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Insights into the adsorption capacity and breakthrough properties of uranium onto rice straw based activated carbon impregnated with ionic-liquid

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ABSTRACT

This study is concerned with uranium adsorption on KOH-oxidized rice and impregnated with ionic-liquid straw-based carbon (RSK carbon) in adsorption contacting systems of batch-type and fixed bed. In this concern, experiments were performed using uranium solution of various initial concentration (100, 200, 400 mg/L); different flow rates (3, 5, 10 ml/min) and different bed depths (3 cm, 6 cm and 12 cm). The data indicated that the adsorbed uranium quantity increased with increasing bed depth, decreasing inlet concentration and flow rate. The difference between isotherm and column values is reasonable due to inherent difference in the nature of batch and continuous operations, in the batch mode equilibrium takes place and there is not continuous feeding from solution but in fixed bed, solution was fed continuously without sufficient time to attain equilibrium. Although the predictive model has been failed in producing breakthrough data on high level of accuracy, the study provided useful information's for design of fixed bed column for uranium-activated carbon system.

Keywords: Breakthrough curve; Fixed-bed column; Activated carbon; Uranium adsorption

1. Introduction

Uranium is radioactive toxic element to human being [1] and its radioactive pollution is hard to prevent [1–3]. Uranium containing wastewater comes mainly from mining/milling and radioactive activities [4] and it was needed an effective method to for uranium removal. The well-known method includes precipitation, ionic liquid solvent extraction, ion exchange, and adsorption [5]. Adsorption method appears to be the most promising approaches due to it is easy operation, low cost and high efficiency [5,6].

Adsorption from solution can be done through batch and column modes [7]. Column mode is easy and flexible to be used in large-scale water treatment applications [2]. Adsorption column is recognized as a non-linear and a plot of the effluent concentration versus the volume of liquid treated (or time) usually yield S-shaped curve referred to as breakthrough curve. "The point on the S-shaped curve at which the solute concentration reaches its allowable maximum value" is referred to as breakthrough point. "The point where the effluent solute concentration reaches 95% of its influent" is usually called exhaustion point [8]. The time for breakthrough

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appearance and its shape are essential characteristics for determining the dynamic response and operation for adsorption column adsorption. Breakthrough time is the time when effluent concentration reaches 5% of feed one, i.e., $C_t = 0.05\ C_o$ and the exhaustion time when $C_t = 0.95\ C_o$ [9]. The shape of breakthrough curve depends on the i) feed concentration, ii) flow rate and iii) bed depth. The breakthrough would a step function for favorable separation i.e. effluent concentration quickly increases from zero to the feed concentration at the moment the column adsorption capacity is reached [10].

In the previous paper, we have reported the batch experimental removal of uranium (VI) by rice straw based activated carbon [11–14]. Batch mode provides important information on the efficiency of the uranium (VI)/carbon system. It gives certain initial information such as equilibrium time, maximum adsorption pH, maximum initial concentration, and lower dose for maximum adsorption of uranium (VI) ions in addition to the adsorption capacity of the adsorbent. But the adsorption behavior in column mode was not investigated. As a continuation of our previous batch experiments, present study aim to utilize RSK carbon for uranium adsorption in fixed-bed column. The effects of main variables such as bed depth, flow rate, and initial uranium concentration on the shape of the breakthrough curve were examined.

2. Experimental

2.1. Preparation and characterization of activated carbon

KOH-oxidized rice straw-based activated carbon was synthesized according to the method that was reported in our previous paper [11–13] and impregnated by ionic liquid using previously published procedure [14]. All main physicochemical properties including for ex. Porosity, FTIR and SEM images of RSK carbon were discussed in details in our previous publications [11–13]. As well as the relation between RSK carbon porosity and surface chemistry with uranium (VI) adsorption from aqueous solution was given in our earlier article [15].

2.2. Adsorption experiments

2.1 gm of uranyl nitrate was dissolved in 1 L DDW water to prepare 1000 mg/l stock uranium solution. 2 ml nitric acid was added to prevent the hydrolysis. Adsorption experiments of uranium were done by the addition of 20 ml uranium solution (100 mg/L and pH 5.5) to appropriate amount of RSK carbon. After 3 h of shaking, solutions were separated by filtration and uranium concentration was measured using coloring agent (arsenazo III) by the mean of UV spectrophotometer [16]. The activated carbon adsorption capacity was calculated using following equation:

$$q_e = \frac{V(C_i - C_e)}{m} \tag{1}$$

where C_o and C_e are initial and equilibrium concentration (mg/l) respectively, V (ml) is the solution volume, and m (g) is adsorbent mass used.

2.3. Column studies

In the column experiments, a predetermined amount of RSK carbon was sieved to a constant particle size of 590 µm washed by distilled water to remove fine particles then added to glass column (i.d. 0.8 cm) by the slurry method [17] to avoid the introduction of air bubbles in the column before adsorption experiment began. The presence air decreases the bed performance. Uranium solution of different concentrations (100, 200, 400 mg/L) is passed through the column at different flow rates (3, 5, 10 ml/min) using metering pump (Milton roy-USA) up to breakthrough happens. In all the column experiments, the effluent solutions were collected using fraction collector (spectra/Chrom CF-1) and uranium concentration measured by the UV spectrophotometer. The column experiments are summarized in Fig 1.

3. Results and discussion

Uranium sorption on RSK carbon under optimum conditions of equilibrium time (1 h) and pH (5.5) with various carbon quantities (5–100 mg) were performed that gave adsorption isotherm with the corresponding Freundlich and Langmuir parameters are shown in Table 1. According to the correlation coefficients (R^2), Langmuir isotherm fits experimental data fine with maximum adsorption capacity of 100 mg/g. These results demonstrating that homogenous uranium adsorption on RSK carbon. Uranium adsorption in

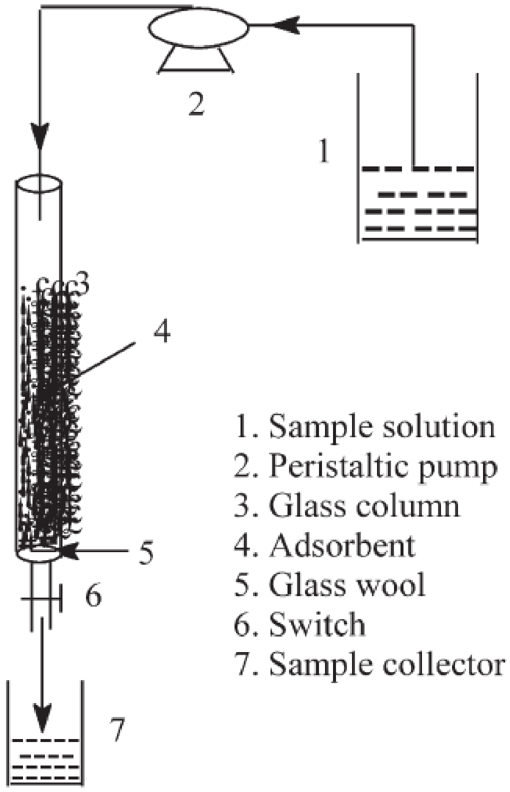

Fig. 1. Column experiments setup.

Table 1
Freundlich and Langmuir parameters of uranium adsorption onto RSK carbon

Model	Parameter	value
Freundlich	K (mg/g)	33.7
	n	3.5
	R^2	0.90
Langmuir	q^o (mg/g)	100
	b (1/mg)	0.28
	R^2	0.999

Table 2
Column parameters of uranium at different bed-depths (L) with $C_o = 100$, $Q = 3$ ml/min

Process parameters	L (cm)		
	3	6	12
Breakthrough			
V_b (ml)	175	390	780
t_b (min)	58.3	130	260
q_b (mg/g)	84.5	77.8	76.5
Exhaustion			
V_E (ml)	723	930	1530
t_E (min)	241	310	510
q_E (mg/g)	349.3	185.6	150

batch was discussed in details in our previous publications. [11,15,18]. The adsorption capacity value obtained in that study (100 mg/g) is higher than other previously reported low-cost adsorbents such as dried tea wastes [19], activated carbon [20], Diarylazobisphenol modified activated carbon [21] ionic liquid modified diatomite [22] with adsorption capacity of 59.5, 34.8, 28.5, 18.72 and 88 mg/g respectively.

3.1. Effect of bed depth on uranium breakthrough curve

In this concern we conduct uranium adsorption at different 3-bed depths (3 cm, 6 cm and 12 cm) with corresponding carbon mass are (0.2, 0.5, and 1.0 g) respectively. All column performance data were described in Table 2. As expected from uranium breakthrough plots in Fig. 2, as the mass of carbon (column depth) increases, the contact time increases and subsequently breakthrough curve becomes gentler. The breakthrough $t_b = 58.3$ min at $L = 3$ cm, $t_b = 130$ min at $L = 6$ cm and $t_b = 260$ min at $L = 12$ cm as shown in Fig. 2. i.e. the breakthrough times increase with bed depths, inducing larger treated volumes (175, 390, 780 ml respectively). The adsorption capacities are 84.5, 77.8 and 76.5 mg uranium per gm carbon for the bed depth 3, 6 and 12 cm, respectively i.e. the three column length showed an average value of $q_b = 79.6$ mg/g.

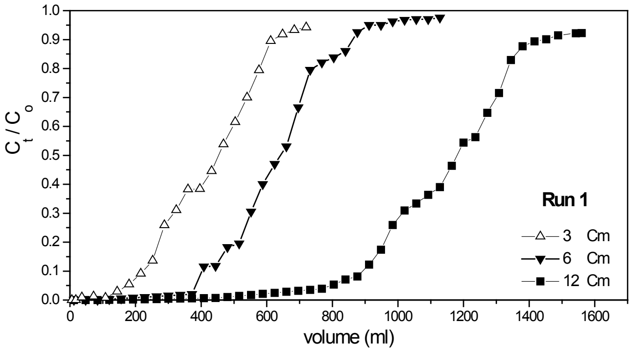

Fig. 2. Experimental breakthrough curves of uranium at different bed depths (3, 6, 12 cm) with respect to volume-treated (ml) **Conditions:** $C_o = 100$ ppm and $Q = 3$ ml/min.

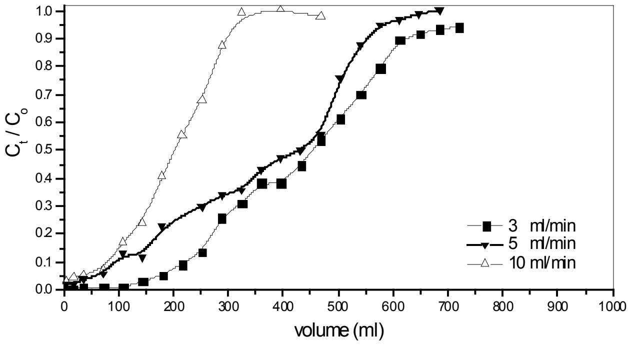

Fig. 3. Experimental breakthrough curves of uranium at different flow rates (3, 5, 10 ml/min) with respect to volume-treated (ml) **Conditions:** $C_o = 100$ ppm and $L = 3$ cm.

Increasing bed depth leads to increasing number of adsorption sites. Thus a large bed depth takings long time to be saturated with the same amount of uranium ions at constant conditions of flowrate and concentration [23]. Alternatively, increasing column bed depth increases the fluid residence time in the column, allowing adsorbate ions to diffuse deeper in adsorbent [24].

3.2. Effect of flow rate

In column experiment with 0.2 g of RSK carbon, the solution flow rate was changed from 3 ml/min to 10 ml/min with constant 100 mg/l feed uranium concentration. Comparative normalized uranium concentration vs. effluent volume at different flow rates is shown in Fig. 3. The column parameters are given in Table 3. The lowest flow rate of 3 ml/min gave the highest uranium ($q_b = 84.5$ mg/g at $t_b = 58.3$ min). But, as solution continued to flow, effluent uranium concentration of rapidly increased, the bed come to be saturated with uranium and solute effluent concentration rapidly rose to inlet concentration. Sharp breakthrough curves got by RSK carbon at higher flow rates (5 ml/min and 10 ml/min). The breakpoint time and adsorbed uranium also reduced with rising flow rate ($q_b = 26.4$ mg/g at $t_b = 10.6$ min at flow rate 5 ml/min and $q_b = 12.7$ mg/g at $t_b = 2.5$ min at flow rate 10 ml/min). This behavior indicate that uranium sorption by RSK carbon is influenced by (i) inadequate column residence time (ii) sorbent pores diffusion (iii) small number of active adsorption sites and (iv) biomass ionic groups available for sorption [10].

Table 3
Column parameters of uranium at different flow rates at C_o = 100 mg/l, L = 3 cm

Process parameters	Q (ml/min)		
	3	5	10
Breakthrough			
V_b (ml)	175	53	25
t_b (min)	58.3	10.6	2.5
q_b (mg/g)	84.5	26.4	12.7
Exhaustion			
V_E (ml)	723	570	315
t_E (min)	241	114	31.5
q_E (mg/g)	349.3	283.6	160

Table 4
Column parameters of uranium at different initial concentration at L = 3 cm, Q = 5 ml/min

Process parameters	C_o (mg/l)		
	100	200	400
Breakthrough			
V_b (ml)	53	27.5	15
t_b (min)	10.6	5.5	3
q_b (mg/g)	26.4	28.3	31.1
Exhaustion			
V_E (ml)	570	342.5	190
t_E (min)	114	68.5	38
q_E (mg/g)	283.6	353.1	393.8

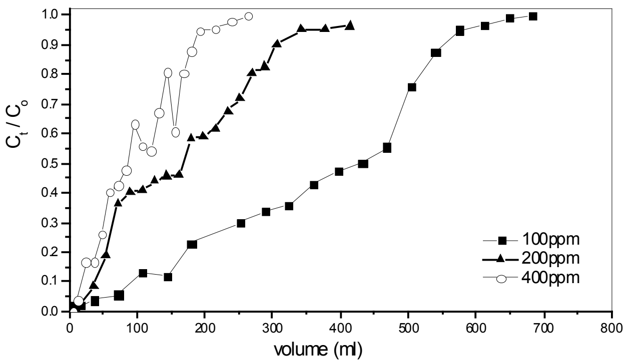

Fig. 4. Experimental breakthrough curves of uranium at different initial concentrations (100, 200 and 400 ppm) with respect to volume-treated (ml). **Conditions:** Q = 5 ml/min and L = 3 cm.

3.3. Effect of the influent concentration

Alteration in the influent uranium concentration influence on the column operating characteristics [25]. The sorption performance of RSK carbon was tested at various feed uranium concentrations (100, 200 and 400 mg/L). The sorption breakthrough curves got by altering feed uranium concentration from 100 to 400 mg/l at the flow rate (5 ml/min) and the bed depth (3 cm) are given in Fig. 4. Decrease of feed uranium concentration cause the latest breakthrough curve, and subsequently increasing treated effluent volume. Low concentration gradient produced slow transfer owing to reduced diffusion coefficients or mass transfer coefficient reductions [10]. The break point time declined at high feed uranium concentration as the adsorption binding sites come to be more rapidly saturated. As shown in Fig. 4, the break point time appeared after 10.6 min (match to 53 ml of effluent solution volume) at 100 mg/l feed uranium concentration while as break point time takes place after 5.5 min (match to 27.5 ml) at feed uranium concentration of 200 mg/l and appeared after 3 min (match to 15 ml) at 400 mg/l feed uranium concentration.

As shown in Table 4, the column performance parameters at breakthrough and exhaustion linked to feed uranium concentration are presented and also compared. In this concern, though the break and exhaustion time decreases with increasing feed uranium concentration, the adsorption capacity (q_b and q_E) showed the opposite trend. For the inlet uranium concentration of 100, 200 and 400 mg/l, q_b = 26.4, 28.3, 31.1 mg/g and q_e = 283.6, 353.1, 393.8 mg/g respectively. Adsorption driving force is the difference between solution solute concentration and solute on the sorbent [10]. High difference in their concentration give a high adsorption driving force and this can explain why high adsorption capacity was attained in the column fed with a high uranium concentration.

3.4. Modeling of breakthrough curve using predictive approach

Such models are based on deriving breakthrough volume and time solely from batch experimental isotherm. This approach saves a lot of time spent on column experimentation.

Using Freundlich equation ($x/m = K_f C^{1/n}f$) the constants K_f and n_f can be determined by conducting batch adsorption isotherm. A procedure for identifying the breakthrough volume and time described by EPA/NSF report (2000) [26] is outlined below:

1. Choosing C_b as the required effluent concentration, compute the estimated adsorbent loading at breakthrough as: $(x/m)_b = K_f (C_b) 1/n_f$
2. Determine the amount of removal required to meet the C_b by subtracting the C_b concentration from the initial concentration: $\Delta C_b = C_o - C_b$
3. Calculate the volume of water treated at breakthrough per unit weight of adsorbent by dividing the carbon loading at breakthrough by required removal: $(V/m)_b = (x/m)_b / \Delta C_b$
4. Knowing the value of mass of adsorbent (m) and the required flow rate (Q) then Volume treated at breakthrough, $V_b = (V/m)_b{}^* \, m$

Run time at breakthrough, $t_b = V_b / Q$

The predicted breakthrough volume and time and corresponding experimental values for different RSK carbon masses; m (bed height), different initial concentrations; C_o and various flow rates; Q, of uranium solutions are given in Table 5

As seen, the predictive model though advantageous, has been failed in producing breakthrough data (V_b and t_b) on high level of accuracy and these calculations should only used as

Table 5
Predicted and experimental V_b and t_b of uranium: RSK carbon adsorption system

M (g)	C_o (mg/l)	Q (ml/min)	Experimental		Predicted	
			V_b	t_b	V_b	t_b
0.207	100	3	175	58.3	117	39
0.501	100	3	390	130	283.4	94.5
1.02	100	3	780	260	577	192
0.201	100	5	53	10.6	113	22.7
0.495	100	5	335	67	280	56
0.94	100	5	380	76	531.7	106
0.194	200	5	27.5	5.5	67	13.4
0.507	200	5	115	23	175	35
0.965	200	5	155	31	333.7	66.7

rough prediction [26]. The difference between isotherm and column values is reasonable owing to inherent variance in the nature of batch and continuous operations [27]. In the batch mode equilibrium takes place and there is not continuous feeding from solution but in fixed bed, solution was fed continuously without sufficient time to attain equilibrium.

4. Conclusion

Uranium adsorption behavior on RSK carbon was investigated using continuous fixed-bed column. High influent concentration, high solution flow rate and low bed depth increased adsorbates breakthrough. Initial uranium concentration significantly influence on adsorption performance compared with bed depth and flow rate. Thus, this study gave valuable information for the design of fixed-bed column for uranium removal from aqueous solution using activated carbon.

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