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Single and two-stage batch adsorber design for efficient uranium removal by activated carbon

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ABSTRACT

Empirical adsorber design using adsorption equilibrium conditions is necessary to predict its size and performance. Single-stage batch adsorption is the most commonly method used by researchers to evaluate their adsorbents for commercial usage. However, further studies are needed to assess the adsorbent application at industrial field. KOH-oxidized rice straw-based carbon (RSK) has *been investigated for* adsorption of U(VI) in a single batch adsorber. An initial uranium concentration of 100 mg/l is assumed and the required amount of carbon to recover U(VI) content by 5%–95% was calculated. For example, the required masses of RSK carbon to treat 50 L of 100 mg/l of uranium solution are 4.0, 13.0, 24.0, 39.0, 69.0 and 89.0 g for 5%, 10%, 30%, 50%, 70%, and 90% U(VI) removal, respectively. Through such a projection, a real single stage adsorption system can be design. Two-stage batch adsorber design model was further developed to predict the minimum amount of RSK carbon necessary to reach a specific uranium removal percentages at a given volume of wastewater effluents. The replacement of single-stage system with two-stage system results in significant reduction (25%) of the overall required sorbent amount that balances the higher cost of the two-stage plant.

Keywords: Adsorption; Batch adsorber; Batch design; Single stage

1. Introduction

Uranium is a heavy metal occurs naturally in the earth's crust in various chemical forms. In addition, it found in food and drinking water. In nature, uranium have different oxidation states from 2^+ to 6^+, but 6^+ is the most commonly exist valence stat that is frequently combined with oxygen to form uranyl ion, UO_2^{2+}. Natural uranium composed of three radionuclides mixture (234U, 235U and 238U) disintegrates by both gamma and alpha emissions [1].

In the environment, uranium come by discharge from natural deposit, mill tailing, nuclear industries, military application, cigarette smoking, coal combustion and other fuels [2]. High uranium in phosphate fertilizers at concentrations of 150 mg/kg, might also play big role to groundwater uranium content of [3].

Uranium radiological and toxicity properties represents its main health threat [4] with the most sensitive toxicological endpoint is kidney illness through chemical interactions [5]. Exposure to high uranium level was associated with carcinogenicity and genotoxicity than its chemical toxicity [6]. The new federal standard, known as the "maximum contaminant level" (or MCL), is 30 ug/l which is equivalent to an activity of 20 pCi/L for uranium in public water supplies [7].

One of the most effective method for uranium removal from water is anion exchange that is able to remove ura-

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nium to concentrations as low as 1 µg/L (>99% removal). Nevertheless this method need regeneration that may be difficult [8]. Furthermore coagulation, ionic liquid solvent extraction, activated alumina, lime softening and reverse osmosis, used for effective uranium removal in laboratory and pilot plant studies. However, all of these technologies fails in areas with high natural uranium levels. Therefore, cation exchange and granular activated carbon can remove uranium effectively [8]. Inorganic adsorbent showed high selectivity towards toxic cations mostly for U(VI) like zirconium hydrophosphate nanoparticles [9] and magnetic chitosan resin [10].

The preconcentration of uranium based on adsorption is found many applications in nuclear industry. From an environmental point of view, adsorption with activated carbon can be considered as the most effective and economic process for removing trace metals from water [11].

In this study, the equilibrium adsorption of U(VI) removal by KOH-oxidized rice straw-based carbon (RSK) has been considered and based on the equilibrium studies. This paper developed a single and two-stage batch adsorber design model. A design analysis method was used to estimate the least amount of adsorbent necessary to reach a specific uranium removal percentage at a known volume of wastewater in the single and two-stage batch adsorber adsorption process. The minimum adsorbent quantity required make best use of adsorbent efficiency and therefore reduces capital expenditure.

2. Methods

Activated carbon was produced by steam pyrolysis according method described elsewhere [12]. The obtained carbon was oxidized using potassium hydroxide (KOH) in the presence of ionic liquid to produce modified activated carbons as stated by the procedures described earlier [13,14] and denoted as RSK. Surface area and pore characteristics of the prepared carbons were determined by nitrogen adsorption at 77K using Quantachrome Instruments, Model Nova1000e series, USA. Simple mass titration method was used to estimate the pH_{pzc} of RSK carbon as reported [15]. The Boehm titration method was used to estimate the acidic and basic properties of RSK carbon [16]. All details about the Effect of porosity and surface chemistry on the adsorption of uranium(VI) from aqueous solution are given in our previous article [6].

2.1. Adsorption experiments

Stock solution (1000 ppm) of Uranium was prepared by dissolving 2.10 of uranyl nitrate in 1 L distilled deionized water acidified by 2 ml nitric acid to prevent uranium hydrolysis.

Uranium adsorption experiments were done using 20 ml solution of 100 ppm initial concentration uranium using RSK carbon. 100 ppm U(VI) was chosen as initial concentration which represent U(VI) concentration in mill tailings [33]. The pH was adjusted to pH 5.5 (maximum adsorption) by adding microvolumes of 0.05 N LiOH or 0.05 N HNO_3 solutions. No precipitation was observed at this pH value. After each experiment, solution was filtered and uranium concentration remaining in the solution was measured using UV spectrophotometer and arsenazo III as color producing reagent [17].

Adsorption capacity of RSK adsorbent was calculated by:

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

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

3. Results and discussion

3.1. Batch operation

The full details of uranium batch adsorption on activated carbons were described in our previous work [12,18]. In this concern, KOH-oxidized rice straw-based carbon activated carbon (RSK) was determined to be superior in removal of uranium. Uranium removal by RSK carbon was maximum at pH 5.5 and equilibrium time of 40 min. with maximum adsorption capacity 100 mg/g. Uranium adsorption capacity were found to be 58.0 mg/g on silica [19], 18.7 mg/g on d modified carbon [20], 28.30 mg/g onto activated carbon [21] and 88 mg/g on ionic liquid modified diatomite [30]. Thus, RSK carbon is more effective for uranium removal. As a continuity of our work, the present study will try to evaluate RSK carbon as commercial adsorbents through the design of a single and two-stage batch adsorption system.

In a typical batch process, the effluent to be treated and the adsorbent were mixed together in a suitable reaction vessel (agitated contacting tank) for a set of time until solute level has been reduced to the desired level and the system approach equilibrium. This is followed with filtration to separate the solid adsorbent and adsorbate from the liquid [22]. The design in the batch adsorption may be single or multi stage depending on wastewater volume, so one tank reactor or more is used in which the agitation should be vigorous to ensure rapid contact of the adsorbent particles with the liquid [22].

Most batch adsorption systems are operated on a fill-and-draw basis i.e. once the reaction vessel is filled, carbon can be added and mixture agitated until adsorption is complete. The vessel can then be drained and prepared to receive another quantity of wastewater. If wastewater is generated continuously, two or more tanks may be used and alternated in the fill-and-treat modes.

3.2. Single-stage batch adsorption

For predicting the design of a single-stage adsorber model for a batch-adsorption study, the adsorption equilibrium data is useful [23]. Designing a batch adsorber model is essential for extrapolation the results of the lab-bench-scale experiments to a large-scale real systems, which in turn could be utilized in designing an industrial wastewater treatment system.

The Empirical design procedure is important to evaluate the adsorbent from economical point of view. Thus, to predict adsorber size and its efficiency for U (VI) removal by RSK carbon adsorbent from wastewater streams, an empirical procedure depends on the adsorption equilibrium is designed. The systematic diagram for a single-stage adsorption process is given in Fig. 1. The objective of the design is to decrease U (VI) in a solution of volume V (L) from an initial concentration of C_o to C_e (mg L^{-1}).

The mass of RSK carbon used is M (g) and U (VI) loaded onto RSK carbon changes from q_0 to q_e (mg/g). At time zero time, q_o = zero that increase with time and amount of U (VI) removed equates to that adsorbed by the adsorbents.

Considering the mass balance inside the sorbent, the amount of U(VI) removed from the solution should equal to amount of U(VI) adsorbed onto RSK carbon [24].

$$V(C_o - C_e) = m(q_e - q_o) \tag{2}$$

with q_o = the sorption capacity at the start of the process, mg/g; q_e = the sorption capacity at equilibrium, mg/g; V = solution volume, l; m = adsorbent mass, g; C_o = the initial concentration, mg/l; C_e = the equilibrium concentration, mg/l.

Rearrangement Eq. (2) gives

$$(q_e - q_o) = -\frac{V}{m}(C_e - C_o) \tag{3}$$

Eq. (3) represents a straight-line equation, i.e. line from the starting point (C_o, q_o) on the isotherm plot and have slope of ($-V/m$) is termed the operating line of this stage and its intersection with adsorption isotherm at point (C_e, q_e) [25,26]. Some of important advantages of Eq. (3) are as follows: (V/m) for a desired purification can be calculated. (C_e, q_e) values at desired V/m value can be determined from adsorption isotherm plot as shown in Fig. 2.

Adsorption isotherm can be used to predict the design of single-stage batch adsorption [27]. For the of U(VI) adsorption on RSK carbon, the relation of C_e and q_e obeyed Freundlich isotherm well with constants as seen in Table 1. Based on this, Freundlich equation was used to estimate RSK carbon amount necessary to remove a definite percentage of U(VI) from different volumes of solutions. With

$$q_e = KC^n \tag{4}$$

Freundlich data may be applied to Eq. (4) and substitution q_e and rearranging gives

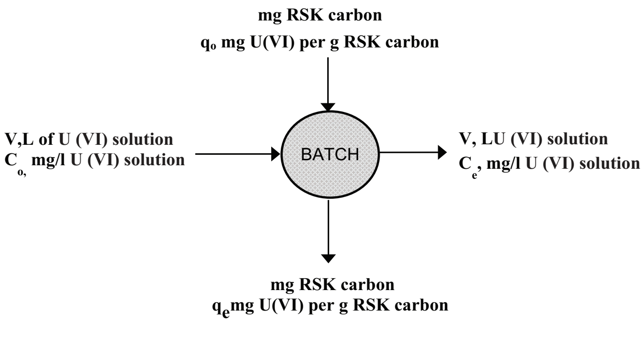

Fig. 1. Single-stage batch adsorption.

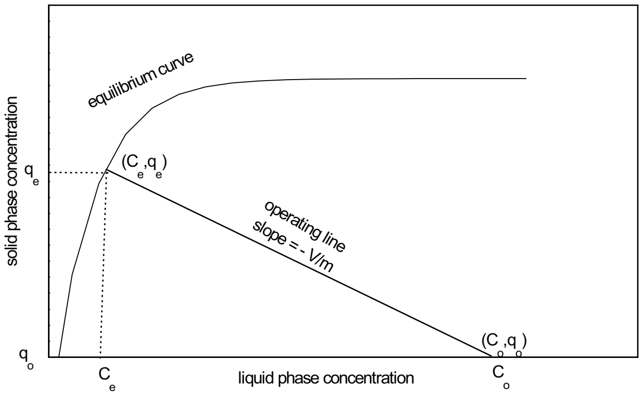

Fig. 2. Operating line for single-stage batch adsorption.

Table 1
Freundlich parameters for adsorption of U(VI) onto RSK carbon

Parameter	Value
K_f (mg/g)	33.73
n	3.4
R^2	0.999

$$\frac{m}{V} = \frac{C_o - C_e}{K_f C_e^{1/n}} \tag{5}$$

where k_f and n are the Frendulich constants.

Eq. (5) permits the analytical calculation of adsorbent: solution ratio for a given change in solution concentration C_o to C_e [28]. Fig. 3 displays a series of plots resulting from Eq. (5) for adsorption of U (VI) (C_o = 100 mg/l) on RSK carbon. Fig. 3 shows effluent amounts that could be treated to decrease the U (VI) content by 90%, 80%, 70%, 60% and 50% using different masses of adsorbent. For example, 50 L of100 mg/l of uranium solution is to be treated. The required masses of RSK carbon are 4.0, 13.0, 24.0, 39.0, 69.0 and 89.0 g for 5%, 10%, 30%, 50%, 70%, and 90% U (VI) removal, respectively.

The results in Fig. 3 are used to expect the design of single-stage batch adsorbers with low accuracy. Owing

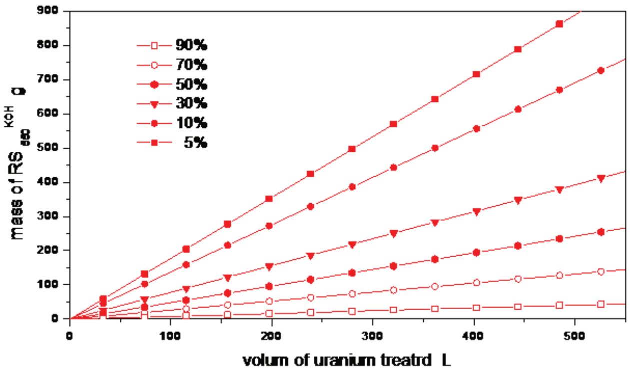

Fig. 3. RSK mass against volume of solution treated at various percentages of uranium removal (C_o = 100 mg/l).

to problem of predicting scale up conditions, no experiments was undertaken to test this model [28]. The solute removal efficiency can be enhanced if the solution is treated with separate small batches of adsorbent better than in single batch process. However, this maximizes operation cost. Therefore, usually only two stages are used [29].

3.3. Two-stage batch adsorption

In some cases, a single-stage batch adsorber cannot achieve the high levels of metal removal but these can be readily achieved using an optimized two-stage batch adsorber design. The schematic for this type of process is shown in Fig. 4 [29]. Stage 1 and stage 2 treat the same quantity of solution, V. The operating diagram can be constructed as shown in Fig. 5 for a two-stage process. The approach is the same as for the single-stage operating diagram, and the operating lines will be parallel when the same quantity of adsorbent is used. Using two stages batch adsorption have advantages of (1) reduce metal effluent concentration to much lower level than in one stage using the same sorbent amount, (2) decrease sorbent consumption and disposal, and (3) removal of different metals with different maximum removal pH ranges [29].

The operating diagram assumes fresh adsorbent at each stage and therefore $q_o = 0$

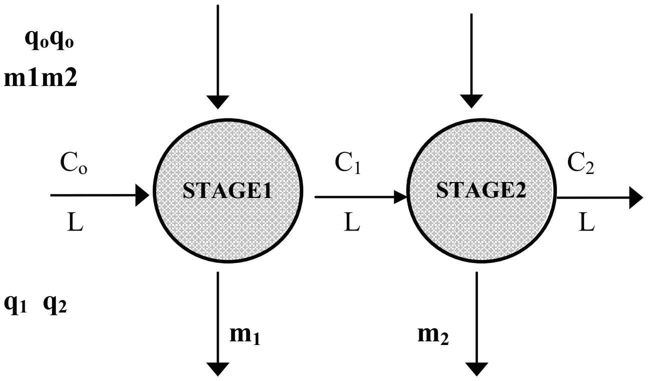

Fig. 4. Two-stage batch adsorption.

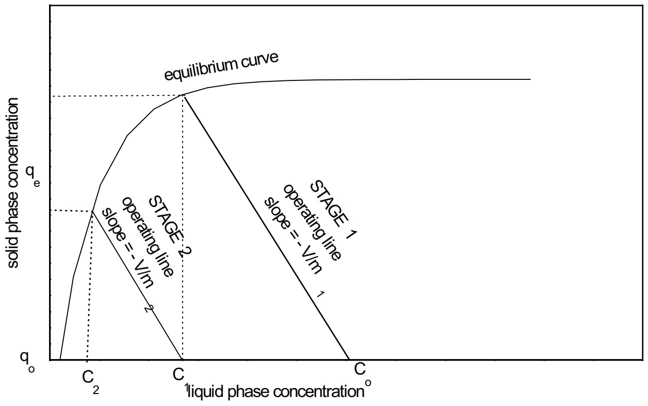

Fig. 5. Operating lines for two-stage batch adsorption.

The mass balance equation for stage 1 is

$$V(C_0 - C_1) = m_1(q_1 - q_0) \tag{6}$$

And for stage 2

$$V(C_1 - C_2) = m_2(q_2 - q_1) \tag{7}$$

An important economic factor in multistage adsorption is to determine the minimum quantity of adsorbent to treat a fixed volume of effluent. This can be calculated analytically as follows: [22]. When fresh adsorbent is used at each stage q_o = zero and using Freundlich equation in Eq. (5) thus:

$$\frac{m_1}{V} = \frac{(C_0 - C_1)}{q_1} = \frac{(C_0 - C_1)}{K_f C_1^{1/n}} \tag{8}$$

For stage 2

$$\frac{m_2}{V} = \frac{(C_1 - C_2)}{q_2} = \frac{(C_1 - C_2)}{K_f C_2^{1/n}} \tag{9}$$

The total amount of adsorbent used in two stages process

$$\frac{m_1 + m_2}{V} = \left(\frac{C_0 - C_1}{K_f C_1^{1/n}} + \frac{C_1 - C_2}{K_f C_2^{1/n}} \right) \tag{10}$$

Thus for uranium K_f = 33.73 and $1/n$ = 0.29

$$\frac{m_1 + m_2}{V} = \left(\frac{C_0 - C_1}{33.7 C_1^{0.29}} + \frac{C_1 - C_2}{33.7 C_2^{0.29}} \right) \tag{11}$$

However, there are some drawbacks with batch adsorption operation, that is [28]. (a) Time necessary for adsorbent and liquid to come to equilibrium may be quite large. (b) Expensive plant items include agitated tank and a filter press. (c) Extra time is requisite for the filtration process. For these reasons a number of fixed bed experiments were performed.

A series of design aim to treat 50 L of 100 mg/L U(VI) solution to 5 mg/L in 10 decrements was considered in stage 1 of a two-stage system. In adsorption system 1, the objective was to decrease initial uranium concentration from 100 to 95 mg/L. In the same way, the design objective of the first stage in systems 2, 3, 4, 5, 6, 7, 8, 9 and 10 was to decrease initial uranium concentration from 100 to 90, 80, 70, 60, 50, 40, 30, 20, 10 and 5 mg/L, respectively. The second stage in all adsorption systems aims to decrease uranium concentration in stage 1 to 5 mg/L. The equivalent amount of RSK carbon necessary for uranium removal in stage 1 and stage 2 were calculated using Eq. (11). Depends on the adsorption system number that used minimum RSK carbon mass to decrease the uranium concentration from C_1 to C_2 (mg/L) was expected from the plot of mass of RSK carbon necessary two-stage adsorption system against equilibrium uranium concentration in stage 1 (Fig. 6).

Obviously, increases in the RSK carbon used in first stage led to reduce its amounts in the second stage. It is worth noting that the 7th two-stage adsorption with equilib-

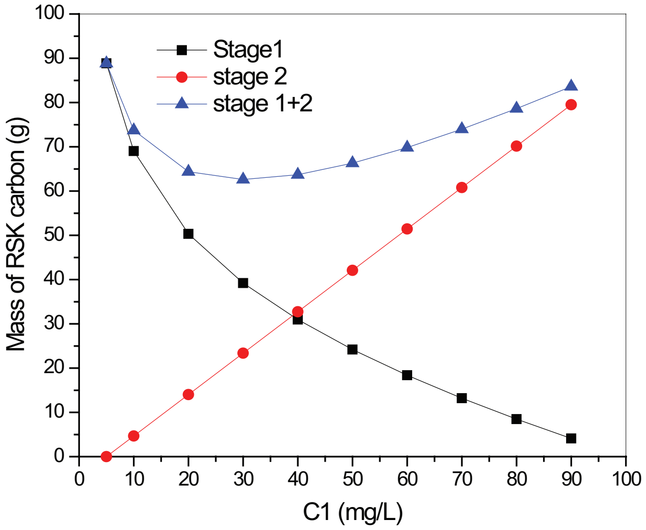

Fig. 6. Optimization of carbon dosage in a two-stage batch adsorption system.

rium uranium concentration of 30 mg/L in stage 1 utilized lowest amount of the carbon (62.6 g) to achieve the desired objective of reducing 50 L of metal solution from 100 to 5 mg/L U(VI) concentration.

The minimum quantity of the adsorbent necessary for 50 L of U (VI) metal solution to be treated was calculated from the total quantity of adsorbent necessary at both the stages vs. adsorption system number. The expected improved adsorbent required for a two-stage adsorption system to decrease the metal concentration from 100 to 5 mg/L for 50 L is given in Table 2. Two-stage sorption system decreased RSK carbon dose by around 25 % in relation single-stage adsorption system. Furthermore, when RSK carbon is used to adsorb uranium, the adoption of double-stage adsorber improves the economic balance of the process, down to the significant reduction of the needed amount of adsorbent

Table 2
Mass of carbon required for a series of adsorption systems (C_0 = 100 mg/L; C_1 = 5 mg/L)

Sorption system	C_1	Stage 1, M_1 (g)	Stage 2, M_2 (g)	$M_1 + M_2$ (g)
		50L	50L	50L
1	90	4.1	79.5	83.6
2	80	8.5	70.2	78.6
3	70	13.2	60.8	74.0
4	60	18.4	51.4	69.8
5	50	24.2	42.1	66.3
6	40	31.0	32.7	63.7
7	30	39.2	23.4	62.6
8	20	50.3	14.0	64.4
9	10	69.0	4.7	73.7
10	5	88.9	0.0	88.9

4. Conclusion

The design of single- and two-stage adsorption plants was carried out for the adsorption of U(VI) ions onto KOH-oxidized rice straw-based carbon (RSK). Depends on well-correlated adsorption isotherm, a two-stage batch adsorption process design was displayed and results analysis showed that two-stage batch could save more adsorbent than single-stage batch. It is principally suitable for optimizing the use of RSK carbon to minimize capital investment costs particularly when high uranium removal efficiency is extremely needed.

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