



Adsorption of uranium from aqueous solution using chitosan-tripolyphosphate (CTPP) beads

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ABSTRACT

Chitosan-tripolyphosphate (CTPP) beads were prepared using in-liquid curing method and used for the adsorption of uranium from aqueous solution. Beads were prepared at two different cross-linking densities by adjusting the pH of the tripolyphosphate solution. The synthesized beads were characterized using FTIR spectroscopy before and after adsorption of uranium. Beads having higher cross-linking are found to have better adsorption capacity for uranium. Factors that influence the uranium adsorption onto CTPP beads such as solution pH, contact time and initial uranium concentration were studied in detail. The experimental results were fitted into Langmuir and Freundlich adsorption isotherms. From Langmuir adsorption model the adsorption capacity of CTPP beads for uranium is estimated as 236.9 mg/g. Pseudo-first order, pseudo-second order and intraparticle diffusion model were applied to the observed kinetics data and the results shows that the pseudo-second order model is more suitable to explain the kinetics of adsorption of uranium on CTPP beads. FTIR spectroscopic characterization of the beads showed that the phosphate groups may be more responsible for the adsorption of uranium on CTPP beads.

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1. Introduction

Chemical and radiotoxicity of uranium is well documented [1]. Based on the radiological risks by the radiation of uranium isotopes and chemical risks from heavy metals, the health effects of uranium can be divided into carcinogenic and non-carcinogenic effects. Nephritis is the primarily chemically induced effect of uranium in humans, whereas USEPA has classified uranium as a confirmed human carcinogen and suggested that zero tolerance is the only safe acceptable limit [2]. They prescribed that maximum contaminant level goal (MCLG) for uranium as zero in 1991. In addition, the EPA finalized a realistic regulation level of 30 µg/L as the maximum contaminant level. Though stringent environmental regulation exists against the release of uranium contaminated solution into the environment, effluents from nuclear and many other conventional industries are found to have significant quantity of uranium present in it [3]. Therefore it is desirable to develop efficient and economically viable methods for the treatment of water contaminated with uranium. Different methods have been used for cleaning solutions contaminated with uranium such as co-precipitation, ion exchange, membrane based separation and sorption on various surfaces [4–7]. In acidic solutions, uranium

exists as U(VI), whereas in neutral or basic pH conditions, it normally exist as neutral or anionic species by complex formation with anionic ligands such as OH⁻ or CO₃²⁻ [8]. Thus in neutral pH ranges, processes such as ion exchange is less effective for the removal of uranium from aqueous medium whereas membrane separation suffers many practical difficulties such as membrane fouling, which requires frequent maintenance. Thus sorption on various media is getting increasing interest as a suitable remediation process for the treatment of uranium contaminated solutions [9]. In past several decades, environmental friendly and potentially inexpensive biosorbents have attracted significant interest as suitable materials for the development of new environmental remediation technologies [10,11]. Chitin is the most abundant biopolymer after cellulose, and its partially deacetylated form, chitosan is found to have excellent sorption capacity for various heavy metals including radionuclides [12–17]. Chitosan is the copolymer composed of β-2-amino-2-deoxy-D-glucopyranose units and the residual 2-acetamido-2-deoxy-D-glucopyranose units and the metal uptake by it is primarily attributed to the amine and hydroxyl groups present in the polymer chain, which can interact with various metallic species through ion exchange and/or chelation mechanism. Two types of modifications are commonly adopted for the preparation of chitosan based sorbents. Cross-linking to improve its solubility and engineering properties and grafting of functional groups for enhancing the adsorption capacity and/or selectivity. Various reports have been published on the use of modified and

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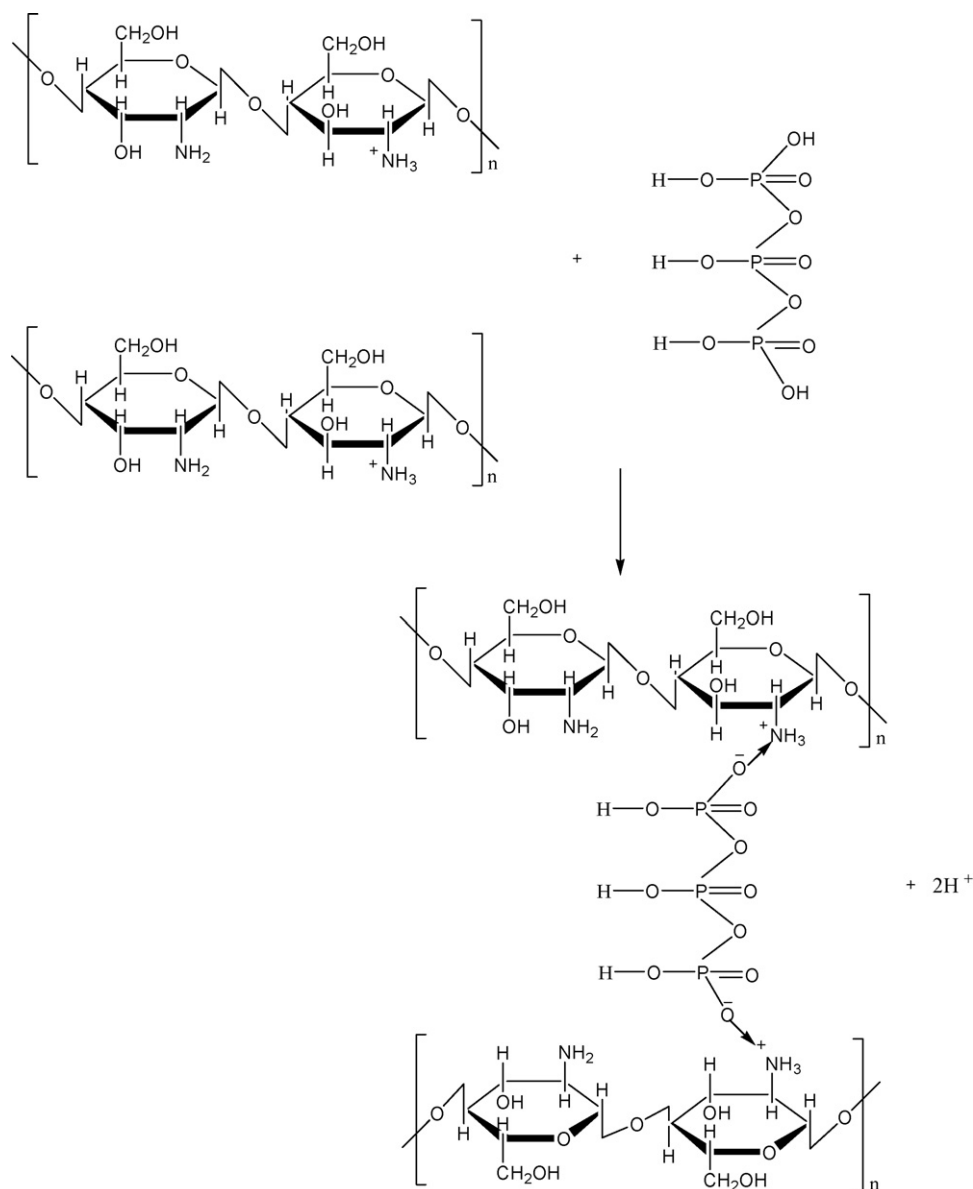


Fig. 1. Schematic representation of cross-linking of chitosan with sodium tripolyphosphate.

unmodified chitosan derivatives for analytical preconcentration [18–20] and sorption of uranium from aqueous solution [21–25]. However all these previous reports, dealing with sorption of uranium on chitosan derivatives; cross-linking agents used were toxic chemicals such as glutaraldehyde (GLA), epichlorohydrin (ECH) or ethylene glycol diglycidyl ether (EGDE).

From the environmental safety point of view, it is preferred to use non-toxic and environmentally benign substances for developing future technologies. Tripolyphosphate (TPP) mediated ionic cross-linking of chitosan is thus a suitable alternative to the use of toxic chemicals for the modification of chitosan. Cross-linking of chitosan by TPP can be achieved by a single-step process, where the formation of intra- and intermolecular cross-linking leads to solidification of chitosan into chitosan-tripolyphosphate (CTPP) beads [26]. Recently Ngah and Fatinathan [27] has reported the adsorption of Pb(II) and Cu(II) on CTPP beads from single and binary metal systems. Since phosphate groups are also known to have good affinity for uranium, CTPP beads may be a good adsorbent for uranium from aqueous solution. In the present work, we studied the adsorption of uranium onto CTPP beads. CTPP beads of two

different cross-linking densities were prepared and the sorption of uranium is studied as a function of contact time, pH and concentration of uranium. The experimental results were fitted into Langmuir and Freundlich isotherm models. Kinetics of the adsorption process was analysed using pseudo-first order, pseudo-second order and intraparticle diffusion models. To understand the mechanism of adsorption of uranium onto CTPP beads, the beads were characterized using Fourier transform infrared (FTIR) spectroscopy before and after adsorption of uranium.

2. Experimental

2.1. Materials

Chitosan (medium molecular weight) and sodium tripolyphosphate (STPP) ($\text{Na}_5\text{P}_3\text{O}_{10}$) were purchased from Aldrich Chemical Company, USA. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ACS grade) was purchased from Merck, Germany. 2-(5-Bromo-2-Pyridylazo)5-diethylaminophenol (Br-PADAP), triethanolamine, CDTA, NaF and sulphosalicylic acid used for analysis uranium were analytical grade and were pur-

chased from Merck, Germany or Sigma–Aldrich, USA. 2000 mg/l U(VI) standard solution was prepared by dissolving appropriate quantity of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionised water. All other chemicals used in the experiments were of analytical grade. Deionised water used for all experiments was obtained from Milli-Q (Millipore Corporation, USA) water purification system.

2.2. Preparation and characterization of CTPP beads

CTPP beads were prepared using the method described by Lee et al. [26]. Chitosan (10 g) was dissolved in 500 ml of dilute acetic acid (1%, v/v) to prepare the chitosan solution. The STPP solution was prepared by dissolving 10 g of the solid in 100 mL of water. The chitosan solution was added/poured into the TPP solution drop wise using a PVC tip, with an opening of 1 mm. The beads were prepared at two different pH for the TPP solution; pH = 8.6 (original pH of the STPP solution) and pH = 3.0 adjusted by adding 1 M HCl, in order to obtain beads with different cross-linking densities [28]. The formation of cross-linked CTPP beads by the interaction between phosphate groups of tripolyphosphate and amino group of chitosan is schematically represented in Fig. 1. The beads were cured for 12 h, separated by filtration, washed four times with deionised water and air dried before use in adsorption experiments. Dried beads were spherical and slightly yellowish in colour. FTIR spectra of the powdered beads before and after adsorption of uranium were recorded as KBr pellets using JASCO 6200 model FTIR spectrophotometer.

2.3. Uranium measurement by Br-PADAP method

Concentration of dissolved uranium after the equilibration was determined using the spectrophotometric method using Br-PADAP as the complexing agent at pH = 7.8 [29,30]. Triethanolamine buffer (TEA-buffer) for pH adjustment was prepared by diluting 14 mL of the triethanolamine in 80 mL of deionised water, adjusting the pH to 7.8 by adding concentrated HClO_4 and finally made up to 100 mL. Complexing solution for removing the interference of other bivalent cations was prepared by dissolving 3.5 g of sulphosalicylic acid, 0.5 g of NaF and 1.25 g of CDTA in 40 mL water and adjusting pH to 7.8 by the addition of sodium hydroxide pellets and finally made up to 100 mL. For the measurement of uranium, 1 mL of complexing solution, 20–100 μL of aliquot of the sample, 1 mL TEA-buffer, 4 mL of ethanol and 0.5 mL of Br-PADAP were added into the 10 mL volumetric flask and made up to 10 mL using deionised water. The solution was allowed to develop colour for 30 min and optical density is measured at 578 nm using UV540 double beam spectrophotometer (Thermo Spectronic, USA).

2.4. Sorption of uranium on CTPP bead

For batch equilibration studies, experimental solutions containing measured concentration of uranium and the adsorbent were adjusted to the required pH and equilibrated in 100 mL Erlenmeyer flask at 250 rpm using a horizontal orbital shaker. Temperature during the adsorption experiments were controlled at $25 \pm 0.5^\circ\text{C}$. All pH adjustments were carried out with 1 M $\text{HNO}_3/\text{Na}_2\text{CO}_3$. After fixed time of equilibration, 20–100 μL of the solution was withdrawn from the experimental mixture and uranium concentration was estimated using the spectrophotometric method as described in Section 2.3. The amount of uranium adsorbed onto the CTPP bead at time t , was calculated by:

$$q_t = \frac{(c_0 - c_t)V}{w} \quad (1)$$

where q_t (mg/g) is the quantity of uranium adsorbed on CTPP bead at time t (h), c_0 is the initial concentration (mg/L) of uranium used in the experiment, c_t is the measured concentration (mg/L) of uranium

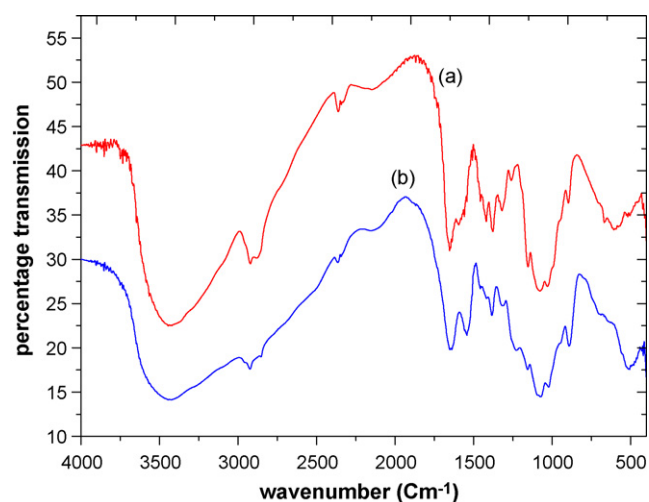


Fig. 2. FTIR spectra of (a) chitosan and (b) CTPP beads cross-linked at pH = 3.

presented in the liquid phase after equilibration time t ; V is the volume of the solution (L); w is the mass of the CTPP beads (g). For kinetic investigations, the adsorption experiments were conducted at a stirring speed of 400 rpm, using a magnetic stirrer, in order to minimize the effect bulk and film diffusion on sorption process [31].

3. Results and discussion

3.1. Characterization of CTPP beads

CTPP beads prepared were characterized using FTIR spectroscopy. The IR spectra of chitosan powder and the CTPP bead is provided in Fig. 2. The main differences in the IR spectra is the additional peak in the CTPP bead spectrum at 1230 cm^{-1} , which can be assigned to the $\text{P}=\text{O}$ stretching vibration indicating the presence of phosphate group in the prepared beads. Peak at 1694 cm^{-1} corresponding to NH_2 group and 1419 cm^{-1} corresponding to NH deformation vibration of NH_2 groups, present in the original chitosan spectrum is completely disappeared in the spectrum of CTPP bead, with appearance of a fresh peak at 1541 cm^{-1} which can be assigned to NH_3^+ [26,27]. The beads are prepared at pH = 3 where the amino group are mostly protonated. From the spectral information it can be concluded that the cross-linking is taking place through the ionic interaction between the negatively charged $\text{P}-\text{O}^-$ moieties of the phosphate group and protonated NH_3^+ moieties of the chitosan molecule.

3.2. Effect of cross-linking and solution pH on uranium sorption

Chitosan is brittle, where most of the active functional groups are deeply embedded inside the crystalline phase which leads to reduced adsorption capacity for the adsorbent. Cross-linking of chitosan with various cross-linking agents is found to improve its amorphous character. In order to investigate the effect of cross-linking and solution pH on the uranium sorption process, two sets of experiments were conducted, one using higher cross-linked beads and the other with lower cross-linked beads. Equilibration studies were carried out with 50 ml of 200 ppm U (VI) solution containing 50 mg of the adsorbent in each case and varying the initial pH of the solution from 3 to 9. Fig. 3 presents the uranium adsorption on lower and higher cross-linked beads, as a function of the solution pH. Under identical experimental conditions, beads with higher cross-linking showed higher adsorption capacity for uranium. The pH dependence also differs significantly with the extent of cross-linking of the CTPP beads. The uranium adsorp-

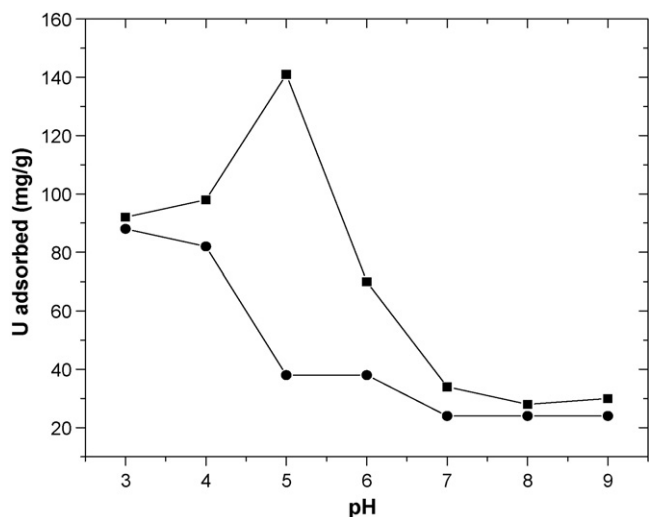


Fig. 3. Effect of pH on the adsorption of uranium on CTPP beads: lower cross-linked beads (●) and higher cross-linked beads (■) (volume = 50 ml, $U = 200$ mg/L, CTPP = 50 mg and $T = 25^\circ\text{C}$).

tion capacity of lower cross-linked beads decreased monotonously with pH of the solution. Though for lower cross-linked beads, both amino and phosphate groups may be available for the adsorption of uranium, it is reported that they are more amenable to swelling in acidic solution [26]. In such case, as the pH of the solution increases, due to reduced swelling, more and more active sites may not be reachable by uranium species for adsorption, resulting in lower adsorption capacity. On the other hand beads with higher cross-linking showed maximum adsorption at pH = 5. The swelling behavior of higher cross-linked beads is nearly independent of pH and other factors determine the adsorption dependence of uranium on pH of the solution. At lower pH, the amino groups are protonated whereas phosphate groups remain undissociated. Thus at lower pH, the positively charged uranyl ion is not favored by the positive or neutral binding groups on the adsorbent, resulting in lower adsorption capacity. At neutral to alkaline pH, uranium is present as anionic hydroxyl-carbonate complexes such as, $\text{UO}_2\text{CO}_3\text{OH}^-$, $(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$, $(\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-}$, etc. [32], and thus not favorable for adsorption onto the neutral/negatively charged functional groups of CTPP beads, which explain the reduction in adsorption at higher pH. Thus the maximum adsorption capacity observed at pH = 5 for the higher cross-linked CTPP beads is the result of pH-dependent speciation of the uranyl ion and the pH-dependent dissociation behavior of CTPP functional groups responsible for uranium adsorption. Due to the higher adsorption capacity, beads with higher cross-linking and the optimum pH = 5 were used for further experiments.

3.3. Effect of contact time on uranium sorption

To understand the effect of contact time on uranium adsorption onto CTPP beads, experiments were conducted with 100 mL of solution having 400 mg/L uranium and 100 mg of adsorbent. 100 μL of the sample were analysed at various intervals to estimate the concentration of dissolved uranium as a function of equilibration time. Fig. 4 shows that the process is characterized by a rapid adsorption in the initial 4 h of equilibration time, followed by a slow process, leading to equilibrium adsorption in around 3 days. The initial fast sorption might be due to the surface adsorption of uranium on the CTPP beads. Uranyl ion is a bulky cation and the diffusion of the bulk ion into the CTPP beads is a slow process leading to the overall slow kinetics of the adsorption process. During longer stay of the beads in the experimental solution, they become swollen, but no

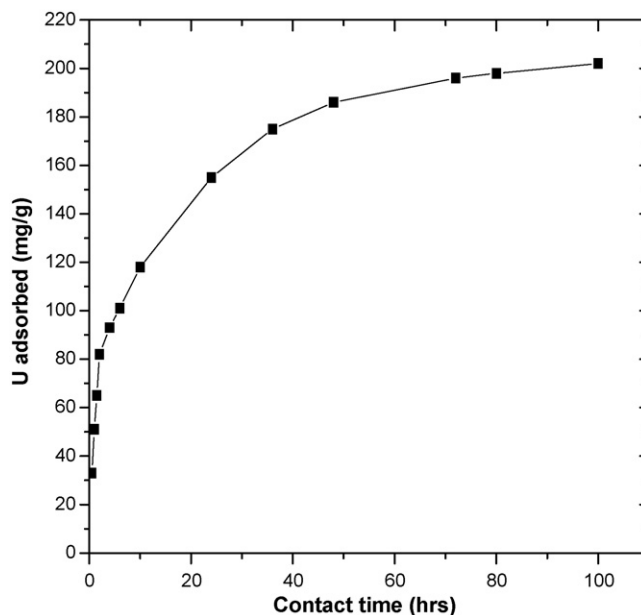


Fig. 4. Effect of contact time on the adsorption of uranium on CTPP beads (volume = 100 ml, $U = 400$ mg/L, CTPP = 100 mg, pH = 5 and $T = 25^\circ\text{C}$).

solubility of the beads was observed even after 5 days of equilibration. Concentration of dissolved uranium measured after 10 days of equilibration was in the same range (within 5%) of the concentration measured after 72 h of equilibration, showing that for practical purposes 72 h can be taken as the time required for completing the adsorption equilibrium.

3.4. Effect of initial uranium concentration

The relation between the adsorbed amount and the equilibrium concentration in the aqueous phase is very important in optimizing the sorption process and understanding the sorption behavior. For investigating the effect of initial uranium concentration on the adsorption of uranium onto CTPP beads, experiments were con-

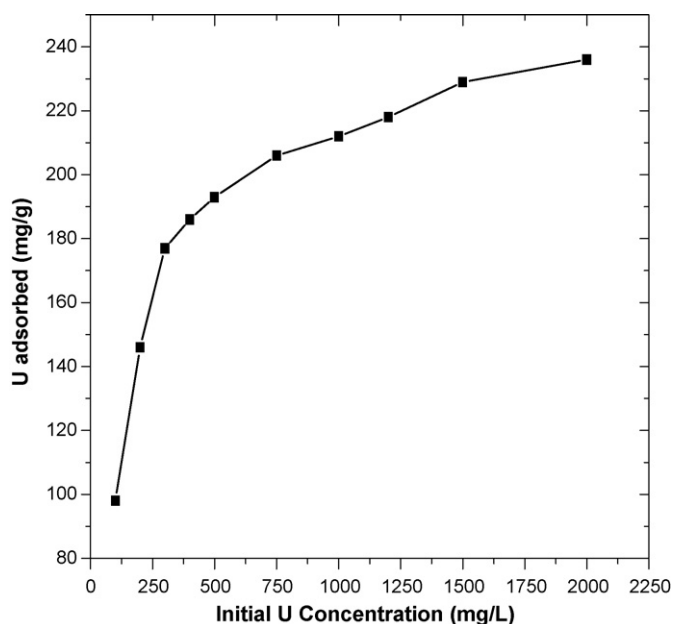


Fig. 5. Effect of initial uranium concentration on adsorption on CTPP beads (volume = 50 ml, CTPP = 50 mg, pH = 5, and $T = 25^\circ\text{C}$).

Table 1
Model constants and correlation coefficients for adsorption of uranium by CTPP beads.

Isotherm model					Experimentally observed saturation capacity (mg/g)	
Langmuir			Freundlich			239.9
Q (mg/g)	b (mL/mg)	R ²	k _F (mg/g)	n	R ²	
236.9	0.019	0.997	89.9	7.65	0.991	

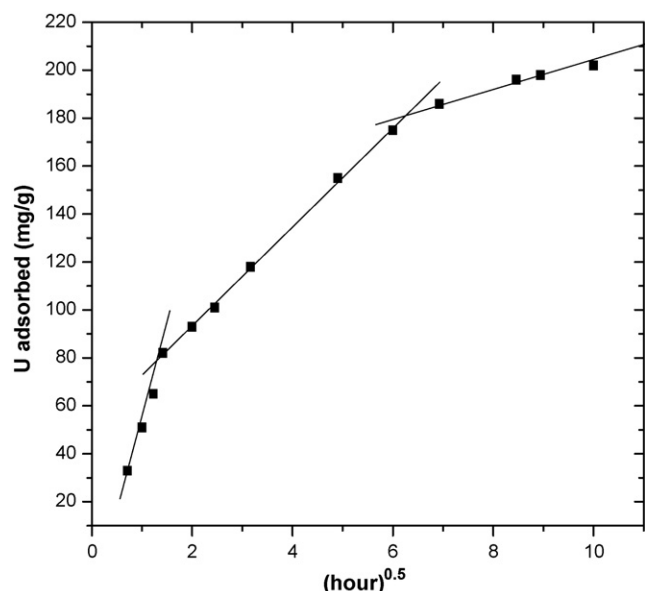


Fig. 6. Intraparticle diffusion kinetics of the adsorption of uranium on CTPP beads.

ducted with 50 mL solutions having initial uranium concentration varying from 100 mg/L to 2000 mg/L and a fixed mass of 50 mg of adsorbent. Fig. 5 shows the amount of adsorbed uranium after equilibrium versus the initial uranium concentrations. As expected the adsorption capacity increased with the initial metal concentration. With more uranium present in solution, larger fraction of the active sites is involved in the adsorption process. At higher uranium concentrations adsorption capacity reached a plateau indicating saturation of the available binding sites on the adsorbent. The steep slope at initial uranium concentrations is a desirable feature of the sorption system and the results indicates that a CTPP bead is an efficient adsorbent for uranium.

3.5. Sorption isotherm

Adsorption isotherm is fundamental in understanding the distribution of the adsorbate on adsorbent surface once the equilibrium is established [33]. The simplest adsorption model is Langmuir isotherm in which it is assumed that the adsorbate form a monolayer on the adsorbent surface and the adsorption energy decreases as the distance from the surface increase, making multilayer adsorption process less favorable. The linear form of the Langmuir

Table 3
Kinetics parameters of uranium adsorption by CTPP beads.

Kinetic model						Experimentally observed adsorption capacity (mg/g)	
Pseudo-first order			Pseudo-second order			Intraparticle diffusion model	
k ₁ (h ⁻¹)	q _e (mg g ⁻¹)	R ²	k ₂ (g mg ⁻¹ h ⁻¹)	q _e (mg g ⁻¹)	R ²	k _{id} (mg g ⁻¹ h ⁻¹)	R ²
0.045	141.6	0.995	9.4 × 10 ⁻⁴	209.2	0.997	19.6	0.993
							202.4

Table 2
R_L values for uranium adsorption obtained from Langmuir equation.

Initial U concentration (c ₀) (mg/L)	Separation factor (R _L)
10	0.840
50	0.512
100	0.256
500	0.095
1000	0.050

isotherm can be expressed as:

$$\frac{c_e}{q_e} = \frac{1}{Qb} + \frac{c_e}{Q} \quad (2)$$

where q_e is the amount of metal ion adsorbed at equilibrium (mg/g), c_e is the equilibrium metal ion concentration remaining in solution, Q (mg/g) is the amount of metal ion adsorbed at complete monolayer coverage, and b is the Langmuir constant related to the affinity of the binding site (mL/mg). The monolayer adsorption capacity, Q and the Langmuir constant b can be obtained from the linear plot of c_e/q_e against c_e . Other commonly used adsorption model is the Freundlich isotherm which is an empirical model used to explain the adsorption on heterogeneous surfaces. The Freundlich isotherm can be expressed as:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e \quad (3)$$

where k_F (mg/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively, and can be obtained from the linear plot of $\ln q_e$ against $\ln c_e$. The model parameters obtained by applying both Langmuir and Freundlich model to the experimental data are given in Table 1. From the better correlation coefficient and the fact that the equilibrium adsorption capacity (Q) obtained from Langmuir model (236.9 mg/g) is close to the experimentally observed saturation capacity (239.9 mg/g), it can be concluded that the monolayer Langmuir adsorption isotherm is more suitable to explain the adsorption of uranium onto CTPP beads.

The favorability of the CTPP beads as an adsorption medium for uranium can be obtained from the Langmuir adsorption constant b ; which is related to the separation factor R_L defined as:

$$R_L = \frac{1}{1 + bc_0} \quad (4)$$

where c_0 is the initial metal ion concentration. $0 < R_L < 1$ indicates that the adsorbent is a favorable medium for the adsorption of the given metal. Table 2 presents the calculated R_L values at five different initial uranium concentrations. For all the tested uranium concentrations, $0 < R_L < 1$ which proves that CTPP bead is a favorable adsorbent for uranium. The same conclusion can be arrived

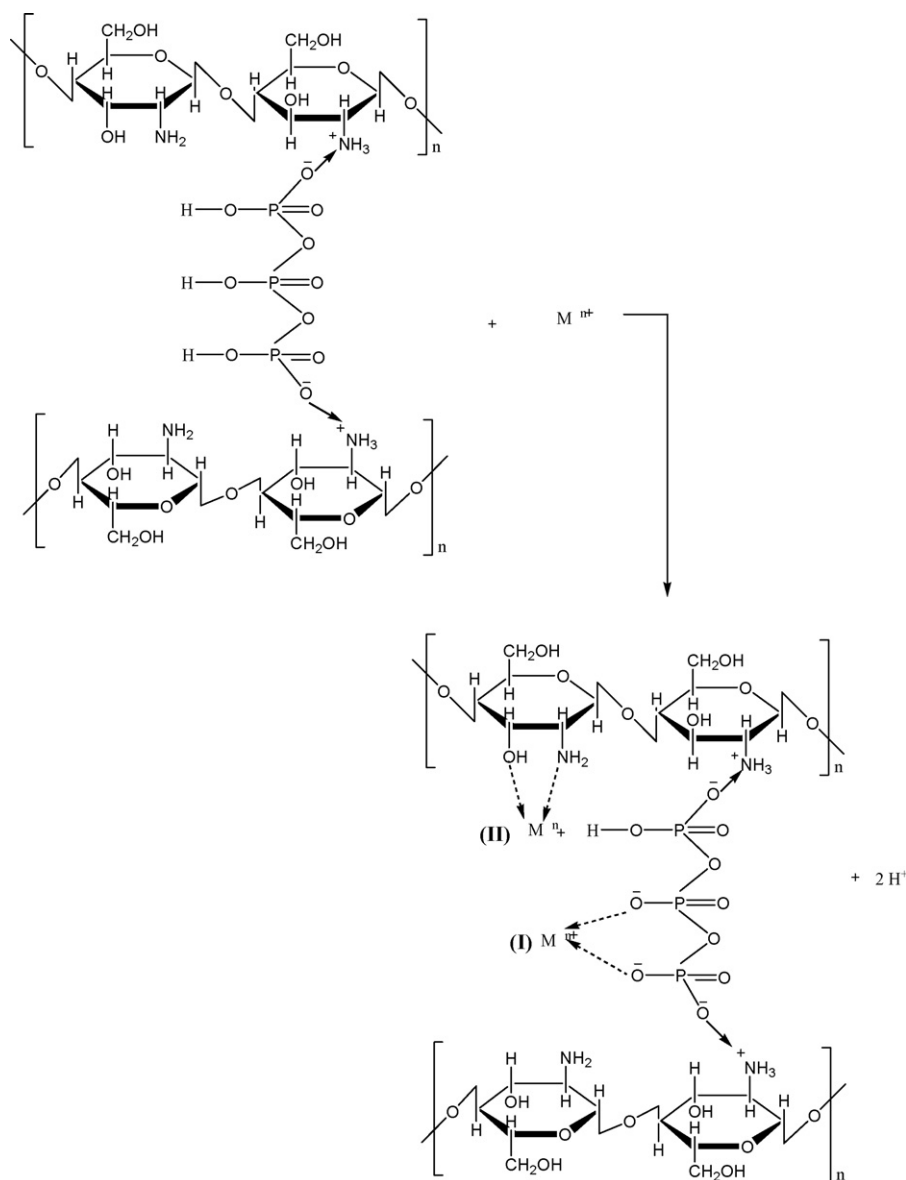


Fig. 7. Schematic presentation of binding of uranium by CTPP beads.

from the Freundlich constant n in which case a value of n between 1 and 10 indicates the acceptance of the medium as the suitable adsorbent.

3.6. Sorption kinetics

Experiments for studying the adsorption kinetics were carried out at higher agitation speed in order to minimize the effect of bulk diffusion and film diffusion on the adsorption process. It is assumed that at the experimental agitation rate of 400 rpm, intraparticle diffusion or chemical reactions may be the rate limiting step. Both pseudo-first order and pseudo-second order kinetics were applied to analyse the experimentally observed kinetic data [34]. Pseudo-first order kinetic model can be expressed as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t \quad (5)$$

where q_e and q_t are the concentration of uranium adsorbed on CTPP beads (mg/g) at equilibrium time, and time t (h) respectively, and k_1 is the pseudo-first order rate constant (h^{-1}) for the adsorption of

uranium onto CTPP beads. The model parameters q_e and k_1 can be obtained from the linear plot of $\log(q_e - q_t)$ against time. Pseudo-second order kinetics can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where q_e (mg/g) and q_t (mg/g) have the same meaning as earlier and k_2 is the rate constant ($\text{g mg}^{-1} \text{h}^{-1}$) of the pseudo-second order kinetic model. The equilibrium adsorption capacity q_e and the second order rate constant k_2 can be obtained from the plot of t/q_t against t . The model parameters and the equilibrium concentration obtained by both the models are given in Table 3. From the results it can be observed that both pseudo-first and pseudo-second order models are matching with the experimental kinetics data. From the better correlation coefficient and the fact that the equilibrium concentration obtained by the pseudo-second order plot (209 mg/g) is more close to the experimental value than that obtained from the pseudo-first order plot (141.5 mg/g), it can be concluded that pseudo-second order model is more relevant to explain the kinetics of adsorption of uranium on CTPP beads.

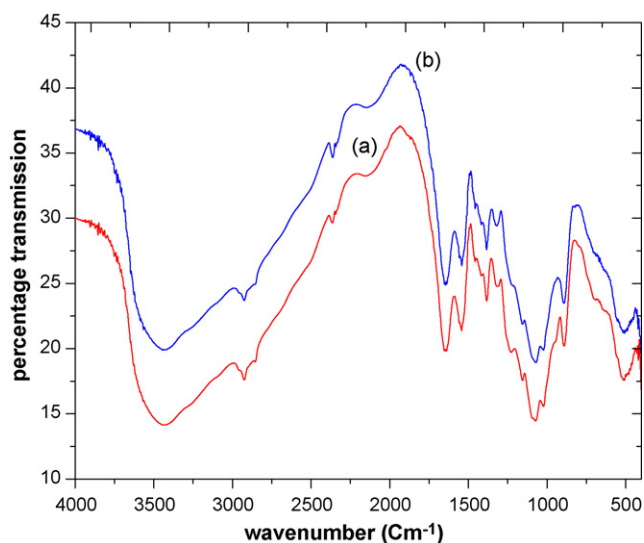


Fig. 8. FTIR spectra of CTPP beads before (a) and after (b) adsorption of uranium.

Adsorption of the metal ions to the active sites of the adsorbent depends on the concentration level of metal ions near the vicinity of the binding sites. Concentration distribution within the beads is controlled by the intraparticle diffusion and in many cases the Fickian diffusion equation is applicable to explain the sorption process [34], which can be expressed as:

$$q_t = k_{id} \times t^{1/2} \quad (7)$$

where q_t is the adsorption capacity (mg/g) at time t , and k_{id} is the intraparticle diffusion constant ($\text{mg g}^{-1} \text{h}^{-1}$). The plot of quantity adsorbed (q_t) at time t as a function of \sqrt{t} gives a straight line, from which the intraparticle diffusion constant, k_{id} can be obtained. The experimental curve (Fig. 6) gives three straight lines with three different slopes (all with $r^2 \geq 0.97$). Thus it is clearly evident that intraparticle diffusion is not applicable to the entire time scale of the adsorption process. The initial straight line, which corresponds to the fast adsorption, could be due to the surface adsorption on the dried beads where intraparticle diffusion has no significant contribution. Similarly the last straight line might be corresponding to the chemical equilibration of uranium in the swollen CTPP beads. Among the three lines, one corresponding to the intermediate time scales has the best statistical fit as per the intraparticle diffusion model. Thus it can be assumed that uranium diffusion inside the beads have significant influence in controlling the kinetics of uranium sorption at intermediate time scales. However it should be noted that this straight line does not pass through the origin which means intraparticle diffusion is not the sole rate determining factor controlling the adsorption of uranium onto CTPP beads. Similar three-stage kinetics was earlier reported for the sorption of humic acid by cross-linked chitosan beads [34].

3.7. Mechanism of uranium adsorption on CTPP beads

Two potential binding sites in CTPP beads available for the adsorption of uranium is presented in Fig. 7 [27]. Highly cross-linked beads used for the adsorption studies were prepared at pH = 3, where most of the amine groups are protonated. Ionic cross-linking with tripolyphosphate might have consumed most of these amino groups, thus not available for binding of uranium. Thus the principal functional groups responsible for uranium adsorption by CTPP beads might be the phosphate group. In order to identify the functional groups responsible for the adsorption of uranium onto CTPP beads, FTIR spectra of the CTPP beads were recorded

after the adsorption of uranium. Fig. 8 presents the FTIR spectra of the CTPP beads before and after adsorption of uranium. Significant decrease in the peak at 1230 cm^{-1} corresponding to $-\text{P}=\text{O}$ stretching vibration in the spectrum after adsorption of uranium indicates that phosphate groups are affected due to the adsorption process. Though the peak at 1319 cm^{-1} corresponding to $-\text{C}-\text{N}$ stretching vibration is slightly shifted, no significant change is observed in the peak position of any other major peaks corresponding to nitrogen and oxygen functional groups. Thus from the spectral characterization of the beads, it is evident that phosphate groups are the major contributor for the adsorption of uranium (binding site I), though it does not preclude some involvement of the amino groups (binding site II) in the adsorption process.

4. Conclusion

CTPP beads were found to have good adsorption capacity for uranium from aqueous solution. Adsorption capacity is found to be more for higher cross-linked CTPP beads than that for the lower cross-linked beads, regardless of the pH of the experimental solution. For beads with higher cross-linking, adsorption capacity is found to depend on the solution pH, and maximum adsorption capacity is observed at pH = 5. Langmuir adsorption isotherm is found to be more suitable to explain the adsorption of uranium onto CTPP beads than Freundlich model. Kinetics of adsorption of uranium by CTPP beads is found to be slow, taking around 3 days to complete the equilibrium, probably due to slow diffusion of the bulky uranium species into the beads. The observed adsorption kinetics data matches with the pseudo-second order model, indicating that the adsorption is dominated by chemisorption. Application of the intraparticle diffusion model gave three straight line portions in the experimental curve, showing the limited utility of this model, in explaining the observed kinetics. From characterization of the beads before and after uranium adsorption using FTIR, it is concluded that phosphate groups are more responsible for the uranium uptake by CTPP beads than the amino groups.

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References

- [1] D. Brugge, J.L. de Lomos, B. Oldmixon, Exposure pathways and health effects associated with chemical and radiological toxicity of natural uranium, *Rev. Environ. Health* 20 (2005) 177–193.
- [2] USEPA, EPA Integrated Risk Information System (IRIS), Electronic Database, USEPA, Washington, DC, 1996.
- [3] S.M. Grashchenko, Naturally occurring radionuclides of uranium and thorium series in non nuclear industrial process, *Radiochemistry* 47 (2005) 614–618.
- [4] A.P. Kryvoruchko, L.Y. Yurlova, I.D. Atamanenko, B.Y. Kornilovich, Ultrafiltration removal of U(VI) from contaminated water, *Desalination* 162 (2004) 229–239.
- [5] X. Shuibao, Z. Chun, Z. Xinghuo, Y. Jing, Z. Xiaojian, W. Jingsong, Removal of uranium(VI) from aqueous solution by adsorption on hametite, *J. Environ. Radioact.* 100 (2008) 162–166.
- [6] S.Y. Lee, E.A. Banditti, Removing uranium from drinking water by metal hydroxide and anion exchange resin, *J. Am. Water Works Assoc.* 75 (1983) 536–542.
- [7] D. Clifford, Z. Zhang, Modifying ion exchange for combined removal of uranium and radium, *J. Am. Water Works Assoc.* 86 (1994) 214–227.
- [8] I.A. Katsoyiannis, H.W. Althoff, H. Bartel, M. Jekel, The effect of groundwater composition on uranium(VI) sorption onto bacteriogenic iron oxides, *Water Res.* 40 (2006) 3646–3652.
- [9] S. Yusan, S. Akyil, Sorption of uranium (VI) from aqueous solution by akaganeite, *J. Hazard. Mater.* 160 (2008) 388–395.
- [10] C. Gok, S. Aytas, Biosorption of uranium (VI) from aqueous solution using calcium alginate beads, *J. Hazard. Mater.* 168 (2009) 369–375.

- [11] T.S. Anirudhan, C.D. Bringle, S. Renjith, Removal of uranium (VI) from aqueous solution and nuclear industry effluents using humic acid immobilized zirconium-pillared clay, *J. Environ. Radioact.* 101 (2010) 267–276.
- [12] D. Chauhan, N. Shankaramakrishnan, Highly enhanced adsorption for decontamination of lead ions from battery wastewaters using chitosan functionalized with xanthate, *Bioresour. Technol.* 99 (2008) 9021–9024.
- [13] X. Liu, Q. Hu, Z. Fang, X. Zhang, B. Zhang, Magnetic chitosan nanocomposite: a useful tool for heavy metal ion removal, *Langmuir* 25 (2009) 3–8.
- [14] E. Guibal, Interaction of metal ions with chitosan based sorbents: a review, *Sep. Purif. Technol.* 38 (2004) 43–74.
- [15] P.A. Miretzky, F. Cirelli, Hg(II) removal from water by chitosan and chitosan derivatives: a review, *J. Hazard. Mater.* 167 (2009) 10–23.
- [16] E. Metwally, S.S. Elkholy, H.A.M. Salem, M.Z. Elsabee, Sorption behavior of ^{60}Co and $^{152+154}\text{Eu}$ radionuclides on to chitosan derivatives, *Carbohydr. Polym.* 72 (2009) 622–631.
- [17] J. Cao, Y. Tan, Y. Che, H. Xin, Novel complex gel beads composed of hydrolysed poly acrylamide and chitosan: an effective adsorbent for the removal of heavy metal form aqueous solution, *Bioresour. Technol.* 101 (2010) 2558–2561.
- [18] A. Sabarudin, M. Oshima, T. Takayanagi, L. Hakim, K. Oshita, Y.H. Gao, S. Motomizu, Functionalisation of chitosan with 3,4-dihydroxy benzoic acid for the adsorption/collection of uranium in water samples and its determination by inductively coupled plasma mass spectrometry, *Anal. Chim. Acta* 581 (2007) 214–220.
- [19] S. Dutta, P.K. Mohapatra, S.P. Ramnani, S. Sabharwal, A.K. Das, V.K. Manchanda, Use of chitosan derivatives as solid phase extractors for metal ions, *Desalination* 232 (2008) 234–242.
- [20] K. Oshita, M. Oshima, Y. Gao, K.H. Lee, S. Motomizu, Synthesis of novel chitosan resin derivatized with serine moiety for the column collection/concentration of uranium and the determination of uranium by ICP-MS, *Anal. Chim. Acta* 480 (2003) 239–249.
- [21] G. Wang, J. Liu, X. Wang, Z. Xie, N. Deng, Adsorption of uranium(VI) from aqueous solution onto cross-linked chitosan, *J. Hazard. Mater.* 168 (2009) 1053–1082.
- [22] E. Guibal, M.J. Charrier, I. Saucedo, P.L. Cloirec, Enhancement of metal ion sorption performance of chitosan: effect of the structure on the diffusion properties, *Langmuir* 11 (1995) 591–598.
- [23] R.A.A. Muzzarelli, Removal of uranium from solutions and brines by a derivative of chitosan and ascorbic acid, *Carbohydr. Polym.* 5 (1985) 85–89.
- [24] R. Akkaya, U. Ulusoy, Adsorptive features of chitosan entrapped in poly acrylamide hydrogel for Pb^{2+} , UO_2^{2+} and Th^{4+} , *J. Hazard. Mater.* 151 (2008) 380–388.
- [25] A.A. Atia, Studies on the interaction of mercury(II) and uranyl(II) with modified chitosan resin, *Hydrometallurgy* 80 (2005) 13–22.
- [26] S.T. Lee, F.L. Mi, Y.J. Shen, S.S. Shyu, Equilibrium and kinetic studies of copper(II) uptake by chitosan-tripolyphosphate chelating resin, *Polymer* 42 (2001) 1879–1892.
- [27] W.S.W. Ngah, S. Fatinathan, Adsorption characterisation of Pb(II) and Cu(II) ions onto chitosan tripolyphosphate beads: kinetic, equilibrium and thermodynamic studies, *J. Environ. Manage.* 91 (2010) 958–969.
- [28] F.L. Mi, S.S. Shyu, S.T. Lee, T.B. Wong, Kinetic study of chitosan-tripolyphosphate complex reaction and acid-resistive properties of the chitosan-tripolyphosphate gel beads prepared by in-liquid curing method, *J. Polym. Sci. B* 37 (1995) 1551–1564.
- [29] A. Suresh, D.K. Pâté, T.G. Srinivasan, P.R. Vasudeva Rao, A new procedure for the spectrophotometric determination of uranium(VI) in the presence of large excess of thorium(IV), *Spectrochim. Acta A* 58 (2002) 34–347.
- [30] S.K. Das, S.G. Rege, A. Mukherjee, A. Ramanujam, R.K. Dhumwad, Direct spectrophotometer method for the determination of microgram quantities of uranium with Br-Padap in aqueous and organic waste streams of PUREX and THOREX process. BARC Report No. 1593, 1991.
- [31] E. Guibal, C. Milot, J.M. Tobin, Metal anion sorption by chitosan beads: equilibrium and kinetics studies, *Ind. Eng. Chem. Res.* 34 (1998) 1463–1554.
- [32] L. Maya, Hydrolysis and carbonate complexation of dioxouranium(VI) in the neutral-pH range at 25 °C, *Inorg. Chem.* 21 (1982) 2895–2898.
- [33] B. Kannamba, K.L. Reddy, B.V. Apparao, Removal of Cu(II) from aqueous solutions using chemically modified chitosan, *J. Hazard. Mater.* 175 (2010) 935–948.
- [34] W.S.W. Ngah, M.A.K.M. Hanafiah, S.S. Yong, Adsorption of humic acid from aqueous solution on cross-linked chitosan-epichlorohydrin beads: kinetic and isotherm studies, *Colloids Surf. B* 65 (2008) 18–24.