{OH})^+$  and further to  $\text{UO}_2(\text{OH})_2$ , a colloidal precipitate, with increase in pH of the solution, thereby decreasing the sorption.

Further, extraction of uranium by the EIPBs has been carried out from solutions with different nitric acid concentrations. The

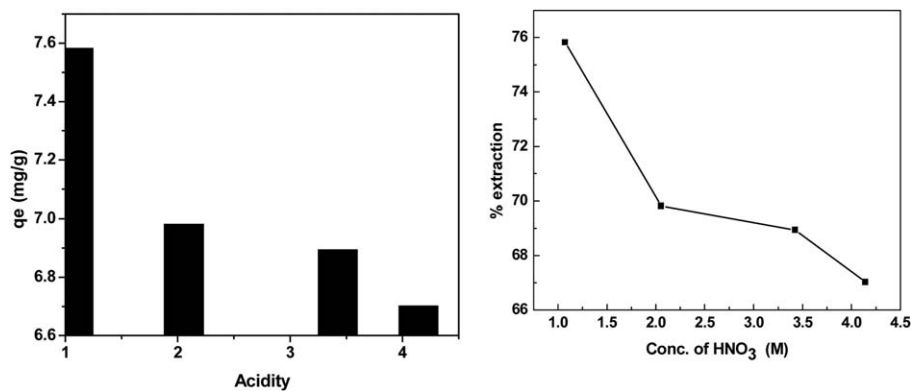
equilibrium capacity ( $q_e$ ) and percentage extraction (%E) values for uranium from the different nitric acid solutions are given in Figure 5. The extraction of uranium, with good efficiency (~67% or more), could easily be accomplished by maintaining  $\text{HNO}_3$  concentration between 1.0 and 4.0M. The higher  $q_e$  and %E values of uranium were obtained at lower strength of nitric acid. The increasing  $\text{NO}_3^-$  ion concentration could be the retarding force for the metal ions to get complexed with the extractant molecule, thereby decreasing the extraction of



**Figure 3.** FTIR spectra of (a) D2EHPA pure liquid, (b) blank PES beads, and (c) synthesized EIPBs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** The effect of pH on the sorption of  $\text{UO}_2^{2+}$  ions on to 0.05g EIPBs,  $\text{U(VI)} = 100$  ppm (with tracer of  $^{233}\text{U}$ ), equilibration time = 3 h, and  $T = 298 \pm 0.5$  K.



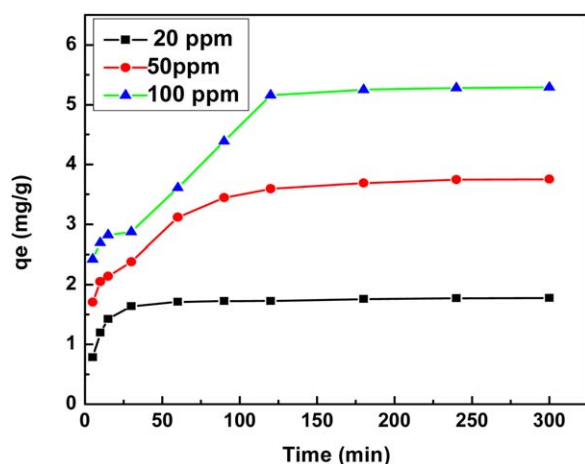
**Figure 5.** The effect of HNO<sub>3</sub> concentration on the adsorption of UO<sub>2</sub><sup>2+</sup> ions on to 0.05g EIPBs, U(VI) = 100 ppm (with tracer of <sup>233</sup>U), equilibration time = 3 h, and T = 298 ± 0.5 K.

uranium into the polymeric beads. The observed *q<sub>e</sub>* values vary from 7.6 to 6.7 at the studied acid strength of 1.0–4.0M HNO<sub>3</sub> indicating that these beads can be used with minimum adjustment of feed HNO<sub>3</sub> concentration in the usual acidic waste.

#### Effect of Sorption Time

Kinetics of sorption is one of the important parameters in the sorption process because it helps in determining the contact time needed for optimum sorption, which depends on the nature of the system used.

The effect of the contact time on the sorption of uranyl ions onto the EIPBs, at three different concentrations, is presented in Figure 6. The sorption mixtures, set at constant temperature (T = 298K) and at pH = 4, were sampled at different times, ranging from 1 to 300 min, to investigate the effect of contact time on the sorption of uranyl ions. It can be seen that the extent of uranyl ions removal increases with contact time up to certain value, and then there is no further increase in sorption. Experimental results indicate that the maximum amount of the sorption is reached in about 120 min for 50 and 100 ppm uranium solutions, and 40 min for 20 ppm solution, at the studied



**Figure 6.** The effect of equilibrium time on the sorption of UO<sub>2</sub><sup>2+</sup> ions on to EIPBs, at different concentration, at T = 298 ± 0.5 K. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

temperature. We can conclude that the equilibrium is achieved in 120 min, which can be considered neither too slow nor too fast for practical utility of the synthesized beads. Therefore, the time period of 120 min has been used in further sorption experiments, as the optimum contact time for the maximum sorption.

#### Sorption Kinetics Models

The uptake of uranyl ions by the EIPBs involves diffusion of the sorbate to the surface of the beads, intrabead 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 sorption process of uranium ions onto the EIPBs, four kinetic models, namely, pseudo-first-order model, pseudo-second-order model, intraparticle diffusion model, and Boyd's plot are used. Table I presents the results obtained on fitting experimental data into these models.

Pseudo-first-order model: The pseudo-first order model of Lagergren is given as<sup>26</sup> follows:

$$\frac{dq}{dt} = k_1(q_e - q_t), \quad (3)$$

where *q<sub>e</sub>* and *q<sub>t</sub>* are the amounts of metal ions sorbed onto EIPBs in (mg/g), at equilibrium and at time *t*, respectively, and *k<sub>1</sub>* is the first-order rate constant (min<sup>-1</sup>).

The integrated form of eq. (3) can be written as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t. \quad (4)$$

The linear pseudo-first-order plot of log (*q<sub>e</sub> - q<sub>t</sub>*) versus *t*, is shown in Figure 7(A). It has correlation coefficient values in the range of 0.50–0.98 (Table I), which indicates that the rate of sorption of uranyl ions onto the EIPBs cannot be explained by the pseudo-first-order kinetic model for the entire studied range of the initial uranyl ion concentration.

Pseudo-second-order model: The pseudo-second-order kinetics model has been used, which is given by the following equation<sup>26</sup>:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2, \quad (5)$$

where, *k<sub>2</sub>*, (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of second-order sorption. The integrated form of eq. (5) is given as follows:

**Table I.** Pseudo-First-Order, Pseudo-Second-Order, and Intraparticle Diffusion Constants and Values of  $R^2$  for the Adsorption of Uranium onto EIPBs

Kinetics model	Parameters	$C_0 = 20$ ppm	$C_0 = 50$ ppm	$C_0 = 100$ ppm
Pseudo-first-order	$K_1$ ( $\text{min}^{-1}$ )	-0.0088	-0.0366	-0.0524
	$q_e$ ( $\text{mg g}^{-1}$ )	2.6	82.97	2949.6
	$R^2$	0.50975	0.95473	0.98544
Pseudo-second-order	$K_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	0.1228	0.0212	0.0067
	$q_e$ ( $\text{mg g}^{-1}$ )	1.80	3.91	6.15
	$R^2$	0.9999	0.9987	0.9871
Intraparticle diffusion	$K_{id}$ ( $\text{min}^{-1/2}$ )	0.008	0.047	0.1898
	$I$ ( $\mu\text{mol g}^{-1}$ )	1.65	3.02	2.64
	$R^2$	0.93685	0.88754	0.96607

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t. \quad (6)$$

It can be rearranged to obtain the equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t. \quad (7)$$

The plot of  $t/q_t$  versus  $t$  gives a straight line, as shown in Figure 7(B). The values of  $R^2$  for this model are 0.9999, 0.9987, and 0.9871 for 20, 50, and 100 ppm, respectively, which are higher than those for the pseudo-first-order kinetic model at all the studied concentrations of uranium. The pseudo-second-order model assumes that chemisorption is the rate-controlling step. Additionally, in comparison to the first-order kinetic model, the values of  $q_e$  obtained from the second-order model are in good accordance with the experimental  $q_{exp}$  values of 1.84, 3.66, and 5.92 mg/g, respectively, at the three studied initial concentrations of 20, 50, and 100 ppm. Therefore, this model can be applied to the sorption process in the entire studied concentration range and we can conclude that the pseudo-second-order model explains the kinetics of the process in a better way.

The kinetic results were further analyzed by intraparticle diffusion model to understand the diffusion mechanism. According to this model, the plot of uptake versus the square root of time should be linear if intraparticle diffusion is involved in the sorption process and if these lines pass through the origin then

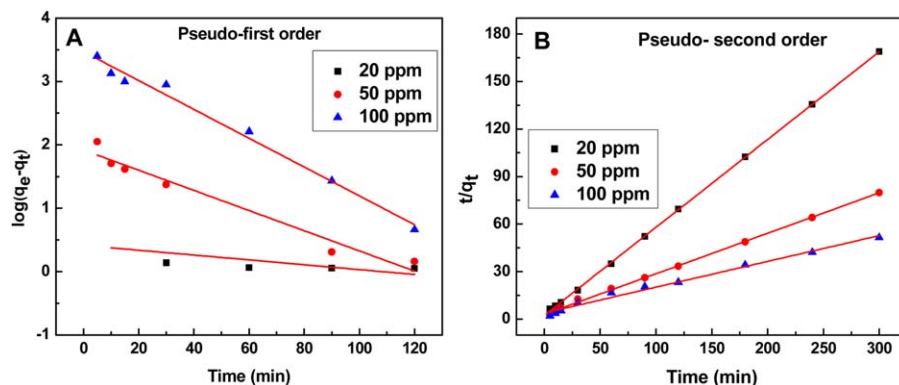
intraparticle diffusion is the rate-controlling step.<sup>27</sup> When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and these further shows that the intraparticle diffusion is not the only rate-limiting step, but other diffusion mechanisms may also control the rate of sorption, all of which may be operating simultaneously.

Intraparticle diffusion model is represented by the following equation:

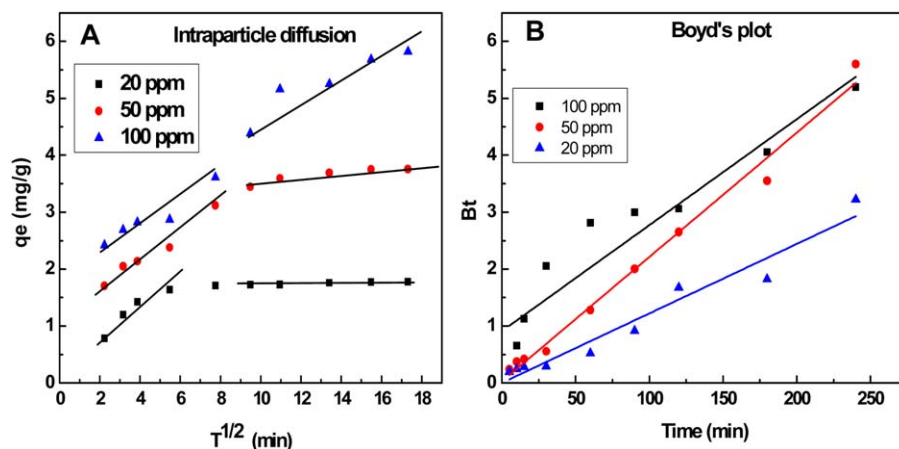
$$q_t = k_{id} t^{1/2} + I, \quad (8)$$

where  $k_{id}$  is the intraparticle diffusion rate constant, the value of intercept  $I$  give the idea about the thickness of boundary layer. These sorption data is fitted in the intraparticle diffusion model. The larger the intercept  $I$  (the thickness of boundary layer), the greater is the boundary layer effect. The deviation of straight line from the origin may be because of difference in initial and final stages of the sorption.

The intraparticle diffusion plot for the sorption of uranium onto EIPBs is shown in Figure 8(A). It is observed that there are two linear portions which elucidate the two sorption stages, namely, external mass transfer at initial period followed by intraparticle diffusion of uranium onto the EIPBs. The slope of the second linear portion gives the intraparticle diffusion rate constant, listed in Table I, shows that  $k$  increases with increasing initial uranium concentration. The equilibrium concentration  $q_e$



**Figure 7.** (a) Pseudo-first-order and (b) pseudo-second-order plots for uranyl ion sorption onto the EIPBs, at three different initial U(VI) concentrations. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** (a) Intraparticle diffusion plots and 9(b) Boyd's plots for the Cs<sup>+</sup> ion sorption onto EIPBs at three different initial concentrations of uranyl ions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

increases accordingly with the increase in initial uranium concentration. In order to further confirm whether the sorption proceeds via film diffusion or intraparticle diffusion mechanism, the kinetic data can be analyzed, using the kinetic expression given by Boyd et al.<sup>28</sup> is as follows:

$$F = 1 - \frac{6}{\pi^2} \exp(-Bt), \quad (9)$$

where  $F$  is the fraction of solute sorbed at different time  $t$  and  $Bt$  is a mathematical function of  $F$ .

$$F = \frac{q_t}{q_e}, \quad (10)$$

where,  $q_t$  and  $q_e$  represents the amount sorbed (mg/g) at any time  $t$  and at infinite time (in the present study 300 min.), respectively. Solutions to eq. (9), depending on the value of  $F$ , are given as eqs. (11) and (12).

$$Bt = 2\pi - \frac{\pi^2 F}{3} - 2\pi \left(1 - \frac{\pi F}{3}\right)^{1/2} \quad (11)$$

$$Bt = -0.4977 - \ln(1 - F) \quad (12)$$

Thus, the value of  $Bt$  can be calculated for each value of  $F$ , using eq. (11) for  $F$  values up to 0.85 and, eq. (12) for higher  $F$  values.

The linearity of  $Bt$  versus  $t$  plot provides useful information to distinguish between the film diffusion and the intraparticle diffusion mechanism of sorption. A straight line passing through the origin is indicative of the sorption processes only governed by intraparticle diffusion mechanisms; otherwise, it is governed by film diffusion. The Boyd's plot of  $Bt$  against time ( $t$ ) is shown in Figure 8(B). The fitted lines, for all the concentrations studied, do not pass through the origin, indicating that the sorption process is also governed by the external mass transport, and intraparticle diffusion may not be the only rate-controlling step in the removal of the sorbate.

### Sorption Isotherms

The analysis and study of equilibrium data is very important in view to develop a model equation, which can accurately repre-

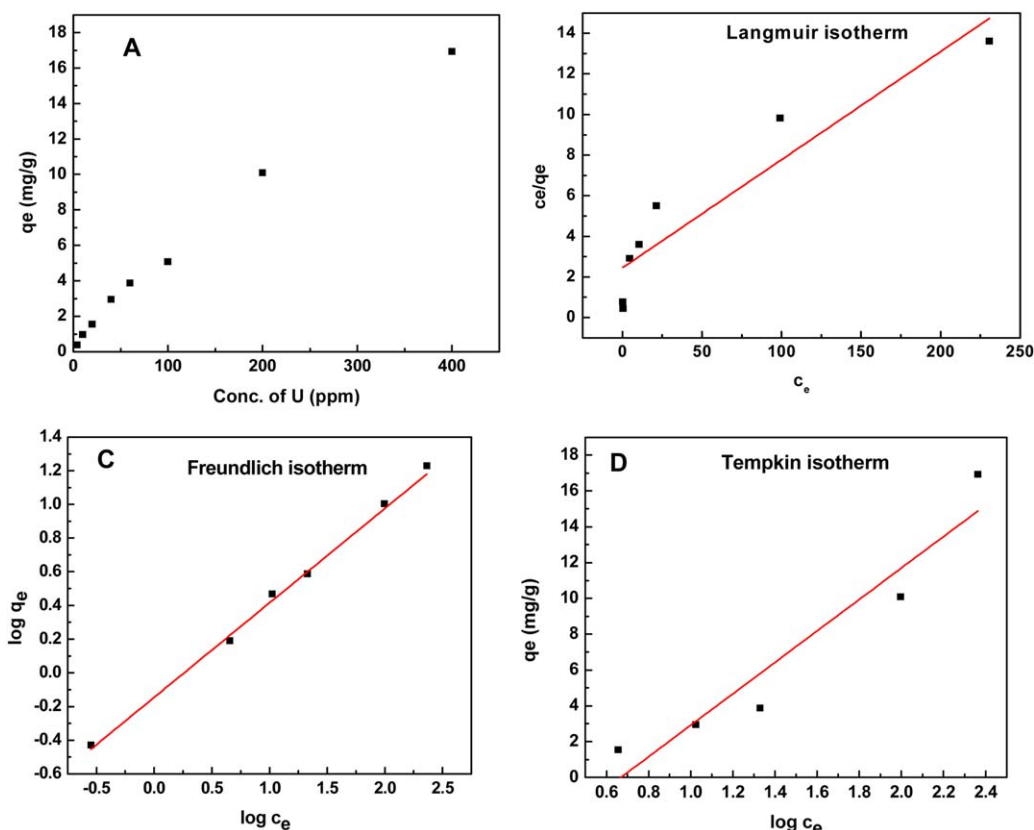
sent the results and could be used for the design purposes. Results of the sorption of urinal ions onto the EIPBs have been subjected to different sorption isotherms, namely, the Freundlich, Langmuir, and Tempkin models. These models suggest different sorption mechanisms, with different interactions between the sorbate and the sorbent. The Freundlich isotherm is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of sorption over the surface. Whereas in the Langmuir theory, basic assumption is that the sorption takes place at specific homogeneous sites within the sorbent. Temkin isotherm contains a factor that explicitly takes into account the sorptive-sorbent interactions. This isotherm assumes that (i) the heat of sorption of all the molecules in the layer decreases linearly with coverage because of sorbent-sorbate interactions, and that (ii) the sorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

The results of Figure 9(A) clearly indicate that, with an increase in the initial uranyl ions concentration, the amount of sorbed uranyl ions increases significantly. At lower initial metal ions concentration, the sorption increases linearly with the initial metal ions concentration, suggesting that the sorption sites on the EIPBs are sufficient, and in this case, the amount of uranyl ions sorbed is dependent on the number of the metal ions transported from the bulk solution to the surfaces of the beads. At higher initial metal ions concentration, however, the sorption no longer increases proportionally with the initial metal ions concentration, indicating that the number of sorption sites on the surfaces of the EIPBs actually limits the amount of sorbed uranyl ions.

**The Langmuir Model.** The widely used Langmuir isotherm, in the form of eq. (13) has been successfully applied in many real sorption processes<sup>29</sup>

$$q_e = q_{\max} \left( \frac{bc_e}{1 + bc_e} \right) \quad (13)$$

Here,  $b$  (L/mg) is the Langmuir equilibrium constant, which is related to the affinity of the binding sites, and  $q_{\max}$  (mg/g) is the maximum sorption capacity (theoretical monolayer saturation capacity). The main characteristics of the Langmuir



**Figure 9.** (a) Effect of initial concentration on the uptake of metal ion, (b) Langmuir isotherm plot, (c) Freundlich isotherm plot, and (d) Temkin isotherm plot for sorption of U(VI) on to the synthesized EIPBs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

equation, the constants  $b$  and  $q_{\max}$ , can be determined from the linear form of the Langmuir equation, as follows:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} b} + \frac{c_e}{q_{\max}} \quad (14)$$

A linear plot of  $(c_e/q_e)$  versus  $c_e$  as shown in Figure 9(B) indicates that the sorption behavior follows the Langmuir sorption isotherm. The values of  $q_{\max}$  and  $b$  were found to be 18.87 mg/g and 0.022 L/mg, from the slope and the intercept, respectively.

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

$$R_L = \frac{1}{1 + bc_0} \quad (15)$$

The value of  $R_L$  for the entire studied concentration range lies between 0 and 1 indicating favorable sorption, as reported by McKay et al.<sup>30</sup>

**The Freundlich Isotherm.** The Freundlich model is often used for sorption on a heterogeneous surface. It is given by the following equation<sup>31</sup>:

$$q_e = k_f c_e^{1/n}, \quad (16)$$

where,  $k_f$  and  $n$  are empirical constants, characteristics of the system indicating the sorption capacity and the sorption inten-

sity, respectively. The above equation can be represented in the following linear form, to confirm the applicability of the model to the present data.

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad (17)$$

Freundlich isotherm plot is shown in Figure 9(C). The plot is linear, with the correlation coefficient ( $R^2$ ) of 0.9892. The values of the Freundlich constants,  $k_f$  and  $n$ , are given in Table II.

**The Temkin Isotherm.** The Temkin isotherm<sup>32</sup> has also been used in many sorption processes. A linear form of the Temkin isotherm can be expressed as follows:

$$q_e = \left(2.303 \frac{Rt}{b}\right) \log A + \left(2.303 \frac{Rt}{b}\right) \log c_e \quad (18)$$

It can be simplified to eq. (19) by substituting  $B$  for  $2.303RT/b$ .

$$q_e = B \log A + B \log c_e \quad (19)$$

Therefore, a plot of  $q_e$  versus  $\log c_e$  gives a straight line that enables one to determine the constants  $A$  and  $B$ . Figure 9(D) shows the plot of this isotherm. From the slope, the value of  $B$  was determined to be 8.78, and the value of  $A$  was calculated to be 0.215 from the intercept. The values of the Temkin constants  $A$  and  $B$  along with the correlation coefficient are given in Table II.

Comparing the  $R^2$  values, given in Table II, for different isotherms, it can be concluded that the Freundlich isotherm is a



**Table II.** Isotherm Constants and Corresponding  $R^2$  Values for the Sorption of Ions onto EIPBs

Metal ion	Langmuir parameters			Freundlich parameters			Temkin parameters		
	$B$ ( $L\ mg^{-1}$ )	$q_{max}$ ( $mg\ g^{-1}$ )	$R^2$	$k_f$ ( $mg\ g^{-1}$ )	$n$	$R^2$	$B$	$A$ ( $L\ g^{-1}$ )	$R^2$
Uranyl ion	0.022	18.87	0.8589	0.72	1.78	0.9892	8.78	0.215	0.9365

better fit for the given sorption process. Langmuir isotherm is not fitting perfectly under the testing conditions and it is clear from the plot that the Temkin isotherm also cannot be used to describe the sorption isotherm properly.

#### Determination of Experimental Capacity, Chemical Stability, Leaching Study, and Reusability of EIPBs

The experimental loading capacity of the EIPBs for U(VI) was determined at pH 4. A known quantity of swollen beads was equilibrated with uranyl solution of 400 ppm concentration and known volume, and after 120 min of equilibration, an aliquot from the aqueous phase was removed and analyzed, to determine U, loaded into the EIPBs. Under optimized conditions, experimental loading capacity for U(VI) was found to be  $\sim 17$  mg/g of swollen beads. Because water content in these beads is around 75%, as per the TGA, hence, their capacity may be accounted as  $\sim 68$  mg/g of the dry beads. The chemical stability of the EIPBs in the presence of acids is very important for the recovery of uranyl ions, and their reusability. The beads were immersed in different concentrations of hydrochloric acid, 1–4M, for various periods of time (up to 8 h), to test their acid stability. No significant structural changes, or weight loss, of the beads was observed. These results indicate that beads are having good chemical stability in acidic medium, and can be considered for the recovery of uranium in multiple cycles.

In order to find out practical applicability of the EIPBs for extraction of U(VI), repeated extraction (at pH 4) and stripping (with 0.1M oxalic acid) experiments were carried out with the same set of beads. The extraction was carried out for 120 min of equilibration, followed by washing with DI water, and three contacts with the stripping solution, to ensure quantitative recovery of the loaded U(VI). The beads were also washed thoroughly with DI water after stripping, to remove oxalic acid from the beads, before repeating the extraction cycle. The synthesized EIPBs beads were equilibrated with uranyl ions for 120 min, leached with 0.1M oxalic acid, and washed with water, and again immersed in uranyl ion solution. This process was repeated up to four cycles. It was found that the beads showed no significant decrease in capacity up to the studied cycles. Hence, these beads can be efficiently used in multiple sorption–desorption cycles, for separation of uranium. The observed small decrease in percent uranyl ions sorption with the number of cycles is probably because of incomplete leaching of the uranyl ions with 0.1M acid. These results confirm stability of the beads under the studied acidic conditions, without any significant leaching out of the D2EHPA extractant from the beads. These beads have most appropriate porosity and hydrophilicity, which facilitate fast exchange of U(VI), without loss of the encapsulated D2EHPA extractant. So, the developed beads can

be used to overcome the usual problem of solvent bleeding from the SLMs.

#### CONCLUSION

In this study, the use of D2EHPA-impregnated beads as a sorbent has been successfully examined in the removal of U(VI) ions from aqueous solution under batch experimental conditions. The pH, initial metal ion concentration, and contact time are found to have a significant effect on the sorption efficiency of U(VI). The sorption capacity is maximum at pH 4.0 and decreases significantly on either side of pH 4.0. The sorption process could be found satisfactorily correlated by the second-order kinetic and chemisorption models. This suggests that the rate-limiting step could be a chemical sorption as well as the mass transport. Sorption equilibrium data have been fitted very well to the Freundlich isotherm model. The kinetics of extraction is very fast because quantitative recovery of U (VI) can be achieved in 120 min. The sorption kinetic data have been respectively analyzed by the Lagergren first-order model, the pseudo-second-order model, and the intraparticle diffusion model. The results indicate that the sorption of Uranium onto EIPBs could be best described by the pseudo-second-order model. The results of the study show that these synthesized beads have good capacity  $\sim 17$  mg/g of swollen beads ( $\approx 70$  mg/g of dry beads), for uranium. The quantitative stripping of the extracted U(VI) can be achieved by using 0.1 M oxalic acid. The extraction performance of EIPBs remains unchanged for four successive cycles of extraction/stripping experiments, reflecting on its desirable recyclability for remediation of radioactive effluents.

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