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Kinetics studies of uranium sorption by powdered corn cob in batch and fixed bed system

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A R T I C L E   I N F O

A B S T R A C T

Sorption of uranium (VI) from aqueous solution onto powdered corn cob has been carried out using batch and fixed-bed technique. The experimental results in batch technique were fitted well with pseudo second-order kinetics model. In the fixed bed technique, Thomas and Bohart–Adams models were evaluated by linear regression analysis for U(VI) uptake in different flow rates, bed heights and initial concentrations. The column experimental data were fitted well with Thomas mode ($r^2 = 0.999$), but the Bohart–Adams model ($r^2 = 0.911$), predicted poor performance of fixed-bed column.

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Introduction

The growth of technology in nuclear industries has led to the emergence of many of environmental pollution problems, it is so important to develop number of methods for removing hazardous elements from industrial liquid wastes. Uranium is the important element in nuclear applications. Nuclear power is derived from uranium, which has no significant commercial use other than as a fuel for electricity generation. For this reason, the recovery, concentration and purification of uranium are of great importance. Because of the expected shortage of uranium in near future, researches are to be directed to the recovery of uranium from nonconventional resources such as sea water, industrial waste waters, mine waste water, and other waste sources in relation to the pollution of the natural environment [1,2]. The most commonly used methods for the removal of heavy metals from wastewater are chemical precipitation; membrane processes, ion exchange, solvent extraction, photocatalysis and adsorption [3]. Adsorption process has long been used in the removal of heavy metals and other hazardous materials such as, color, odor and organic pollution.

Although activated carbon is widely applied for pollutant removal, natural materials which are relatively cheaper and eco-friendly have also been successfully employed as adsorbents for heavy metal removal from aqueous solutions and

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wastewaters due to their availability, low-cost, unique chemical composition and renewability. The reduced running cost has been the focal point for research on application of natural materials. Cost is a very important factor when considering material for use as adsorbents. The recent attention in this field is evident in the number of research currently being done on the use of low cost agricultural wastes for metal removal from aqueous solution. Among the numerous adsorbents, Agriculture material is one of the most widely used and economic adsorbent in the adsorption process such as coir pith [4], orange peels [5], palm-shell [6], rice straw [7], cellulose beads [8] sunflower [9], has been investigated. The objective of this study was to investigate the adsorption potential of uranium (VI) onto powdered Corn cob (PCC) in batch and fixed-bed technique. In batch process kinetics of uranium removal onto PCC at different parameters (temperature, pH, initial concentration, and adsorbent dose) are investigated. The performance of fixed-bed column was evaluated by Thomas and Bohart–Adams models at different flow rates, bed heights and initial concentrations.

Material and methods

Preparation of adsorbent material

Corn cob is an agricultural by-product generated in Middle East. Corn cobs were washed with distilled water several times to remove dirt and particulate materials. The washed Corn cobs were dried at 80 °C. The dried corncobs were ground and sieved to obtain powdered Corn cob (PCC), of a particle size 300–425 μm and stored in dissector for further use.

Preparation of uranium stock solution

All chemicals and reagents used in this work were analytical grade. Stock solution of uranium (VI) was prepared by dissolving appropriate amounts of UO$_2$(NO$_3$)$_2$·6H$_2$O, Aldrich, USA, in distilled water. For experiments the required concentration was prepared by dilution. The concentrations of U(VI) in solution were determined spectrophotometrically employing Shimadzu UV–VIS-1601 spectrophotometer using arsenazo (III) as complexing reagent [10].

Sorption experiments in batch technique

Batch experiments were first carried out to determine the potential of PCC to adsorb U(VI)) from aqueous solution and to investigate the optimum parameters of adsorption (adsorbent dose, contact time, pH, temperature, and initial concentration). 50 mL of different concentrations (25–100 mg/L) of U(VI) solutions with a range of pH values from 3 to 10 was transferred in a conical flask with 0.3 g of PCC. The solution was agitated at 200 rpm in a thermostatic shaker water bath for different time (10–180 min) at different temperature (303, 313, 323 and 333 K). The samples were withdrawn and centrifuged at 5000 rpm for 5 min and the supernatant solutions were analyzed. The pH of the solutions was adjusted with 0.1 M Na$_2$CO$_3$ or 0.1 N HCl.

Sorption capacity and removal efficiency

Sorption capacity (q) of U(VI) was defined as:

$$q = (C_0 - C_e)V/M \tag{1}$$

In addition, the removal efficiency (R_e) is calculated according to the following equation:

$$R_e(\%) = [(C_0 - C_e)/C_0] \times 100 \tag{2}$$

Sorption kinetics in batch technique

Kinetics of sorption of U(VI) onto PCC was analyzed using two kinetic models (pseudo first-order and pseudo second-order models). The comparing between data of experiments and models was analyzed by the correlation coefficients (r^2).

Pseudo-first-order model

Lagergren's equation of pseudo first-order model describes the sorption capacity of solids in solid–liquid systems [11,12]. It is supposed that one adsorbate is adsorbed onto one sorption site on adsorbent surface.

The linear form of pseudo first order model was given by equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

Values of k_1 and q_e were calculated from the slope and intercept values of the straight line of plotting log $(q_e - q_t)$ versus t, respectively.

Pseudo-second-order model

The pseudo second-order model has been applied for the analysis of kinetics of chemisorption from liquid solutions. The linear form of pseudo-second order model [13,14], given by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

The plot of t/q_t versus t should give a straight line and the K_2 and q_e were calculated from the values of intercept and slope, respectively.

Sorption experiments in fixed-bed technique

Glass column of 2 cm internal diameter and 30 cm height was used in fixed bed experiments. PCC was packed with different bed heights (2.5, 5 and 7.5 cm) in the column with a layer of glass wool at the bottom. Three flow rates (1, 2 and 3 mL/min) were pumped to the top of the packed column by using peristaltic pump with different initial ion concentrations (25, 50, 75 mg/L) at 303 K. The effluent samples were collected at regular intervals and analyzed. Fixed bed studies were terminated when the column reached exhaustion.

Kinetic models of break through curves in fixed-bed column

For good design of fixed bed system, it is important to predict the breakthrough curve for effluent parameters. Thomas [16], Bohart–Adams [17] kinetic models were used to predict the dynamic behavior of the column.

Thomas model
Thomas model is one of the most widely used models in column performance studies. Thomas model is given in linear form by the following expression:

$$Ln[(C_0/C_t) - 1] = [(K_{Th}q_e \, x/Q) - K_T h C_0 \, t] \tag{5}$$

The parameters of Thomas model (k_{Th} and q_e) can be determined from a plot of $Ln\,[(C_0/Ct) - 1]$ against time (t) at a given flow rate.

Bohart–Adams model
Bohart–Adams model is used for the description of the initial part of the breakthrough curve. The linear form of Adam-Bohart model is given by the following expression:

$$Ln(C_t/C_0) = [(K_{AB}C_0 \, t) - (K_{AB}N_0 \, Z)/F] \tag{6}$$

The parameters k_{AB} and N_0 were determined from the intercept and slope of linear plot of $ln\,(C_t/C_0)$ against time (t), respectively.

Results and discussion

Characteristics of adsorbent

Fig. 1(a) and (b), represents the SEM photographs of adsorbent before and after sorption with 500× magnification. Fig. 1(a), shows that the adsorbent surface is rough, porous and irregular shapes allowing for good sorption between U(VI) ions and PCC. After sorption, Fig. 1(b), shows the loss of porosity and roughness of the adsorbent surface.

The FTIR spectrum of PCC before and after sorption (Fig. 2) displays a number of sorption peaks, indicating the complex nature of the adsorbent material. The band at $3417\,cm^{-1}$ was assigned to the OH group in free alcohols. The band at $2920\,cm^{-1}$ was assigned to the C—H stretching. The band at $1615\,cm^{-1}$ was assigned to the asymmetric stretching of —COO— in ionic carboxylic group. The band at $1388\,cm^{-1}$ was assigned to the symmetric —COO— stretching in pectin. The band at $1012\,cm^{-1}$ was assigned to the C—OH stretching in alcohols. After metal loading, the C=O deformation band ($1384\,cm^{-1}$) in pectin remained constant while shifts occurred in the wave numbers 3417, 2920 and $1615\,cm^{-1}$ indicating an interaction of these functional groups with sorbed U(VI) and also the appearance of wave number
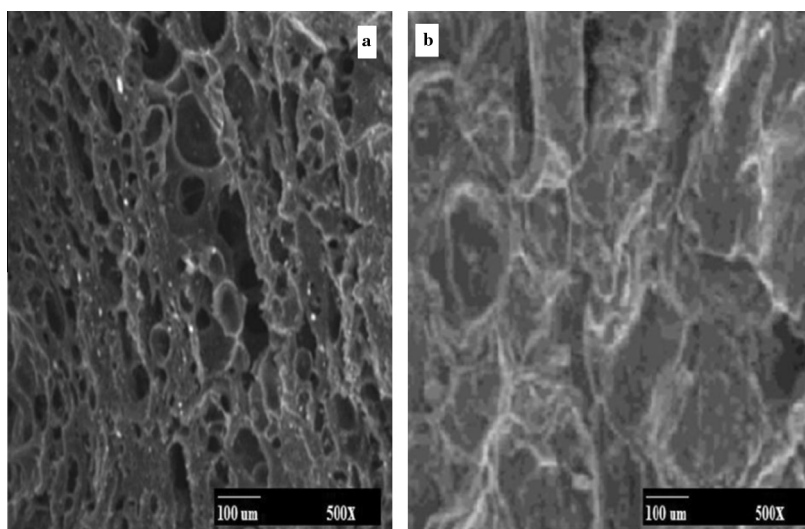

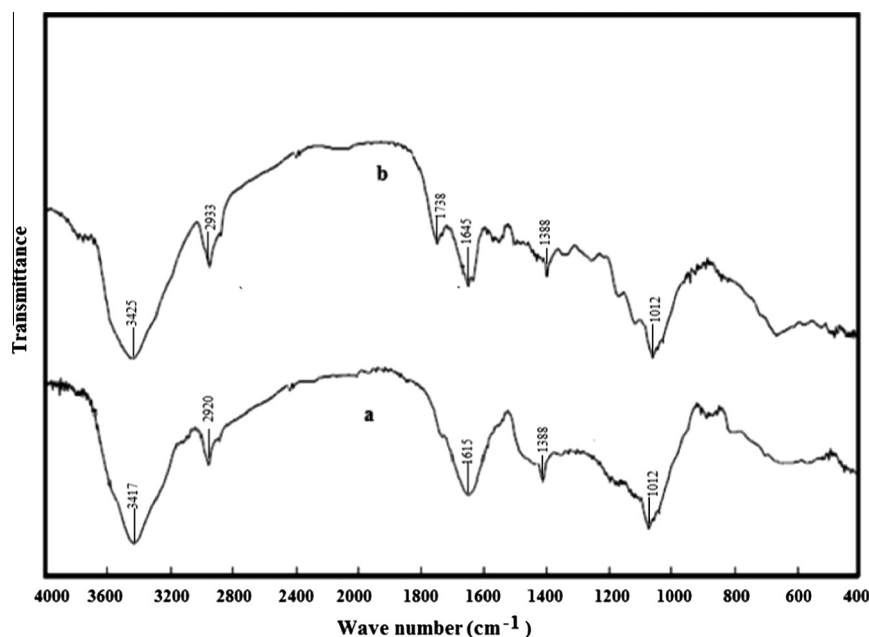**Fig. 1** SEM image of unloaded PCC (a) U(VI) loaded PCC(b).

Fig. 2 FTIR spectrum of unloaded PCC (a) U(VI) loaded PCC (b).

Table 1 Parameters of batch sorption of U(VI) onto PCC.

Parameter		Removal efficiency (Re %)	q (mg/g)
pH:	3	85.55	3.56
(Condition: 25 mg L^{-1}, 0.3 g, 3 h, 303 K)	4	93.20	3.88
	5	98.26	7.22
	6	95.14	4.07
	7	90.21	4.03
	8	70.03	3.13
	10	42.56	1.77
Initial concentration (mg/L):	25	98.26	7.220
(Condition: pH = 5, 0.3 g, 60 min, 303 K)	50	98.39	8.199
	75	98.50	12.31
	100	85.32	14.21
Adsorbent dose (g):	0.1	30.16	11.31
(Condition: 75 mg L^{-1}, 60 min, pH = 5, 303 K)	0.3	98.50	12.31
	0.6	98.50	6.156
	0.9	98.50	4.104
	1.2	98.50	3.07
Temperature (K):	303	98.50	12.31
(Condition: 75 mg L^{-1}, 60 min, 0.3 g, pH = 5)	313	91.58	11.44
	323	80.38	10.04
	333	55.29	6.911

1738 cm^{-1} in the U(VI) loaded spectra may indicate the interaction of this group with U(VI) ion.

Adsorption dynamics

Table 1 shows that the sorption of U(VI) by PCC was found to be increased with increasing the time and attained a maximum value at 60 min (Fig. 3). The U(VI) uptake increased with changing pH of U(VI) solution from 3 to 10. The decreasing of sorption capacity at lower pH is due to the competition between H$^+$ and U(VI) ions. However, with increasing pH

the sorption capacity increased probably due to the decreased H$^+$ concentration that provided more sorption sites for U(VI) ions. The optimum pH for U(VI) uptake by PCC was at pH 5 (Fig. 3). The decreasing in the uptake of U(VI) after pH 5 is due to the formation of stable complexes UO_2CO_3, [UO_2-CO_3]$_{2-}$ [15]. On changing the initial concentration of U(VI) solution from 25 to 100 mg/L, the sorption capacity of U(VI) increased from 7.22 mg/g to 14.21 mg/g. The uptake of U(VI) was studied using different doses of PCC (0.3, 0.6, 0.9 and 1.2 g). The results indicated that the percent of sorption increased with increase PCC dose due to the increasing
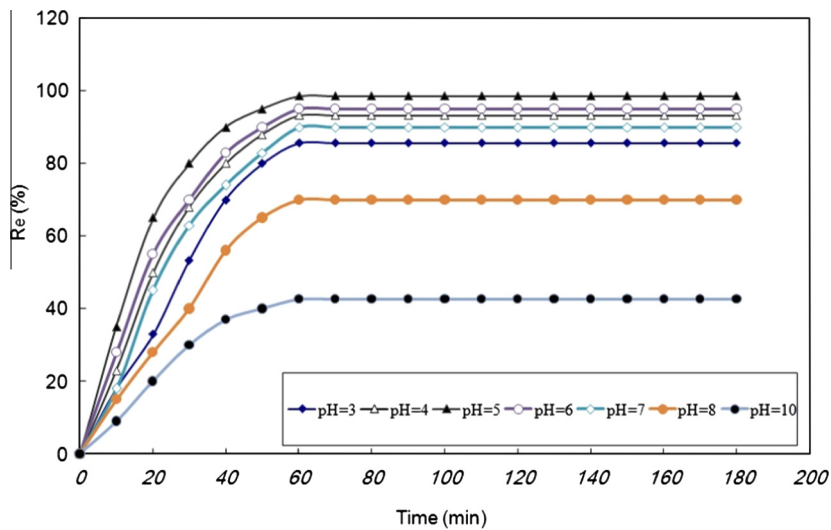
Fig. 3 Effect of pH on the sorption of U(VI) onto PCC at different times.

Table 2 Kinetics data for adsorption of U(VI) onto PCC.

Parameter		Pseudo first-order (Lagergren)			Pseudo second-order		
		K_1	q_e	r^2	K_1	q_e	r^2
pH	3	0.0578	2.786	0.913	0.0409	6.483	0.987
(Condition: 25 mg $^{-1}$, 0.3 g, 3 h, 303 K)	4	0.0786	3.733	0.924	0.0585	6.949	0.986
	5	0.0943	4.363	0.901	0.0725	7.313	0.979
	6	0.1007	4.592	0.826	0.0913	7.273	0.986
	7	0.1089	3.710	0.881	0.1125	7.145	0.987
	8	0.1120	3.080	0.870	0.1289	6.340	0.998
	10	0.1243	2.043	0.899	0.1306	3.240	0.989
Adsorbent dose (mg/L)	0.1	0.0722	4.034	0.756	0.0865	5.254	0.991
(Condition: 25 mg L^{-1}, 60 min, pH = 5, 303 K)	0.3	0.0983	5.223	0.888	0.0981	7.313	0.989
	0.6	0.1121	5.508	0.893	0.1023	8.620	0.988
	0.9	0.1303	6.523	0.865	0.1244	10.932	0.984
	1.2	0.1432	5.587	0.911	0.1336	10.911	0.989
Temperature (°C)	303	0.1132	6.033	0.912	0.0523	7.313	0.998
(Condition: 25 mg L^{-1}, 60 min, 0.3 g, pH = 5)	313	0.1213	4.150	0.915	0.0861	6.012	0.996
	323	0.1345	4.256	0.928	0.1121	4.132	0.999
	333	0.1397	3.143	0.933	0.1253	3.189	0.995
Initial concentration (mg/L)	25	0.0432	6.128	0.821	0.0785	7.313	0.996
(Condition: pH = 5, 0.3 g, 60 min, 303 K)	50	0.1138	7.221	0.901	0.0958	8.874	0.998
	75	0.1302	6.570	0.861	0.1107	10.51	0.998
	100	0.1427	5.335	0.866	0.1203	14.21	0.987

of sorption sites. The effect of temperature on the sorption of was studied from 301 to 333 K. The results indicate that increasing the temperature of the solution decreasing the removal of U(VI) indicating that the process is exothermic in nature. The values of correlation coefficients, (r^2) in the results of kinetics data (Table 2), showed good compliance with the pseudo second-order kinetic model than pseudo first-order kinetic model (Fig. 4).

Column adsorption

Effect of flow rate

The fixed bed study was carried out at different flow rates of 1, 2 and 3 L min^{-1} using 75 mg L^{-1} initial U(VI) concentration,

7.5 cm bed height, pH 5 and at 303 K. Fig. 5 shows that the breakthrough curve occurred faster at higher flow rate. This is because the lower residence time of the influent in the column, thus reducing the contact time between U(VI) and the PCC. Similar trend has been studied by using orange peels to remove U(VI) from aqueous solution [18].

Effect of bed height

The effects of bed heights of 2.5, 5 and 7.5 cm were studied at influent concentration of 75 mg L^{-1}, 1 L min^{-1} flow rate, and pH 5 and at 303 K. Fig. 6 shows that the breakthrough time decreased with increasing the bed height. Increasing the bed height, increase the number of sorption sites and the residence
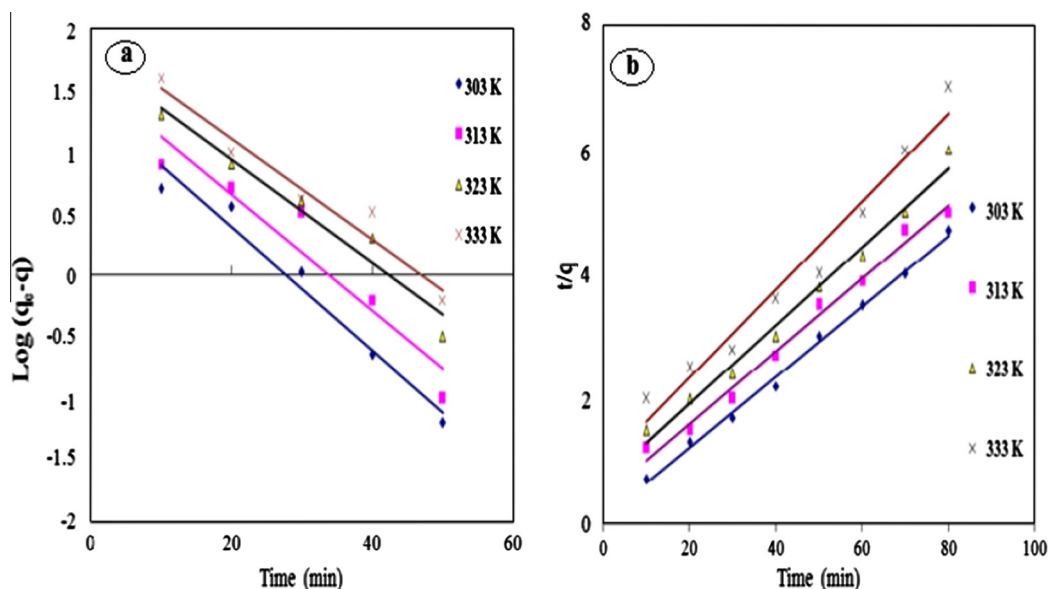
Fig. 4 Pseudo-first order (a) and Pseudo-second order (b) kinetic models for U(VI) onto PCC at different temperatures.
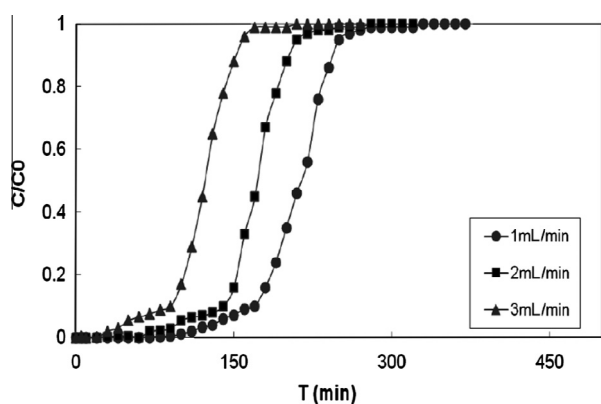

Fig. 5 Breakthrough curves for adsorption by PCC at different flow rates.
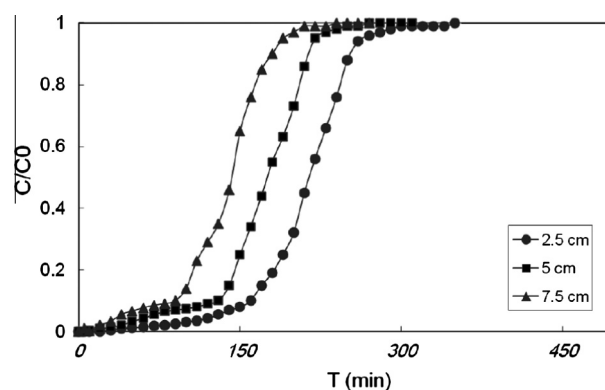

Fig. 7 Breakthrough curves for U(VI) adsorption by PCC at different bed heights.

Effect of initial concentration

The increasing effect of initial U(VI) concentration from 25 to 75 mg/L at constant bed height of 7.5 cm, flow rate of 1 mL/min, pH 5 and at 303 K in the breakthrough curves is shown in Fig. 7. It is observed that the break point time decreased with increased initial U(VI) concentration from 25 to 75 mg/L. On increasing the initial ion concentration, the breakthrough curves became steeper and breakthrough volume decreased because of the lower mass-transfer system from the bulk solution to the adsorbent surface [19,20].

Evaluation of kinetics models in fixed-bed column

Thomas model

The column data were fitted to the Thomas model to determine the Thomas rate constant (k_{Th}) and maximum sorption capacity (q_e). Table 2 shows that the column bed height and initial concentration increased the values of k_{Th} and q_e decreased and increased, respectively. This is due to the dhriving
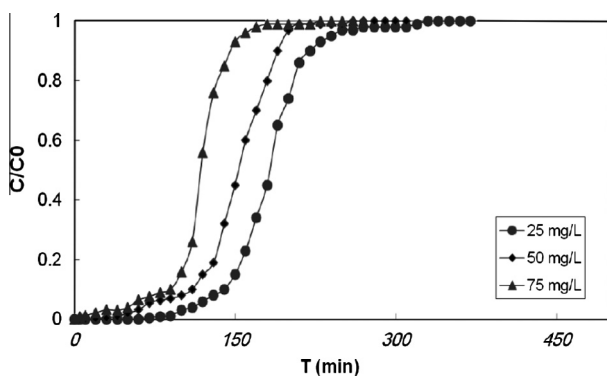

Fig. 6 Breakthrough curves for U(VI) adsorption by PCC at different initial U(VI) concentrations.

time of the U(VI) in the column, thus increasing the removal efficiency of U(VI) in the fixed bed system.

Table 3 Thomas and Bohart–Adams model parameters using linear regression analysis for U(VI) adsorption under various operating conditions.

Model type	Flow rate (mL/min)	Bed height (cm)	Initial concentration C_0 (mg/L)	$q_{e,max}$ (mg/g)	k_{Th} (mL/min mg)	R^2
Thomas model	1	7.5	75	8.054	0.310	0.988
	2	7.5	75	4.321	0.611	0.998
	3	7.5	75	3.331	0.830	0.999
	1	2.5	75	4.230	0.342	0.976
	1	5	75	5.620	0.391	0.989
	1	7.5	50	2.331	0.730	0.988
	1	7.5	25	1.381	1.140	0.989
Bohart–Adams model	Flow rate (mL/min)	Bed height (cm)	C_0 (mg/L)	N_0 (mg/L)	k_{AB} (L/min mg)	R^2
	1	7.5	75	4.133	0.344	0.822
	2	7.5	75	2.560	0.525	0.901
	3	7.5	75	0.980	0.731	0.841
	1	2.5	75	1.933	0.645	0.730
	1	5	75	2.980	0.520	0.911
	1	7.5	25	1.223	0.670	0.867
	1	7.5	50	2.334	0.443	0.854
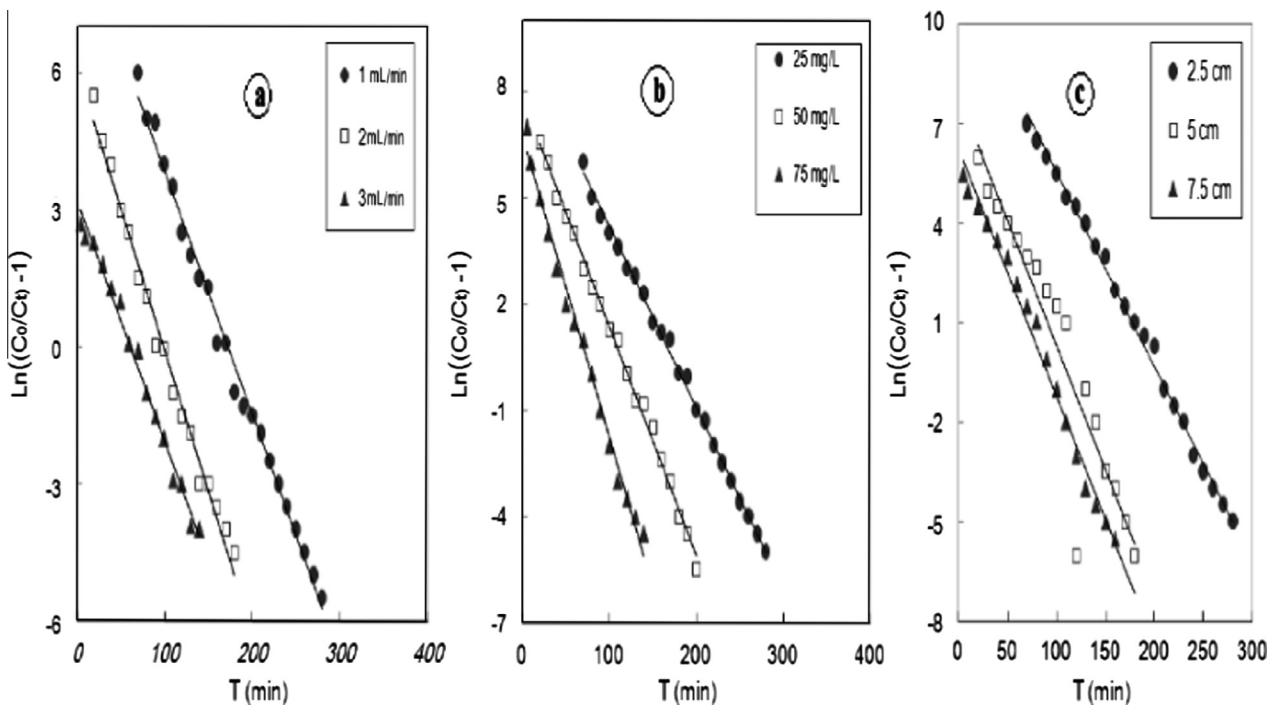
Fig. 8 Linear plot of Thomas model with experimental data at different flow rates, initial U(VI) concentrations and bed heights.

force of adsorption process is the difference between the concentration of uranium ions in the solution and on the adsorbent [21,22]. As the flow rate increased, the value of k_{Th} increased, but the value of $q_{e,max}$ decreased. The values of r^2 of kinetic model ranged from 0.968 to 0.998, indicating good linearity. Table 3 and Fig. 8 indicate that Thomas model is suitable for sorption of U(VI) with PCC.

Bohart–Adams model

Bohart–Adams rate constant, K_{AB} and capacity of the adsorbent (N_0) are dependent on flow rate, initial ion concentration and bed height. From Table 2, it can be seen that the values of kinetic constant (k_{AB}) and capacity of the adsorbent (N_0) decreased and increased with increasing bed height and initial

uranium concentration, respectively. Sorption capacity (N_0) decreased with increasing flow rate, but the value of k_{AB} increased with increasing flow rate (Fig. 9). From results of linear plots of both Thomas and Bohart–Adams model at different heights, flow rates, and concentrations (Table 3), it was observed that Thomas model is appropriate models to describe fixed-bed system. But in the case of Bohart–Adams model, low correlation coefficient ($r^2 = 0.925$) is observed, which indicate that Bohart–Adams model is not as appropriate a predictor for the breakthrough curve, so that the design calculations of large scale were performed using Thomas models. Table 4, shows the comparison between adsorption capacities of PCC and some of available and low-cost adsorbents for U(VI) uptake from aqueous solutions reported in the literature.
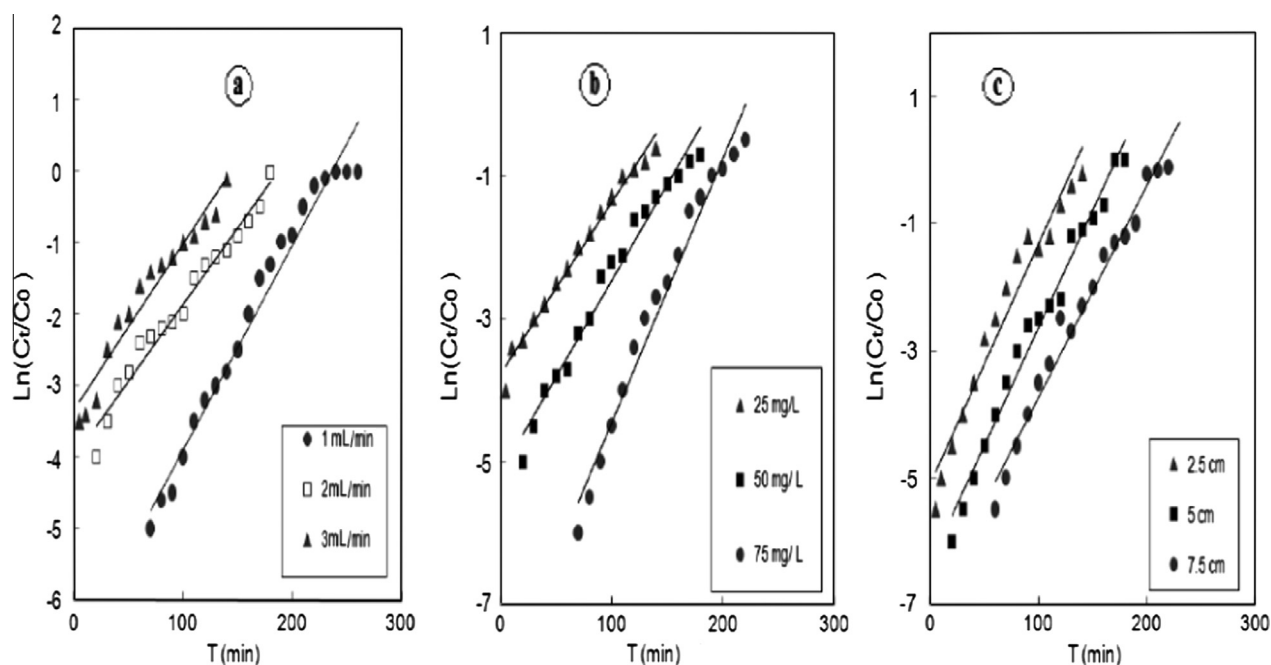
Fig. 9 Linear plot of Bohart–Adams model with experimental data at different flow rates, initial U(VI) concentrations and bed heights.

Table 4 Comparison between adsorption capacities of PCC and some adsorbents for U(VI) uptake from aqueous solutions.

Adsorbents	Adsorption capacity(mg/g)	Reference
Activated carbon	28.50	[2]
Coir pith	28.00	[4]
Orange peels	15.91	[5]
Palm-shell	25.10	[6]
Sunflower	13.45	[9]
Date pits	10.00	[23]
Natural clay	3.53	[24]
Powdered corncob	14.21	The present study

Conclusions

In this work, PCC has good ability to remove U(VI) from aqueous solution in batch and fixed bed system. The experimental results in batch technique were fitted well with pseudo second-order than pseudo first-order kinetics model. The uptake of uranium ions in fixed bed system depends on flow rate, bed height and initial concentration. Thomas and Bohart–Adams kinetic models were used to evaluate the performance of fixed bed column. The value of correlation coefficients of Bohart–Adams model was generally lower than Thomas model under the same experimental conditions. The column experimental data were good fitted with Thomas model, but the Bohart–Adams model predicted poor performance of fixed-bed column.

Conflict of interest

The author has declared no conflict of interest

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects

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