

Study of Uranium Adsorption Using Amidoximated Polyacrylonitrile-Encapsulated Macroporous Beads

Krishankant Singh, Chetan Shah, Charu Dwivedi, Manmohan Kumar, Parma N. Bajaj

Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Correspondence to: M. Kumar (E-mail: manmoku@barc.gov.in)

ABSTRACT: Polyacrylonitrile beads, containing the amidoximated polyacrylonitrile, were prepared for adsorption of uranium. The synthesized amidoximated polyacrylonitrile chelating beads were evaluated, for their ability to adsorb uranium from aqueous solution, at different temperatures and pH values. The kinetic measurement showed that about 120 min of equilibration time was enough, to remove saturation amount of uranium from the solution. The pseudo first-order and pseudo second-order equations were used to analyze the kinetic data, and the rate constants were determined. The equilibrium adsorption data were examined by the Langmuir, Freundlich, and Temkin isotherms. The data showed a better fit to the Langmuir isotherm. The loaded uranium could also be leached out from the beads, by treating with dilute acids. The uranium uptake capacity of the polymeric beads was found to be 3.5 mg/g of the swollen beads. Reusability of the beads was also established by multiple adsorption–desorption experiments. The pore volume and the surface area of the dried beads, measured by BET method, were found to be 1.93 cc/g and 320 m²/g, respectively. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polyacrylonitrile; uranium; adsorption; beads; amidoximation; Br-PADAP

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INTRODUCTION

Uranium is found in the environment, in very small concentrations, mainly in rocks, soil, and water. Uranium is of great importance as a nuclear fuel. Natural uranium, slightly enriched in U²³⁵ (2–3%), is used to fuel nuclear power reactors, to generate electrical power, make isotopes for peaceful purposes, make explosives, etc. Depleted uranium is used as shielding to protect tanks and also used in bullets and missiles. Uranium metal is also used in X-ray targets for generation of high energy X-rays. At the same time, uranium and its compounds are highly toxic, from the chemical, biological, and the radiological standpoints. So, preconcentration and separation of uranium from environmental, biological, and radioactive waste samples is extremely important.

There are many reports on the selective removal of uranium from radioactive waste, water stream, and seawater.^{1–5} Among the different methods for separation of uranium, liquid–liquid extraction is widely used for bulk separation in 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 separation can solve some of these problems and can work in more effi-

cient 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 toward uranyl ions, have been synthesized and used for the separation of uranium. For example, neutral polymer–amberlite polystyrene divinylbenzene (amberlite XAD) series,^{6–8} silica,⁹ octadecyl silica membrane discs,¹⁰ activated silica gel,¹¹ controlled-pore glass,¹² polyurethane foam,¹³ and cationic or anionic exchange resins¹⁴ have been reported to be used for both preconcentration of uranium (VI) from dilute solutions, before determination by a variety of analytical techniques and separation. Among these, functionalized polymeric materials in the form of resins, beads, gels, membranes, etc. are the most important ones, for selective separation of target metal ions from multicomponent aqueous feed solutions, such as radioactive waste and seawater. Preparation of adsorbents by incorporation of modified functional group into the polyacrylonitrile binding matrix and its potential applications in the treatment of radioactive liquid waste streams have been described in a number of articles by Sebesta et. al.¹⁵ Most of the reported methods are for nuclear industry, involving extraction from acidic medium (at relatively higher concentrations), and from sea water at near neutral pH

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condition (from very dilute solutions). Amidoximated polyacrylonitrile (APAN), grafted over nonwoven polypropylene fabric, is one of the important adsorbents, for separation of uranium from very dilute aqueous solutions, at near neutral pH condition. It has been tested upto pilot scale, for separation of uranium from sea water.^{16,17}

Our aim is to separate uranium from aqueous waste of radioactive laboratory, containing low concentration of uranium, before final disposal to environment, to prevent environmental pollution due to both toxic and radioactive nature of uranium. So, in this study, APAN beads have been synthesized for separation of uranium from near neutral aqueous waste of radioactive laboratory. The amidoxime group was introduced by the reaction of a polymer, containing nitrile groups, such as polyacrylonitrile, with hydroxylamine hydrochloride. The effect of various experimental parameters, such as temperature, pH of the solution, uranium concentration and time of equilibration, on the adsorption of uranium has been studied. The kinetics of adsorption has been investigated, and also, the adsorption data have been fitted to known adsorption isotherms to understand the adsorption process.

EXPERIMENTAL

Materials

AR grade acrylonitrile (AN) monomer from S D Fine-Chemicals, *N,N* dimethyl formamide (DMF) and hydroxylamine hydrochloride (NH₂—OH·HCl) from Merck were used as received. Analytical reagent grade uranyl nitrate hexahydrate and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (BR-PADAP) dye were procured from BDH. Triethylamine buffer, NaF, 1,2-cyclohexylene dinitrilotetraacetic acid (CyDTA), sulphosalicylic acid, etc. were procured from local suppliers. Polyacrylonitrile (PAN) was synthesized by gamma irradiation of saturated aqueous solution of acrylonitrile, at a total dose of 2.5 MRad, followed by washing with water and drying at room temperature, to get off-white colored fine powder. Aqueous solutions were prepared, using water purified by Millipore-Q water purification system, having conductivity of 0.6 μS/cm, or lower. A standard solution of uranium [100 ppm (w/v)] was used as a stock solution, and diluted, wherever required, for all the sets of experiments.

Amidoximation of Polyacrylonitrile and Preparation of the Beads

APAN was synthesized by the reaction of PAN with amidoximating reagent solution. Hydroxylamine hydrochloride (4 g) was dissolved in 50% methanol in water (v/v) solvent system, pH adjusted to 7 with KOH, and the volume was made upto 100 mL.¹⁸ The mixture of 3 g PAN powder and the prepared 100 mL amidoximating reagent was heated at 50°C, with constant stirring for 16 h. A water-cooled condenser was used to prevent evaporation of the solvent. On amidoximation, the color of the PAN changed from white to light yellow. Heating of the PAN at higher temperatures and for longer time should be avoided, as this produced yellow modified material, which is very brittle, probably due to thermal degradation. The modified PAN obtained after heating the reaction mixture for 16 h at

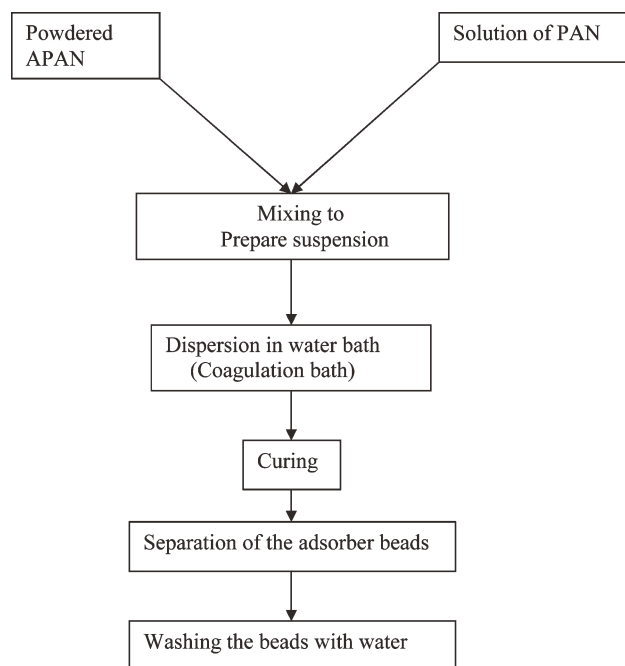
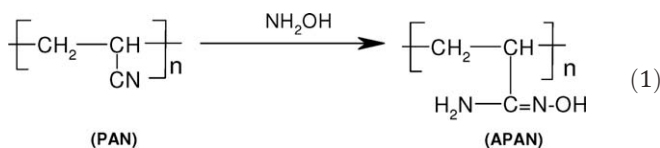


Figure 1. Flow chart for the preparation of composite APAN beads.

50°C retained most of the physical strength of the starting PAN material, without any significant thermal degradation.

The synthesized APAN was separated by centrifuging, washed with water and acetone, and then dried. The reaction of hydroxylamine with the nitrile group can be shown as follows:



The synthesized APAN powder was mixed with a solution of PAN in DMF, and stirred, to form almost homogeneous suspension. This suspension was put into a suitable aqueous bath, containing surfactant, in the form of drops of appropriate size, using a syringe with a needle of suitable diameter. Soft beads of 2 mm diameter were formed almost instantaneously, by phase inversion, which were allowed to cure completely by stirring slowly for about 24 h. These beads were washed with water and used for adsorption of uranium by batch equilibration method.¹⁵ A flow chart of the preparation method is shown in Figure 1.

Characterization of the Synthesized PAN and APAN Beads

The presence of functional groups in the synthesized PAN and the APAN, with and without uranyl ions loading, was confirmed by recording IR spectra in KBr pellets, using Affinity-1 FT-IR spectrophotometer. Morphology of the beads was determined by scanning electron microscope, using Cam scan 3200 LV microscope. The specific surface area and the pore volume measurements of the synthesized APAN beads were carried out by BET method, using "SORPTOMATIC 1990" analyzer, from CE Instruments, Italy. Adsorption-desorption isotherms were

studied for the measurement of specific surface area by multi point Brunauer, Emmett, and Teller (BET) method.¹⁹ The water content and thermal stability of the beads were determined, using METTLER TOLEDO thermo gravimetric analysis instrument, model TGA/DSC 1 STAR^c system, by heating the beads at a constant temperature of 70°C, under nitrogen atmosphere. UV-visible spectra of the beads were recorded on JASCO V 650 spectrophotometer using a quartz cell of path length 2 mm.

Estimation of Uranium by Complexation Method

Br-PADAP is one of the most sensitive reagents that have been used for the spectrophotometric determination of uranium (VI) by several workers.^{20,21} The complexing reagent used for the determination of uranyl ion concentration was prepared by mixing a known concentration of Br-PADAP dye, tri-ethanolamine buffer, and complexing solution. These solutions were prepared as given below. A total of 0.05% Br-PADAP solution was prepared by dissolving 0.025 g of Br-PADAP in 50 mL of double-distilled ethanol. Buffer solution of pH 7.8 was prepared by dissolving 14 g of TEA in 80 mL of distilled water, neutralized with concentrated perchloric acid to adjust pH at 7.8 and allowed to stand overnight. pH of the solution was then readjusted to 7.8, with perchloric acid, and the volume was made up to 100 mL. The complexing solution was prepared by dissolving 5 g of 1,2-CyDTA, 1 g of NaF, and 13 g of sulphosalicylic acid in 40 mL of distilled water, adjusting the pH to 7.8, with NaOH and finally diluting it to 100 mL.²²

A suitable aliquot of U (VI) solution was added to 0.1 mL of the complexing solution in a sample tube of volume 1.5 mL. To the above, the required quantities of the buffer solution (0.1 mL) and the Br-PADAP dye solution (0.1 mL) were added, and the volume was made up to 1 mL, with either ethanol or ethanol/water mixture. This colored solution was then allowed to stand for about 1 h, and the absorbance was measured at 578 nm against a blank reagent solution. Two different calibration graphs were plotted in the concentration ranges of 0–2.5 ppm and 0–25 ppm (plots not shown). The concentration of uranium in the raffinate solution was determined corresponding to the observed absorbance at 578 nm due to the dye-uranyl ion complex, using these calibration graphs. Depending on the absorbance value of the sample, the appropriate calibration graph was used.

Adsorption of UO_2^{2+} Ions by the Beads

A known weight (0.013–0.014 g) of the swollen APAN beads, having PAN to APAN ratio of 1 : 1 (w/w), was added to 0.5 mL of uranyl ion solution of known concentration. After suitable equilibration time, the beads were separated from the solution, and the raffinate solution was treated with complexing reagent. Then, the UV-visible absorption spectrum was recorded, and absorbance at 578 nm was measured. The amount of uranium in the raffinate solution was determined, using the calibration graph obtained with standard solutions of UO_2^{2+} . The amount of uranium adsorbed per unit weight of the APAN beads at equilibrium, q_e , and percentage adsorption (%A) of uranium by the beads were determined using the following equations:

$$q_e = (v/m) \times (C_o - C_e) \quad (2)$$

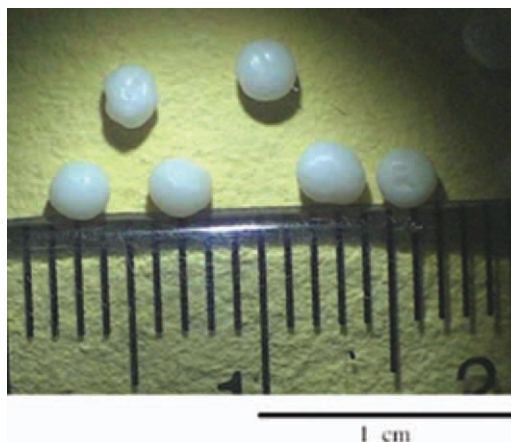


Figure 2. Typical picture of the swollen APAN composite beads. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\%A = \frac{C_o - C_e}{C_o} \times 100 \quad (3)$$

where v is volume of the uranium containing solution in liters, m is the weight of the swollen amidoximated PAN 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

The reaction between APAN and uranyl ions, leading to the formation of APAN–uranyl ion complex, can be represented as

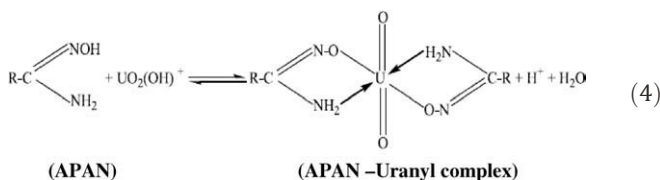


Figure 2 shows the actual picture of the swollen APAN composite beads (average size ~ 2 mm) prepared for the adsorption of uranium from aqueous solution.

Characterization of the Synthesized Beads

Morphology of the beads was examined by scanning electron microscopy (SEM). SEM images of the surface and the cross-section of a dry bead are shown in Figure 3(a,b), respectively. Figure 3(a) clearly shows that the bead surface is rough and has macro pores of diameter ~ 50 nm. All the pores are not visible in Figure 3(a) due to the rough morphology of the surface. The cross-sectional picture [Figure 3(b)] shows the presence of much larger pores in the interior of the beads. The pores seem to be interconnected, and the pore size increases as one moves away from the surface. The pores on the surface of a swollen bead are expected to be much bigger than that of a dried bead. So, the surface of a swollen bead is expected to be macro porous. The specific surface area and the pore volume of the dry beads were determined by BET N_2 adsorption method. The

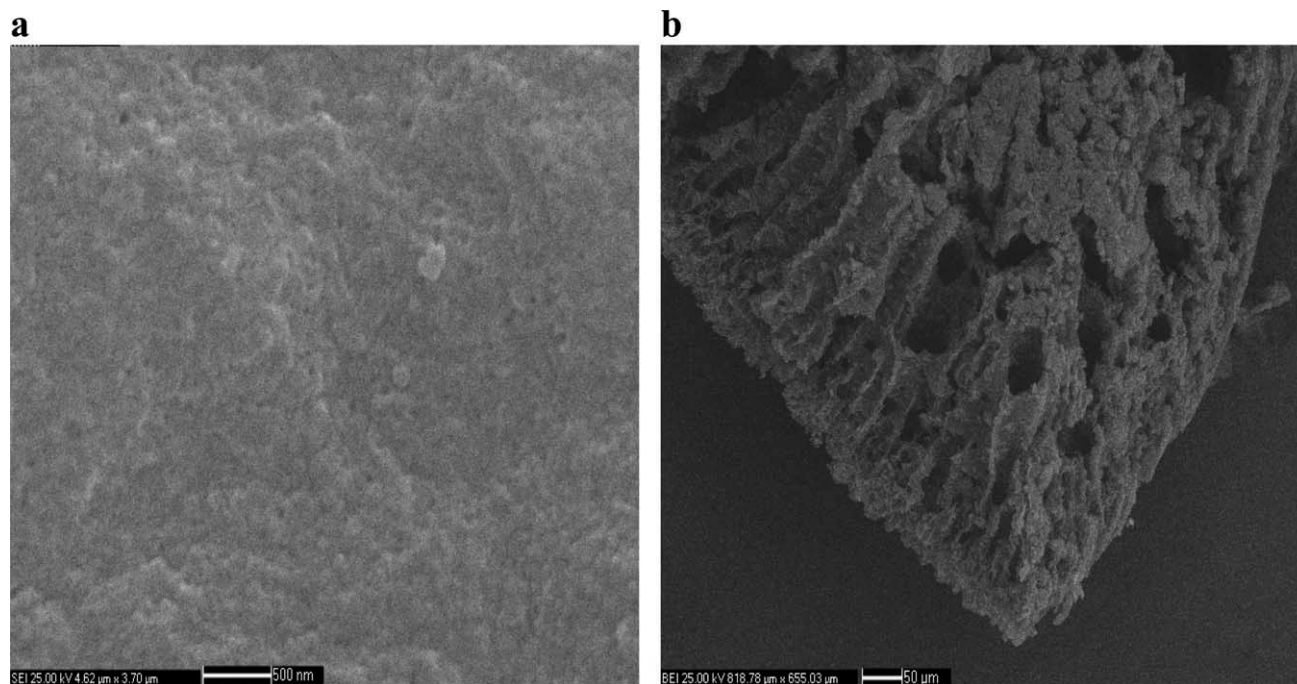


Figure 3. SEM images of (a) the surface and (b) the cross-sectional area of a dry APAN composite bead.

nitrogen adsorption–desorption isotherms were measured at 77 K, using relative partial pressure (i.e., P/P_0) of N_2 of 0.98. The bead samples were degassed at 120°C for 5 h. The surface area was found to be 320 m^2/g , and the pore volume was found to be 1.93 cc/g. As the size of the beads reduces, on drying, the actual pore volume of the swollen beads will be much higher than the value determined here.

Thermo gravimetric analysis of the synthesized beads showed that the beads contain a large amount of water. A weight loss of $80 \pm 4\%$ was observed during the isothermal heating at 70°C, for 30 min, due to evaporation of the water present in the beads. This experiment was done in triplicate, as shown in the Figure 4. Assuming that the volume of the water present in the swollen beads corresponds to the volume of the pores in the

dry beads, the pore volume per unit weight of the dry beads was determined. It is about 4 cc/g based on 80% water content of the swollen beads, as determined by TGA. While in N_2 adsorption method, beads have to be dried, which will result in change in the pore size and pore volume. So, as expected, the pore volume of 1.93 cc/g determined by N_2 adsorption method is lower than the value of 4 cc/g obtained from TGA measurement due to decrease in the size of the beads during the drying process in the former method.

The IR spectra of PAN, amidoximated PAN, and amidoximated PAN beads, with and without UO_2^{2+} ions adsorption, are shown in Figure 5. Amidoximation of the PAN shows that the band associated with the nitrile group at 2244/cm disappears and is replaced by the bands of amidoxime in the region of 3000–

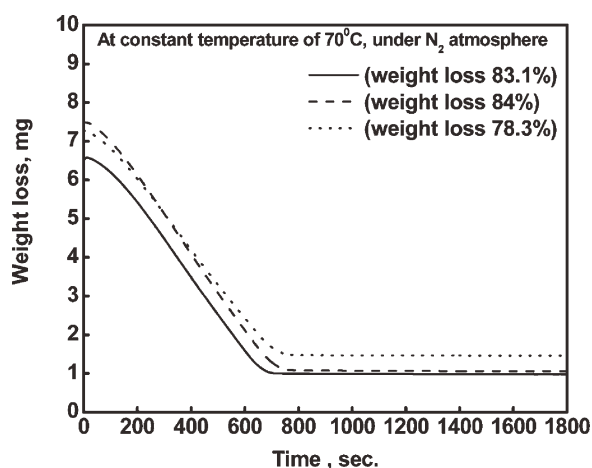


Figure 4. TG curves of the synthesized beads.

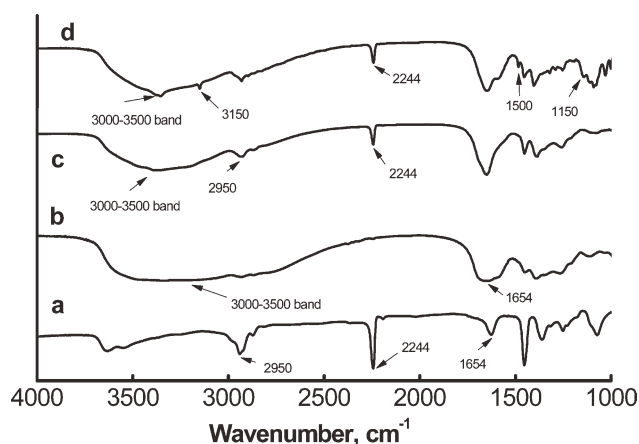


Figure 5. IR spectra of (a) PAN, (b) APAN, (c) APAN beads, and (d) APAN beads loaded with UO_2^{2+} ions.

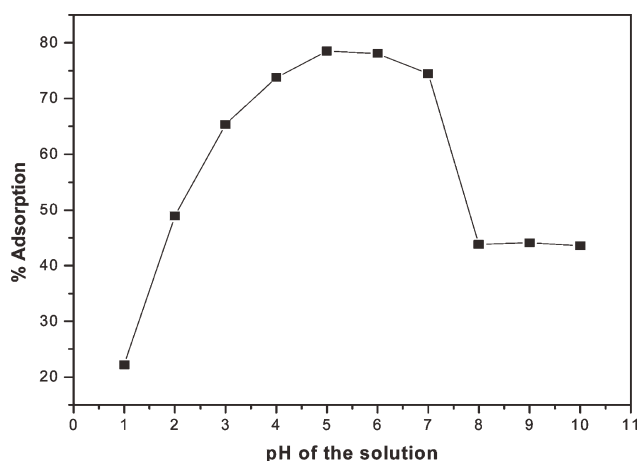


Figure 6. The effect of pH on the adsorption of UO_2^{2+} ions, by equilibrating 0.013 g APAN composite beads with 0.2 mL of 10 ppm aqueous UO_2^{2+} ion solution for 2 h, at room temperature.

3500/cm (broad N—H and O—H stretching vibration), and a band at 1654/cm (C=N stretch vibration), Figure 5(b). The vibrational frequencies observed at 2950 and 2245/cm in the IR spectra of all the samples are due to aliphatic C—H stretching and CN stretching, respectively, of the nitrile functional group. IR spectrum of the synthesized APAN beads shows all the peaks present in PAN and amidoximated PAN. The new peaks at 3150, 1500, and 1150/cm observed in uranyl ions-equilibrated beads are due to adsorption of uranyl ions, which are absent in the IR spectra of all the other samples, namely PAN, amidoximated PAN, and amidoximated PAN beads. This clearly indicates adsorption of uranyl ions onto the amidoximated PAN composite beads.

Effect of pH and Temperature on Adsorption of Uranyl Ions

The effect of pH on adsorption of uranyl ions by the APAN beads was studied, and the results are shown in Figure 6. Adsorption of uranyl ions is found to increase with pH, from 2 to 5, and remain almost constant up to pH 7, before decreasing, on further increase in pH up to 11. The decrease in the adsorption is very sharp, when the pH changes from 7 to 8, while that above pH 8 is very small. The observed lower adsorption of uranyl ions in the acidic pH range is because the H_3O^+ ions present in the solution compete with the UO_2^{2+} ions, for complexation with amidoxime group of the polymeric sorbent. UO_2^{2+} ions gradually hydrolyze to $\text{UO}_2(\text{OH})^+$ and further to $\text{UO}_2(\text{OH})_2$, a colloidal precipitate, with increase in pH of the solution. As the hydrolyzed species, $\text{UO}_2(\text{OH})^+$, can form a strong complex with $\text{R}-\text{C}(\text{NOH})\text{NH}_2$, the adsorption of U (VI) onto APAN adsorbent increases with increase in pH of the solution, especially in the pH range 4.0–6.0. On further increase of pH above 7, the formation of the $\text{UO}_2(\text{OH})_2$ precipitate causes a significant decrease in the adsorption of U (VI), especially at pH above 8.5.

Further, the temperature dependence study was also carried out, by equilibrating the beads with uranyl ion solution at four different temperatures. The percentage adsorption of uranium by

the synthesized beads, after equilibrating at different studied temperatures, is shown in Figure 7. It is found that at 20°C the beads take maximum amount of uranyl ions, in comparison to that at the other studied temperatures, under similar conditions. Among the studied temperatures, the uranyl ion adsorption at 40°C is the lowest. The percentage adsorptions at both 10 and 30°C are very similar, but lower than that at 20°C. Hence, 20°C is the optimum temperature for adsorption of uranyl ions by these beads. The observed change in % adsorption with temperature is the net result of the opposite effects of temperature on the kinetics and the equilibrium constant of the adsorption process. The value of the equilibrium constant decreases with temperature, thereby decreasing the maximum adsorption, resulting in decrease of % adsorption. On the other hand, the rate of the reaction increases with temperature, thereby enabling the equilibrium to be reached faster. The observed lower % conversion at 10°C indicates that the equilibrium has not reached under the experimental conditions of the measurement.

Adsorption Kinetics

The knowledge of kinetics of adsorption of uranyl ions is essential for determining the contact time needed for optimum adsorption, which depends on the nature of the system used. The adsorption mixtures, set at constant temperature ($T = 298$ K), were sampled at different times, ranging from 10 to 200 min, to investigate the effect of the contact time on the adsorption of uranyl ions. The results are plotted in Figure 8. A rapid adsorption is observed at the initial stage, and more than 70% of uranyl ions are adsorbed during the first 60 min. The adsorption equilibrium is established after about 120 min. Therefore, the time period of 120 min has been used in further adsorption experiments, as the optimum contact time for the maximum adsorption.

Adsorption Kinetics Models. To investigate the mechanism of adsorption, the first- and the second-order models were used

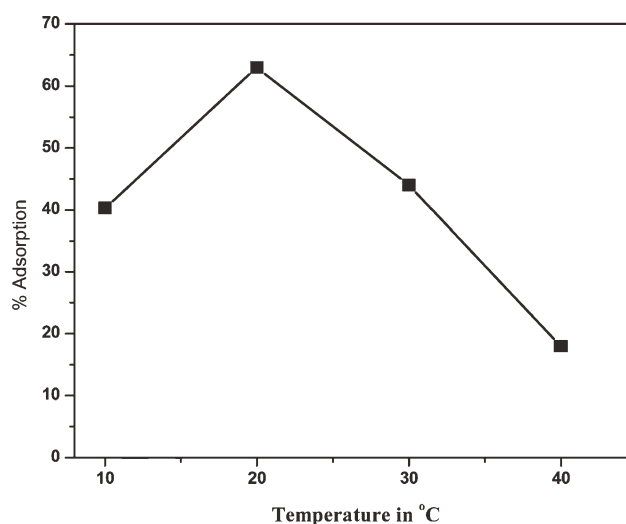


Figure 7. The effect of temperature on the adsorption of UO_2^{2+} ions, after equilibrating 0.013 g APAN composite beads with 0.2 mL of 10 ppm aqueous solution, for 2 h, at different temperatures.

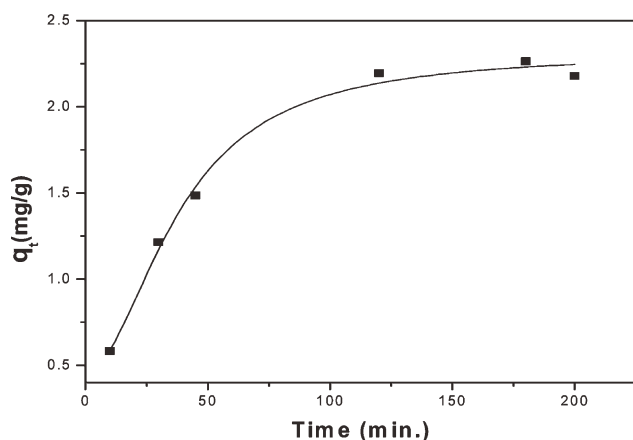


Figure 8. The effect of contact time on the amount of uranium adsorbed onto APAN beads. Initial metal ion concentration 100 mg/L, pH 6 ± 0.1 , amount of APAN beads 0.013 g.

for fitting the experimental data. The pseudo-first-order model of Lagergren is given as²³:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

where q_e and q_t are the amounts of metal ions adsorbed onto the APAN beads (mg/g) at equilibrium and at time t , respectively, and k_1 is the rate constant of the first-order adsorption (/min) process. The integrated form of eq. (5) can be written as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

The plot of $\log(q_e - q_t)$ against t gives a straight line, as shown in Figure 9(a). The values of k_1 and q_e can be obtained from the slope and the intercept, respectively, of the straight line. However, the data plotted as per the first-order model do not fit well in the whole range of the contact time and have correlation coefficient (R_1^2) of only 0.95441, indicating that this model is not appropriate. The values of k_1 , q_e , and R_1^2 obtained are given in Table I. Therefore, pseudo second-order kinetics model has been used, which is given by the following equation.²³

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

where, k_2 (g/mg/min) is the rate constant of the second-order adsorption. The integrated form of eq. (7) is given below.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (8)$$

The above equation can be rearranged as given below.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_0} \quad (9)$$

The plot of t/q_t versus t gives a straight line, as shown in Figure 9(b), with a correlation coefficient of (R_2^2) of 0.98053, indicating

that the second-order model is applicable. The values of q_e and k_2 can be obtained from the slope and the intercept of the plot, respectively, and are found to be 2.67 mg/g and 0.01122 g/mg/min. These values, along with that of R_2^2 , are listed in Table I. From the data in Table I, it is found that the correlation coefficient (R_2^2) for the pseudo second-order kinetic model is more than that for the pseudo first-order kinetic model, which means that the present experimental data fit better to the pseudo second-order kinetic model. The pseudo second-order model assumes that chemisorption is the rate controlling step. Additionally, in comparison to the first-order kinetic model, the value of q_e obtained from the second-order model is in good accordance with the experimental value. This shows that the adsorption of uranyl ions by APAN beads follow second-order kinetics.

Adsorption Isotherms

Adsorption isotherms describe how the adsorbates interact with the adsorbents and are important in optimizing the use of the adsorbents. To investigate the amount of metal ions adsorbed as a function of aqueous concentration of the heavy metals, adsorption isotherms are widely employed for fitting the data, using the representation of the adsorption (expressed as mg of the metal adsorbed per g of solid adsorbent) versus the concentration of uranyl ions in the solution at equilibrium. Adsorption

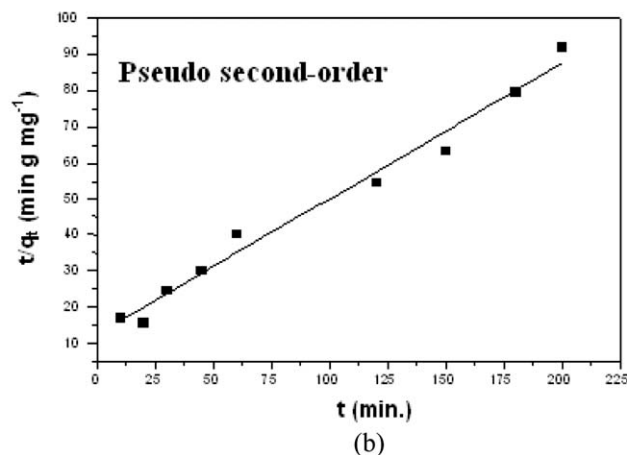
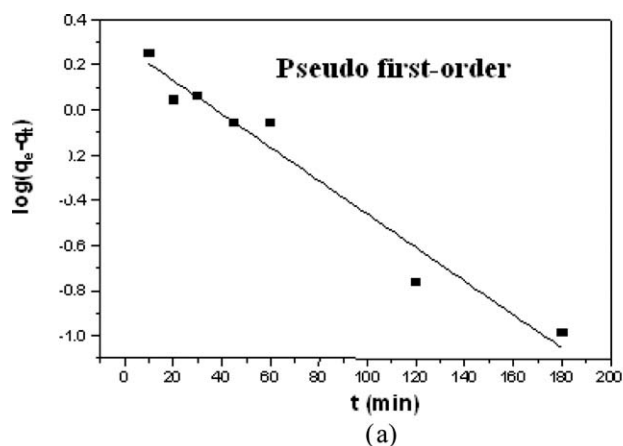


Figure 9. (a) Pseudo first-order and (b) pseudo second-order plot, for the adsorption of uranium onto APAN beads.

Table I. Pseudo-First and Pseudo Second-Order Equation Constants and Values of R^2 for the Adsorption of Uranium onto APAN Beads

Uranium concentration (100 mg/L)	Pseudo first order			Pseudo second order			q_e experimental
	k_1 (1/min)	R_1^2	q_e (mg/g)	k_2 (g/mg/min)	q_e (mg/g)	R_2^2	2.4 (mg/g)
	0.0168	0.9544	1.89	0.01122	2.67	0.9805	

isotherm for uranyl ions on APAN beads is shown in Figure 10(a).

The results clearly indicate that with an increase in the initial uranyl ions concentration the amount of uranyl ions adsorbed increases significantly. At lower initial metal ions concentration, the adsorption increases linearly with the initial metal ions concentration, suggesting that the adsorption sites on the APAN beads are sufficient, and in this case, the

amount of uranyl ions adsorbed 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 adsorption no longer increases proportionally with the initial metal ions concentration, indicating that the number of the adsorption sites on the surfaces of the APAN beads actually limits the amount of uranyl ions adsorbed.

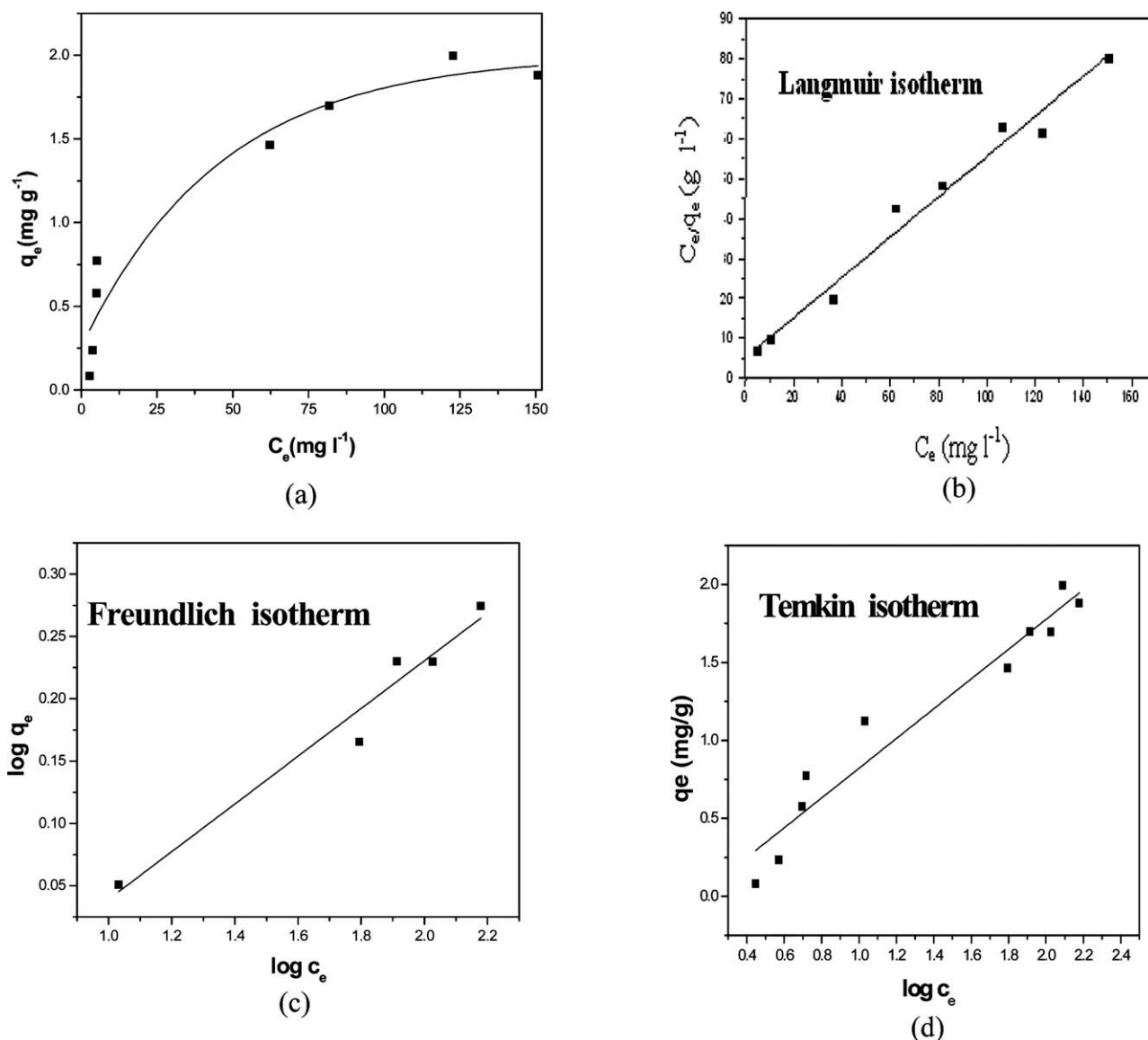


Figure 10. (a) The amount of metal ions adsorbed onto the APAN beads at various equilibrium metal ions concentrations, (b) Langmuir adsorption isotherm, (c) Freundlich adsorption isotherm, and (d) Temkin adsorption isotherm for the adsorption of uranium onto APAN beads; temperature 298 K; pH 6.0 ± 0.1 ; volume 0.5 mL; amount of APAN beads 0.013 g.

Table II. Isotherm Constants and Corresponding R^2 Values for the Adsorption of Uranium onto Swollen APAN Beads

Metal ion	Langmuir parameter			Freundlich parameter			Temkin parameter		
	B (L/mg)	q_{\max} (mg/g)	R^2	k_f (mg/g)	n	R^2	B	A (L/g)	R^2
Uranyl ion	0.0992	1.98	0.9766	1.42	5.22	0.9523	0.95432	0.7269	0.9365

The adsorption data have been subjected to different adsorption isotherms, namely, the Freundlich, Langmuir, and Temkin models. These models suggest different adsorption modes with different interactions between the adsorbate and the adsorbent. In the case of the Freundlich model, the energetic distribution of the sites is heterogeneous due to diversity of the adsorption sites or diverse nature of the metal ions adsorbed (i.e., free or hydrolyzed species). The Langmuir model assumes a monolayer adsorption, with a homogenous distribution of the adsorption sites and the adsorption energies, without interactions between the adsorbed molecules or the ions. The Temkin isotherm model assumes that the heat of adsorption of all the molecules, or ions, in the layer decreases linearly with the thickness of the coverage due to the sorbate/adsorbate interactions.

The Langmuir Model. The widely used Langmuir isotherm, in the form of eq. (10), has been successfully applied to many real adsorption processes.²⁴

$$q_e = q_{\max} \left(\frac{bC_e}{1 + bC_e} \right) \quad (10)$$

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 adsorption capacity (theoretical monolayer saturation capacity). The main characteristics of the Langmuir equation, the constants b and q_{\max} , can be determined from the linearized form of the Langmuir equation given below.

$$\frac{C_e}{q_e} = \frac{1}{(q_{\max}b)} + \frac{C_e}{q_{\max}} \quad (11)$$

The plot of (C_e/q_e) versus C_e , gives a straight line, as shown in Figure 10(b), indicating that the adsorption behavior follows the Langmuir adsorption isotherm. The values of q_{\max} and b were found to be 1.98 mg/g and 0.0992 L/mg from the slope and the intercept, respectively, of the straight line.

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.

$$R_L = \frac{1}{1 + bC_0} \quad (12)$$

The value of R_L , for the entire studied concentration range, lies between 0 and 1, indicating favorable adsorption, as reported by McKay et al.²⁵

The Freundlich Isotherm. The Freundlich model is often used for adsorption on a heterogeneous surface. It is given by the following equation²⁶:

$$q_e = k_f C_e^{1/n} \quad (13)$$

where k_f and n are empirical constants, characteristics of the system representing the adsorption capacity and the adsorption intensity, respectively. The above equation can be represented in the following linear form to confirm the applicability of the model to the present data.

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad (14)$$

Figure 10(c) shows the plot of Freundlich isotherm. The plot is linear, with the correlation coefficient (R^2) of 0.9523. The values of the Freundlich constants, along with that of the correlation coefficient, are given in Table II.

The Temkin Isotherm. The Temkin isotherm²⁷ has also been used in many sorption processes. A linear form of the Temkin isotherm can be expressed as follows:

$$q_e = \left(2.303 \frac{RT}{h} \right) \log A + \left(2.303 \frac{RT}{b} \right) \log c_e \quad (15)$$

where $2.303 RT/b = B$. 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 10(d) shows plot of this isotherm. The values of A and B were determined as 0.7269 and 0.9543 from the intercept and the slope, respectively, of the straight line. The values of the Temkin constants A and B , along with that of the correlation coefficient, are given in Table II.

Comparing the R^2 values given in Table II, it can be concluded that the Langmuir isotherm is a better fit for the given adsorption process. Freundlich 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 adsorption isotherm properly.

Table III. Determination of Maximum Experimental Capacity of the Swollen Beads

No. of stages	Uranium (μg)		Amount of U adsorbed	
	Before equilibration	After equilibration	μg	%
1	50	4.95	45.05	90.1
2	50	37.33	12.68	25.36
3	50	45.78	4.22	8.44
4	50	45.87	4.13	8.26

The maximum experimental capacity of the beads = $(45.05 + 12.68 + 4.22 + 4.13)/0.0186 = \approx 3552 \mu\text{g}\cdot\text{g}^{-1}$ of the swollen beads.

Table IV. Testing of Reusability of the Synthesized Beads

Cycle No.	Amount of uranium (μg)		Amount of uranium adsorbed	
	Before equilibration	After equilibration	μg	%
1	30	2.96	27.04	91.00
2	30	3.75	26.25	88.33
3	30	6.75	23.25	77.50
4	30	6.60	23.40	78.00

Determination of Maximum Capacity, Chemical Stability, Leaching Study, and Reusability of APAN Beads

The loading capacity of the APAN beads was determined, by using the batch equilibration method. The capacity APAN beads was determined by measuring the uranyl ions adsorbed, on equilibrating 0.018 g of the swollen beads with 0.5 mL of 100 ppm uranium containing solution over four consecutive stages. The beads were washed with water, after each stage, to remove the unadsorbed uranyl ions from the surface of the beads. The results obtained in the four consecutive adsorption stages are given in Table III. It is observed that the amount of uranyl ions adsorbed in the second stage is much lower than that in the first cycle, and thereafter, gradually decreases up to the fourth stage, and after that, the beads adsorb negligible amount of uranyl ions. The experimental capacity of the beads as per the first equilibration cycle is found to be 2.4 mg/g, whereas the q_{max} obtained from the Langmuir isotherm is 1.98 mg/g. The maximum experimental adsorption capacity determined by adding the amounts of the adsorbed uranium in each stage comes to 3.5 mg/g of the swollen beads.

The difference between the values of the capacities determined by the repeated equilibration method and that obtained from the kinetics experiment is, because, in the former, the experiment is carried out in four consecutive stages, each of 24 h equilibration time, followed by washing with water, whereas the kinetics experiment is carried out only up to 200 min of contact time.

The chemical stability of the APAN beads 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, 1–5 M, for various periods of time (up to 6 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.

The synthesized APAN beads were equilibrated with uranyl ions for overnight, leached with 0.1 M 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 adsorption–desorption cycles, for adsorption of uranyl ions. The observed small decrease in % uranyl ions adsorption with the number of cycles as shown in Table IV is probably due to incomplete leaching of the uranyl ions with 0.1 M acid.

CONCLUSION

In this study, APAN has been synthesized by the conversion of nitrile groups in the PAN, and further, the APAN has been converted into beads form for adsorption in column mode. The surface morphology of the beads has been investigated by SEM, which shows its porous nature. IR spectra of the beads confirm complete amidoximation of PAN, as well as uranyl ion adsorption on amidoximated PAN beads. These synthesized beads efficiently adsorb uranyl ions from aqueous solution over wide pH and temperature ranges. These beads can be used in many cycles, without much change in the efficiency and the mechanical stability. The amount of uranyl ions adsorbed is found to increase with increase in equilibration time and the initial concentration of uranyl ions. The results of the study show that these synthesized beads have good capacity (3.5 mg/g) for uranium. The most suitable pH for adsorption of uranyl ions is 5–6. The polymeric beads exhibit optimum adsorption at 20°C and at a neutral, or near neutral, pH conditions. Langmuir, Freundlich and Temkin isotherm equations have been used to understand the adsorption of uranyl ions onto APAN beads. Langmuir model shows better correlation coefficient than the other two models at the studied conditions. It is found that the pseudo second-order equation, which assumes chemisorption as the rate determining step, describes the kinetics of adsorption of uranyl ions on APAN beads better than the pseudo first-order equation.

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