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Packed bed column investigation on hexavalent chromium adsorption using activated carbon prepared from *Swietenia Mahogani* fruit shells

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ABSTRACT

The removal of Cr(VI) from aqueous solution by a novel Swietenia Mahogani fruit shell physically activated carbon (SMFS-PAC) was examined in a packed bed column study. The effects of significant parameters such as feed flow rate, bed depth, and initial Cr(VI) concentration were studied. Column data obtained at different conditions were described using the Thomas, Bed depth service time (BDST), Adams–Bohart, and Yoon–Nelson model in order to predict the breakthrough curves and to evaluate the model parameters of the packed bed column studies data. Among the models used, Thomas, BDST, and Yoon–Nelson model, respectively, fitted to the experimental data very well. The SMFS-PAC column study states the value of the good adsorption capacity for the removal of Cr(VI) from aqueous solution.

Keywords: Adsorption; Hexavalent chromium; Packed bed column; Mathematical modeling; Breakthrough curves

1. Introduction

Chromium is a highly toxic metal released by anthropogenic activities of mining, metal plating, glass and ceramics, dyes, pigments, and tanning are the sources for pollution. Mostly chromium exists in the aquatic environment as Cr(III) and Cr(VI). Hexavalent form of chromium is more toxic than trivalent. Cr(VI) affects human physiology and accumulates in the food chain, and strong exposure to Cr(VI) may cause severe health hazards like cancer in the digestive tract and lungs and may cause epigastric pain, vomiting, severe diarrhea, nausea, and hemorrhage [1–3]. Chromium is considered as one of the top 20 contaminants listed under the category of hazardous substances for the past 15 years [4]. The permissible concentration limit of Cr(VI) for discharge into inland surface waters is 0.1 mg/L and for potable water is 0.05 mg/L [5]. Methods such as chemical precipitation, chemical oxidation, ion exchange, electrochemical treatment, membrane filtration were adopted for Cr(VI) removal from industrial wastewater. Nevertheless, these methods associated with the drawbacks such as inefficient metal removal at low concentrations of <100 mg/L, expensive equipment, generation of secondary pollutants and problem of waste disposal [6,7]. Adsorption is an effective method for heavy metal removal. Since this method solves the problems of sludge disposal, flexibility in design and operation, high-quality treated effluent, economical by subjecting low cost adsorbents [8–10]. Agro and natural wastes are considered as the important feed stock for the preparation of activated

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carbon since the waste materials are abundant, renewable and highly economical [11–13]. Adsorbent materials such as coir pith [14], olive pomace [15], sugarcane bagasse [16], rice husk [17], wheat bran [18], hazelnut shell [19], and neem leaves [20] were used as an efficiently adsorbent for the removal of Cr(VI) from aqueous solutions in a batch system. The majority of adsorption studies that appear in the literature have been carried out in batch systems. However, data obtained from batch adsorption systems may not be applied directly to column studies, where contact time is not sufficient for the equilibrium attainment and also restricted to the treatment of small quantities of wastewater. Therefore, for the large scale operations, a packed bed column is preferred, because the column makes the best use of the driving force—the concentration difference responsible for heavy metal adsorption [21–23].

In our previous research, raw form of *Swietenia Mahogani* fruit shell (SMFS) was employed for the biosorption of hexavalent chromium from aqueous solution in a batch study operation [24]. The data of batch conditions are generally not applicable to continuous operations where contact time is not sufficient to reach equilibrium. Thus, it is indispensable to ascertain the practical applicability of the biosorbent in a continuous column operation. Therefore, the present work focuses on the biosorption of hexavalent chromium using *S. Mahogani* fruit shell physically activated carbon (SMFS-PAC) as adsorbent through a continuous column mode operation. The influence of several operational parameters has been analyzed (bed depth, feed flow rate, and inlet Cr(VI) concentration). Also, the fit of the experimental data to various models such as the Thomas, Bed depth service time (BDST), Adams–Bohart, and Yoon–Nelson were subjected to describe the breakthrough curves.

2. Materials and methods

2.1. Preparation of Cr(VI) solutions

Stock solution (1,000 mg/L) of Cr(VI) was prepared by dissolving 2.829 g $K_2Cr_2O_7$ (analytical reagent grade) in 1,000 ml distilled water. All working solutions were prepared by diluting the stock solution with distilled water to the desirable concentration. The pH of the solutions was adjusted with the aliquots of 0.1 M HCl and 0.1 M NaOH solutions, respectively.

2.2. Preparation of adsorbent

Fruit shell of *S. Mahogani* was collected from the National Institute of Technology Calicut. The SMFS was washed thoroughly with distilled water and oven dried at 80˚C for 24 h. The activated carbon was prepared through physical activation, done by carbonization of 300 g of SMFS. Carbonization was performed in a muffle furnace for 1 h at 700˚C in the absence of air by placing the sample in a well-sealed stainless steel tube. The obtained carbon was washed with distilled water and then dried at 120˚C for 2 h. Then, the SMFS-PAC was pulverized, sieved to obtain the adsorbent in the size range of 0.420–0.5 mm. The prepared SMFS-PAC was stored in an airtight plastic container for further use.

2.3. Packed bed column adsorption

Packed bed column studies were conducted in glass column with an internal column diameter of 1 and 15 cm in length. Significant packed bed column adsorption parameters have been represented in Table 1. The SMFS-PAC was packed in the column between glass wool, which prevents the runaway of adsorbent. A schematic of a packed bed column of SMFS-PAC for the adsorption of Cr(VI) is shown in Fig. 1. Column study was carried out by pumping synthetically prepared Cr(VI) solution at the different flow rates 2, 4, and 6 mL/min in an up flow mode using peristaltic pump (Miclins, India). Initial Cr(VI) concentration of 50 mg/L was used in column experiments. The Cr(VI) solutions were maintained at constant pH 2.0. The effect of bed height on adsorption in the packed bed studies was performed with various bed depths of 2, 4, and 6 cm using 0.7544, 1.3334, and 2.1111 g of SMFS-PAC, respectively. Samples were collected at regular intervals during the column adsorption study. The flow in the packed bed column study is carried out continuously until the effluent Cr(VI) concentration approaches the influent concentration, $C_t/C_0 = 1$. The collected samples were analyzed for hexavalent chromium ions using a UV Spectrophotometer (model Systronics 2201, India) at 540 nm [25].

2.4. Column data analysis

The column capacity, q_{total} (mg), for a given set of conditions in the column was calculated from the area

Table 1
Packed bed column adsorption parameters

Total volume (cm^3)	11.78
Column diameter (cm)	1.0
Surface area of the column (cm^2)	48.69
Adsorbent depth (cm)	4
Adsorbent mass (g)	1.3334
Adsorbent surface area (m^2/g)	0.7862
Packing density (g/cm)	0.625

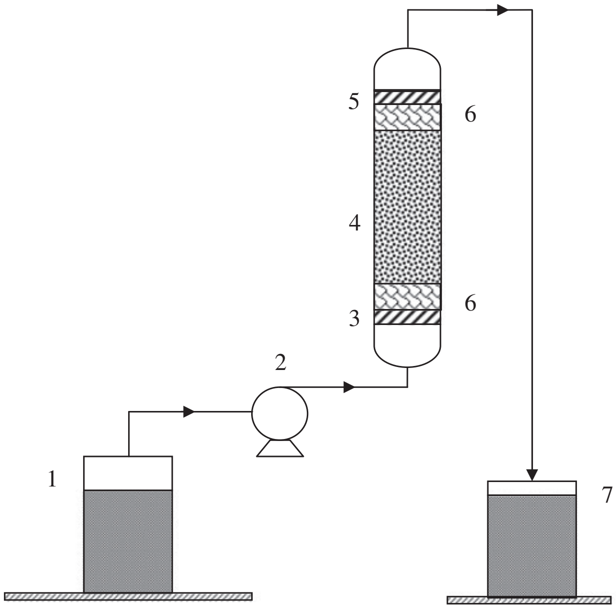

Fig. 1. Experimental setup for the continuous adsorption of Cr(VI) using SMFS-PAC: 1. Influent Cr(VI) solution, 2. Peristaltic feed pump, 3. Bottom sieve, 4. Packed adsorbent, 5. Top sieve, 6. Glass wool, and 7. Effluent Cr(VI).

under the plot of adsorbed Cr(VI) concentration, C_{ads} (mg/L), vs. time multiplied by flow rate, F (mL/min) [26]. The equation for the calculation of maximum packed bed column capacity is represented as follows:

$$q_{\text{total}} = \frac{FA}{1,000} = \frac{F}{1,000} \int_{t=0}^{t=t_{\text{total}}} C_{\text{ads}} \mathrm{d}t \tag{1}$$

where t_{total} represents the total flow time (min), F is the flow rate (mL/min), and A is the area under the breakthrough curve (cm^2).

The equilibrium adsorption capacity $q_{e(\exp)}$ and the weight of Cr(VI) adsorbed per unit weight of adsorbent (mg/g) can be determined as following:

$$q_{e(\exp)} = \frac{q_{\text{total}}}{M} \tag{2}$$

where M is the total mass of the adsorbent in the column (g).

Total amount of Cr(VI) ion entering column (m_{total}) is calculated from the following equation [27]:

$$m_{\text{total}} = \frac{C_0 F t_{\text{total}}}{1,000} \tag{3}$$

and the removal percentage of Cr(VI) ions can be obtained from Eq. (4):

$$Y\ (\%) = \frac{q_{\text{total}}}{m_{\text{total}}} \times 100 \tag{4}$$

The total volume treated, V_{eff} (mL), was calculated from Eq. (5) [28]:

$$V_{\text{eff}} = F t_{\text{total}} \tag{5}$$

2.5. Column data modeling using theoretical models

The packed bed column is described on the basis of breakthrough curve, which is the shape of concentration–time profile. The concept of breakthrough point and curve is a very significant characteristic for the dynamic response, design of process, and adsorption column operation. The parameters of packed bed study are highly dependent on the various experimental operating conditions [29,30]. The experimental data were validated with the theoretical models of Thomas, BDST, Adams–Bohart, and Yoon–Nelson model. These models signify over the investigation of solute interaction behavior and used to estimate the breakthrough curves of the packed bed column adsorption study.

2.5.1. Thomas model

The Thomas model is one of the most widely used models to represent the packed bed column adsorption data. The model assumes Langmuir kinetics of adsorption–desorption and negligible axial dispersion in the column adsorption, since the rate driving force obeys the second order reversible reaction kinetics [31,32]. The expression of the Thomas model for adsorption column is given as follows:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{\text{TH}} q_0 M}{F} - k_{\text{TH}} C_0 t \tag{6}$$

where C_0 is the initial metal ion concentration in the liquid phase (mg/L); C_t is the metal concentration at time t in the solution (mg/L); k_{TH}, the Thomas rate constant (ml/min mg); q_0 is the adsorption capacity (mg/g); M is the amount of adsorbent in the packed bed column (g); and F is the flow rate (ml/min). The value of C_t/C_0 is the ratio of effluent and influent Cr(VI) concentrations. k_{TH} and q_0 are determined from the plot of $\ln\left(\frac{C_0}{C_t} - 1\right)$ vs. t.

2.5.2. BDST model

BDST is a simple model for predicting the relationship between the bed depth and service time. The model is based on physically measuring the capacity of the bed at different values of breakthrough. This model is based on the assumption of forces like intraparticle diffusion and external mass transfer resistance were negligible and that the adsorbate is adsorbed onto the adsorbent surface directly [33]. The BDST model states that bed depth (Z) and service time (t_s) of a packed bed column bears a linear relationship. The equation of BDST model is expressed as follows:

$$t_s = \left(\frac{N_0 Z}{C_0 u}\right) - \left(\frac{1}{C_0 K_a}\right) \ln\left(\frac{C_0}{C_b} - 1\right) \tag{7}$$

where t_s is the service time (min), u is the influent linear velocity of the Cr(VI) solution through the bed (cm/min), N_0 is the adsorption capacity of bed (mg/L), Z represent the bed depth (cm), K_a is the rate constant in BDST model (L/mg min). A plot of t_s vs. bed depth Z yields a straight line, used to determine N_0 and K_a from the slope and intercept, respectively.

2.5.3. Yoon–Nelson model

Yoon–Nelson model is based on the assumption that the rate of decrease in the probability of biosorption of each adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent. In comparison with all the other models, the Yoon–Nelson model is not only less complicated model but also does not requires data of characteristics of adsorbate, adsorbent type, and the physical properties of adsorption bed [34]. The non linear form of Yoon–Nelson equation is expressed as follows:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{\mathrm{YN}} t - k_{\mathrm{YN}} \tau \tag{8}$$

where k_{YN} is the Yoon–Nelson rate constant (1/min) and τ is the time required for 50% adsorbate breakthrough (min). The parameters k_{YN} and τ can be determined from a plot of $\ln(C/(C_0{-}C))$ vs. t.

2.5.4. Adams–Bohart model

The model [35] is based on the surface reaction theory that established a fundamental equation, which describes the relationship between C_t/C_0 and t in a continuous system. This model assumes that that equilibrium is not instantaneous. It is used for the description of the initial part of the breakthrough curve. The expression is as follows:

$$\ln\left(\frac{C_t}{C_0}\right) = k_{\mathrm{AB}} C_0 t - k_{\mathrm{AB}} N_{\mathrm{AB}} \left(\frac{Z}{u}\right) \tag{9}$$

where N_{AB} is the saturation concentration in the Adams–Bohart model (mg/L) and k_{AB} is the mass transfer coefficient (L/mg min). A straight line was attained for this system by plotting $\ln(C_t/C_0)$ against t, which gives the value of k_{AB} from the slope of the line.

3. Results and discussions

3.1. Effect of different bed depths

One of the parameters influencing the breakthrough curve in adsorption studies is height of bed of the packed bed column. The retention of Cr(VI) ions in a packed bed column depends on the amount of SMFS-PAC used or on the bed depth the column functions. The adsorption performance of SMFS-PAC was tested at various bed depths of 2 cm (0.7544 g), 4 cm (1.3334 g), and 6 cm (2.111 g) at flow rate of 2 mL/min and inlet Cr(VI) concentrations of 50 mg/L. Fig. 2 shows the breakthrough profile of Cr(VI) adsorption at different bed heights. The time necessary to attain saturation of the column is higher as the bed depth increases, especially in the case of highest bed depth in this study of 6 cm required a time longer than the 120 min. Nevertheless, when the column works with 2 cm of SMFS-PAC, the adsorbent becomes saturated very soon. This specifies that smaller bed gets saturated faster than the longer bed in packed bed column adsorption (Table 2). The breakthrough curve becomes much steeper with the

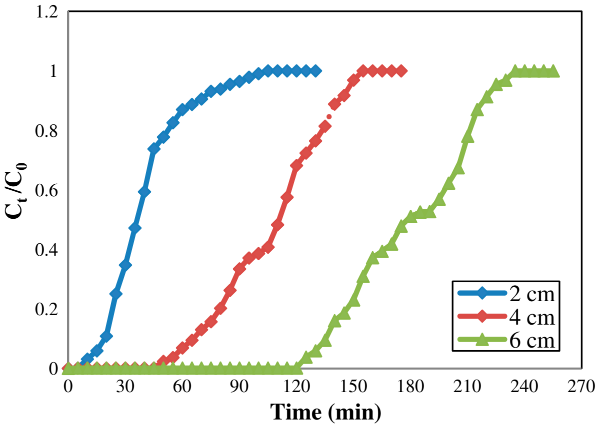

Fig. 2. Breakthrough curves for Cr(VI) adsorption onto SMFS-PAC at different bed depths (inlet Cr(VI) concentration: 50 mg/L, flow rate: 2 mL/min, and pH 2.0).

decrease in bed depth as shown in Fig. 2. This was observed due to the increase in axial dispersion of Cr (VI) ions along the depth of packed bed column causing more Cr(VI) ions adsorption with the increase in bed depth. Also, with the increase in bed depth, there is an increase in Cr(VI) adsorption because of more surfaces available for adsorption and more contact time leading to enhanced adsorption of Cr(VI) ions [36,37].

3.2. Effect of flow rate

The breakthrough curves at three different flow rates (2, 4, and 6 mL/min) are shown in Fig. 3. As expected, an increase in the flow rate produces a diminution in breakthrough and exhaustion times, and as a result, the curves become steeper with a shorter mass transfer zone. The slower flow rate provides more time for mass transfer into the pores of the material, which allows the Cr(VI) ions access to more binding sites within the SMFS-PAC. The percentage of Cr(VI) removal decreased with the increase in flow rate (Table 2), this might be due to less residence time of the Cr(VI) solution through the packed bed column at a higher flow rate [38]. The adsorption capacity was low when the flow rate was higher and vice versa. At a high flow rate, the residence period of Cr(VI) ions in the column was very transitory, which cannot lead to the equilibrium of the adsorption process [39].

3.3. Effect of inlet Cr(VI) concentration

In the adsorption of Cr(VI) to SMFS-PAC, a change in inlet Cr(VI) concentration affected the operating characteristics of the fixed bed column. The adsorption breakthrough curves obtained by changing inlet Cr (VI) concentration from 50 to 150 mg/L at 2 mL/min flow rate and 4 cm bed height are given in Fig. 4. The breakthrough time of the SMFS-PAC was decreased with an increasing initial Cr(VI) concentrations (Fig. 4). This could be explained by the fact that the driving force for adsorption is the Cr(VI) concentration difference between the solution and the SMFS-PAC [40]. Adsorption capacity increased with increasing inlet Cr(VI) concentration (Table 2). This is because of higher concentration gradient caused a faster transport due to an increased mass transfer coefficient [41]. These results showed that the higher inlet metal ion concentration could saturate the adsorbent more rapidly. Therefore, the high Cr(VI) concentration provides sufficient driving force, shorter mass transfer zone, and higher adsorption rate [42].

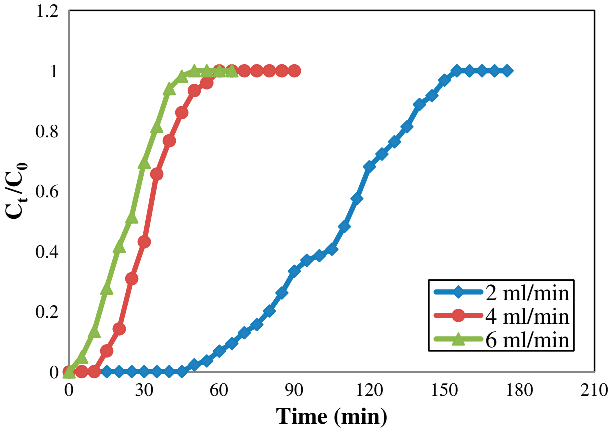

Fig. 3. Breakthrough curves for Cr(VI) adsorption onto SMFS-PAC at different flow rates (inlet Cr(VI) concentration: 50 mg/L, bed height: 4 cm, and pH 2.0).

3.4. Modeling of the breakthrough curves

Four models were proposed to illustrate column breakthrough curve obtained at different inlet metal concentrations, bed height, and flow rates. These are as follows:

Thomas model was fitted to the experimental data in order to determine the Thomas model constants,

Table 2
Parameters in packed bed column for Cr(VI) adsorption by SMFS-PAC.

Z (cm)	F (mL/min)	C_0 (mg/L)	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	$q_{e(exp)}$ (mg/g)	V_{eff} (mL)	Y (%)
2	2	50	100	10	3.6876	4.8881	200	36.87
4	2	50	150	15	10.35	7.7621	300	69.00
6	2	50	230	23	17.6591	8.3652	460	76.77
4	4	50	55	11	5.8623	4.3965	220	53.29
4	6	50	45	13.5	6.2548	4.6908	270	46.33
4	2	100	130	26	21.6580	16.2427	260	83.3
4	2	150	110	33	28.6478	21.4848	220	86.81

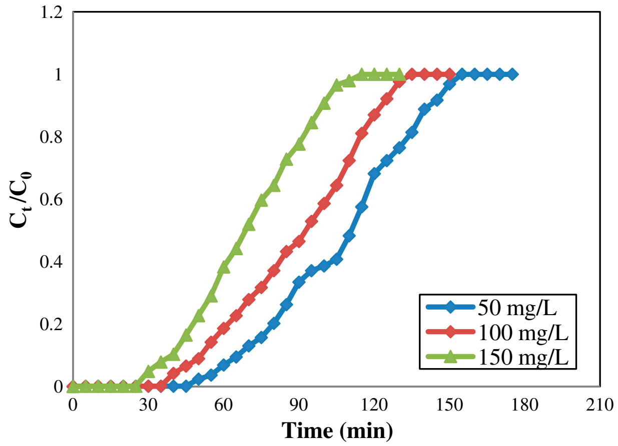

Fig. 4. Breakthrough curves for Cr(VI) adsorption onto SMFS-PAC at different inlet Cr(VI) concentrations (flow rate: 2 mL/min, bed height: 4 cm, and pH 2.0).

k_{TH} and q_0. The calculated constants of this model were represented in Table 3. It was found that the coefficient of determination value of this model was higher and therefore exhibited better fit to the experimental data for all the parameters studied. From Table 3, it can be seen that with the bed depth increasing, the k_{TH} values decreased. As the flow rate increased, the value of k_{TH} increased while the value of q_0 decreased. The value of k_{TH} decreased with increasing initial influent Cr(VI) concentration. It was attributed to the driving force for adsorption in the concentration difference. Thus, the lower flow rate, higher influent concentration, and higher bed depth would increase the adsorption of Cr(VI) on the SMFS-PAC column [22]. The Thomas model was suitable for adsorption process, which indicated that the external and internal diffusions were not the limiting step [43].

The Adams–Bohart model constants k_{AB} and N_{AB} were calculated using linear regression analysis and presented in Table 3. Based on the value of coefficient of determination (R^2), the model is least fitted to the experimental data in comparison with all the other models used in this study. As shown in Table 3, the values of k_{AB} decreased with the increase of both bed depth and influent Cr(VI) concentration, but increased with increasing influent flow rate. It was indicated that the overall system kinetics was dominated by external mass transfer in the initial part of adsorption in the column. This model provides a simple and comprehensive approach to conduct and evaluate adsorption column investigation. However, its validity is limited to the range of conditions used [44].

The constants values of Yoon–Nelson model obtained at various operating parameters were shown in Table 3. The value coefficient of determination (R^2) reveals that this model better fitted with experimental data. The τ value and k_{YN} value increased with the increase in the influent concentration and flow rate. This is because of rapid saturation of SMFS-PAC in the column. The τ value increased and k_{YN} value decreased with increase in bed depth. A similar trend was observed for Cr(VI) adsorption on ozone-treated rice husk carbon [45].

The modeling of the experimental data using BDST model was performed by the plot of service time against bed depths at a flow rate of 2 mL/min and inlet Cr(VI) concentration of 50 mg/L. The equation of linear relationship was obtained with R^2 value of above 0.98. This indicates the validity of BDST model for the present packed bed column system. The BDST model constants are shown in Table 4. Generally, if K_a is large, even a short bed will avoid breakthrough, but as K_a decreases a progressively longer bed is required to avoid breakthrough [46]. The results obtained in this study show possibility of a large scale operation of adsorption process with respect to different bed depths.

Table 3
Thomas, Adams–Bohart, and Yoon–Nelson at different experimental conditions

Experimental conditions			Thomas model			Adams–Bohart model			Yoon–Nelson model		
Z (cm)	F (mL/min)	C_0 (mg/L)	q_0 (mg/g)	k_{TH} (mL/mg min)	R^2	N_{AB} (mg/L)	k_{AB} (L/mg min)	R^2	k_{YN} (1/min)	τ (min)	R^2
2	2	50	5.95	1.8	0.887	5,279	0.48×10^{-3}	0.657	0.078	42	0.955
4	2	50	14.35	1.5	0.943	4,588	0.54×10^{-3}	0.936	0.058	105	0.973
6	2	50	25.56	0.98	0.851	4,641	0.46×10^{-3}	0.873	0.050	180	0.937
4	4	50	5.17	3.94	0.910	3,106	1.24×10^{-3}	0.851	0.143	32	0.995
4	6	50	5.17	3.16	0.980	3,711	1.36×10^{-3}	0.860	0.158	23	0.980
4	2	100	13.73	0.84	0.925	7,752	0.29×10^{-3}	0.931	0.061	89	0.953
4	2	150	15.03	0.68	0.929	9,536	0.23×10^{-3}	0.893	0.076	69	0.978

Table 4
Bed depth service time model constants for adsorption of Cr(VI) ions into SMFS-PAC

N_0 (mg/L)	K_a (L/mg min)	R^2
4,138	−0.0018	0.982

4. Conclusions

Column adsorption of Cr(VI) ions using SMFS-PAC was performed and it reveals that the adsorption of Cr(VI) ions onto SMFS-PAC dependents on the influent flow rate, inlet Cr(VI) ions concentration, and bed depth. The adsorption capacity increased with increased metal ion concentration, bed depth and decreased with flow rate. Modeling column data resulted in better fits with the Thomas model and Yoon–Nelson model. The data also fitted well to the BDST model; which predicts a linear relationship between bed depth and service time. Furthermore, the easy availability and low cost would make SMFS-PAC as an attractive adsorbent for the sequestration of heavy metals.

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Symbols

A — area under the breakthrough curve, cm^2
C_{ads} — biosorbed metal ion concentration, mg/L
C_0 — initial/inlet metal ion concentration, mg/L
C_t — effluent metal ion concentration, mg/L
F — flow rate, ml/min
K_a — rate constant in BDST model, L/mg min
k_{Th} — the Thomas model constant, mL/min mg
k_{YN} — the Yoon–Nelson model rate constant, 1/min
k_{AB} — mass transfer coefficient, L/mg min
m_{total} — total amount of metal ion sent to column, g
M — total mass of the biosorbent packed in the column, g
N_0 — biosorption capacity of bed, mg/L
N_{AB} — saturation concentration in the Adams–Bohart model, mg/L
q_0 — biosorption capacity, mg/g
q_{eq} — equilibrium metal uptake or maximum capacity of the column, mg/g
q_{total} — column capacity, mg
t_{total} — total flow time, min
t_s — service time, min
u — influent linear velocity, cm/min
V_{eff} — total volume treated, mL
Z — bed depth, cm
Y — removal percentage of Cr(VI) ions, %
τ — time required for 50% adsorbate breakthrough, min

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