Removal of Hexavalent Chromium from Aqueous Solution using Natural Adsorbents - Column Studies

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***Abstract*— The packed bed column study was investigated using coconut shell and neem leaf for the removal of Cr(VI) from aqueous solution. The breakthrough characteristics for Cr(VI) removal was reported. The effect of operating parameters like influent Cr(VI) concentration, bed height of the packed column and the flow rate of aqueous solution on the breakthrough curve was studied. Bohart-Adams, Yoon-Nelson, Thomas model,Yan et al. model and Wolborska model were applied to the experimental data for their suitability.**

Keywords*— Hexavalent chromium removal, Column study, Yoon-Nelson model, Thomas model, Adams-Bohart model Introduction

I. INTRODUCTION

The major sources of chromium in water bodies by the human activities are mainly from industrial waste water discharges such as mining, cement, steel and paint industries. Such types of industries discharge Cr(VI) contained water. Cr(VI) has been reported to be toxic to animals, humans and also it is known as carcinogenic (Raji and Anirudhan, 1998). Excessive accumulation of Cr(VI) in human being causes ulcerations, dermatitis and allergic skin reactions. The concentration of Cr(VI) in industrial wastewater remains in the range from 0.5 to 270 mg/L (Casarett and Doul, 1980). According to EPA the maximum tolerance limit of Cr(VI) in drinking water 0.1 mg/L (MINAS, 2001). Tolerance limit of Cr(VI) in drinking water according to Ministry of Environment and Forest, Government of India is 0.01 mg/L (MINAS, 2001).

Several conventional technologies are used to remove the heavy metal from the aqueous solution such as membrane separation, electrochemical precipitation, ion exchange, reverse osmosis, ultrafiltration and adsorption. Major drawbacks of these processes are either high cost or discharge of sludge formed. Ion-exchange is considered a better alternative technique but its operating cost is high. All other techniques have higher operating cost. Hence among these techniques the adsorption method with using low-cost adsorbent is cost effective and extremely useful. Fixed bed column study is more effective for industrial purpose than batch adsorption process. A wide variety of agricultural waste such as rice husk, coconut shell, sawdust, wheat husk, wheat and rice straw abundantly available can be used as low-costadsorbent. Here, coconut shell and neem leaf are used as the adsorbent for Cr(VI) removal in continuous mode operation. The effect of initial pH, flow rate of metal solution, influent metal ion concentration and bed height are studied. Available models, i.e., Thomas model, Yoon-Nelson model, Adams-Bohart model, Yan et al. model, Wolborska model are applied to the experimental data to find out the suitable model. The coconut shell and neem leaf are widely available throughout India. India being a 3rd world country these adsorbent are suitable for the treatment on of Cr(VI) containing wastewater for small to any sized industries.

II. EXPERIMENTAL

Preparation of adsorbent

In the present study coconut shell and neem leaf were used as the adsorbent for the removal of Cr(VI) ions from aqueous solution. Initially adsorbents were collected from local area near Kolkata, West Bengal, India. Initially coconut shell was crushed in roll crusher and then it was grinded. Neem leaves and coconut shell were treated with 0.1N NaOH to remove lignin-based colour materials followed by 0.1N H_2SO_4 (Singha and Das, 2011). Then the adsorbents were washed with distilled water several times and dried at 105°Cfor 6 h. Next the adsorbent was sieved to pass through a -44 +52 mesh screen. After sieving the adsorbent was kept by in an airtight container in a decicator.

Metal solution

1000 mg/L of Cr(VI) solution was prepared by dissolving 2.83 gm of potassium dichromate ($K_2Cr_2O_7$) in double distilled water. Then stock solution of Cr(VI) was diluted to obtain required standard solution containing 5, 10, 15, 20 mg/L of Cr(VI). Throughout the experiment the glass wares were washed with 20% nitric acid followed by washing with deionized water and then the glass wares were dried in oven at 383K.

Reagents and instrument used

The analytical grade reagents were used and obtained from E. Merck Limited, Mumbai, India. WTW pH meter (Multi 340i/SET, Germany) was used to determine the pH of the solution. UV-vis Spectrophotometer (Dr 5000, HACH, U.S.A.) was used to determine the Cr(VI) content in standard and treated solution.

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Experimental procedure

Adsorption experiment was conducted in packed bed column at ambient temperature. Required amount of adsorbent was packed in glass columns to produce desired height. The glass columns had an internal diameter of 2 cm and height of 50 cm. Initially pH of Cr(VI) was adjusted by adding 0.1 N HCl. Cr(VI) solution was pumped through the packed bed column in a down flow direction at a desired flow rate by a peristaltic pump (Cole-Parmer, model-7535-04, USA). Samples were collected from the exit of the column at desired time intervals and 1,5 diphenyl-cabazide is added to produce the complex agent which is analyzed by UV-vis Spectrophotometer to determine the concentration of Cr(VI) (Standard Methods for Examination of Water and Wastewater, 1998). Experimental setup is shown in Figure 1.

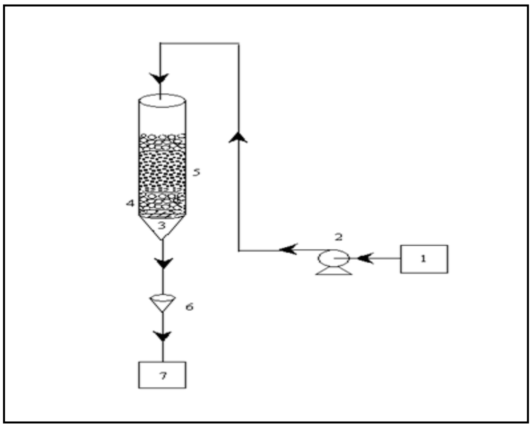

Figure 1 Schematic diagram of experimental set up of column study
1. Reservoir tank with metal solution; 2 Peristaltic pumps; 3. Porous sheet; 4. Glass beads; 5.Adsorbents; 6. Filter; 7. Treated effluent storage.

III. RESULTS AND DISCUSSIONS

Characterization of the adsorbent

Scanning electron microscopic image of the used adsorbents were carried out to see its surface structure. SEM images of adsorbent represented in Figures 2 and 3. The surface of coconut shell and neem leaf is porous and irregular in nature.

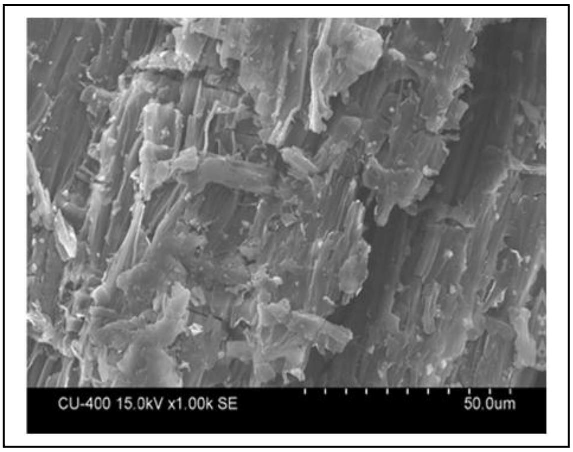

Figure 2. Scanning electron micrograph (SEM) of coconut shell

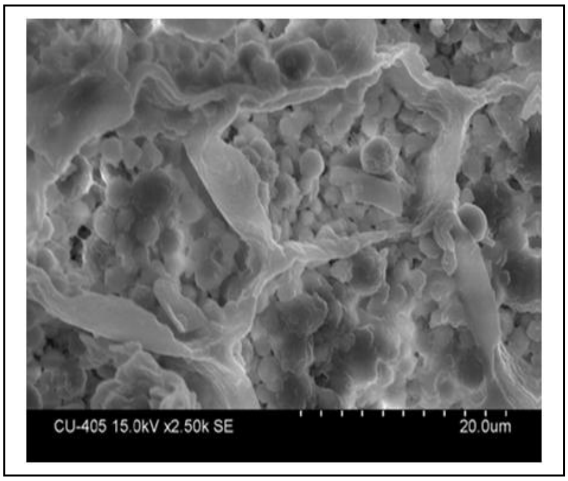

Figure 3. Scanning electron micrograph (SEM) of neem leaf

The FTIR studied indicated that the main functional groups like aliphatic -CH , aliphatic acid, aromatic NO_2, alkane and sulphonyl chlorides stretching are responsible for Cr(VI) binding on neem leaves and similarly phosphate ester, aliphatic acid, aromatic nitro, alkane $–SO_3$ and sulphonic S=O stretching are important for Cr(VI) binding on coconut shell (Singha et al., 2011).

The surface areas are measured in Micromeritics surface area analyzer (ASAP 2010, USA). The point of zero charge was determined by solid addition (Srivastava et al. 2006). Other physical properties of the adsorbents are shown in Table 1.

Table 1 Different physical characteristics of bioadsorbent

Adsorbents	Coconut shell	Neem leaf
Surface area (m^2/g)	0.52	0.57
Bulk Density (g/cm^3)	0.82	0.71
Dry matter (%)	93.84	91.67
Moisture content(%)	6.16	8.33
Point of zero charge	6.62	6.94
Ash content(%)	9.23	13.58

Effects of operating parameters

In our earlier study (Singha and Das, 2011) the effects of pH on the Cr(VI) removal onto coconut shell and neem leaf are reported for batch process. It was observed that for both adsorbents the maximum adsorption observed at pH 2. Cr(VI) exist in different forms in aqueous solution depending on pH. The chromate represented as H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ in solution as a function of pH and concentration [Gurgel et al., 2009].

At pH 1, chromium ions exist in the form of $HCrO_4^-$, while in the pH range 2–6 different forms of chromium ions such as $Cr_2O_7^{2-}$, $HCrO_4^-$,and $Cr_3O_{10}^{2-}$,coexists, of which $HCrO_4^-$ predominates. As the pH increases this form shifts to $CrO_4^{2-}$and $Cr_2O_7^{2-}$ (Singha and Das 2011). At low pH values, the Cr(VI) exists as univalent form, $HCrO_4^-$ and needs only one exchange site. As the pH increased, the overall surface charge on the adsorbents became negative and adsorption decreased.

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The adsorption experiments were operated at flow rate of 10 ml.min^{-1}, 20 ml.min^{-1} and 30 ml.min^{-1}.The breakthrough curve is a plot of dimensionless ratio of concentration (C_t/C_0) versus time and is shown in Figures 4 and 5. The better performance was observed at lower flow rate (10 ml.min^{-1}). At higher flow rate breakthrough occurred more rapidly than the lower flow rate. These figures indicated that with increase in flow rate the breakthrough time decreases. This behaviour occurred because at higher flow rate the Cr(VI) solution had less contact time, i.e., residence time within the column. At lower flow rate the Cr(VI) solution had more time to contact with the adsorbent in the column and hence higher removal of metal ions observed. The best adsorption capacity of the fixed bed column obtained at 10 ml min^{-1} flow rate. Similar results are obtained by other researchers (Hanen and Abdelmottaleb,2013 ; Sivaprakash et al.,2010).

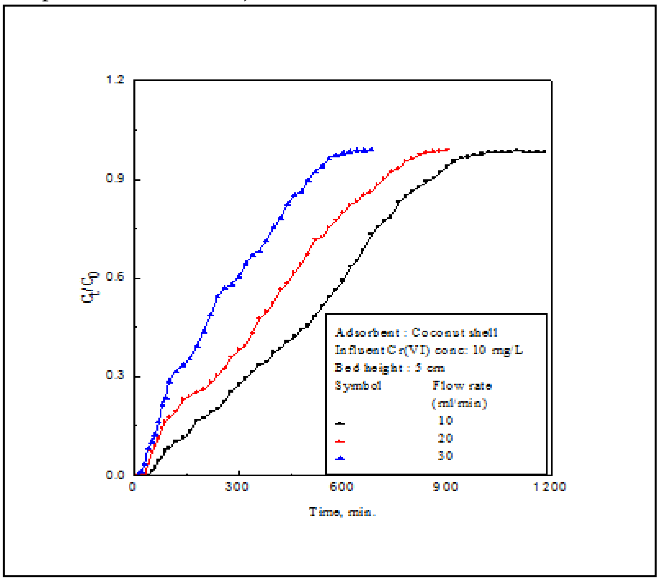

Figure 4 Effect of flow rate for Cr(VI) adsorption on coconut shell at constant bed height and influent metal ion concentration

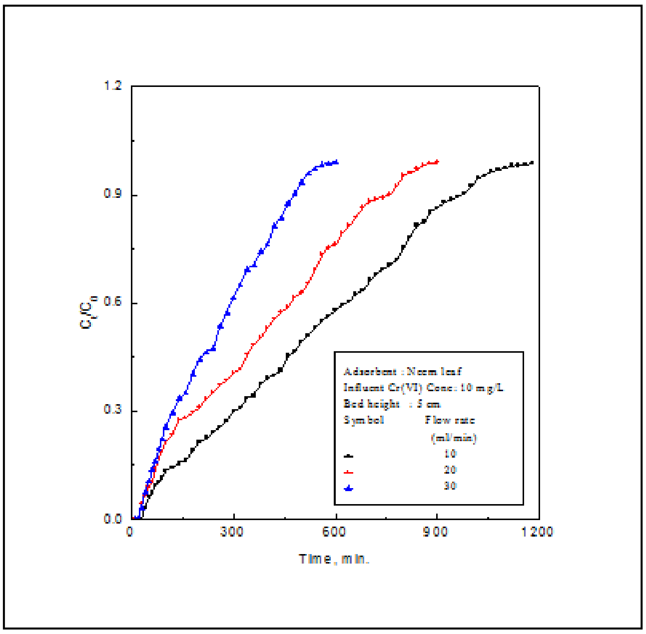

Figure 5 Effect of flow rate for Cr(VI) adsorption on neem leaf at constant bed height and influent metal ion concentration

The effects of bed height were investigated for bed height of 5, 10 and 15 cm at a constant flow rate and influent metal ion concentration. The breakthrough curves are shown in Figures 6 and 7.The removal of heavy metal is entirely dependent on the bed height. From these graphs it was observed that the breakthrough time decreases as the bed height decreases. At higher bed height breakthrough occurred more slowly than the lower bed height because at higher bed height aqueous solution got more binding sites of the adsorbent and this behaviour produced higher removal of metal ions in the column. Similar observations are obtained by other researchers (Hasfalina et al., 2012; Nwabanne et al., 2012).

The effects of metal ion concentration were investigated at different initial Cr(VI) concentration of 10 mg/L, 20 mg/L and 30 mg/L. The breakthrough curves are shown in Figures 8 and 9. From the breakthrough graphs it observed that adsorption capacity of the packed bed increases with the decrease in metal ion concentration. At high influent metal ion concentration adsorption capacity decreased due to earlier saturation of active surfaces. At lower influent metal ion concentration the adsorption capacity increased because the metal ions would react with active binding sites. The breakthrough time increased as the influent metal ion decreased (Deepali, 2011).

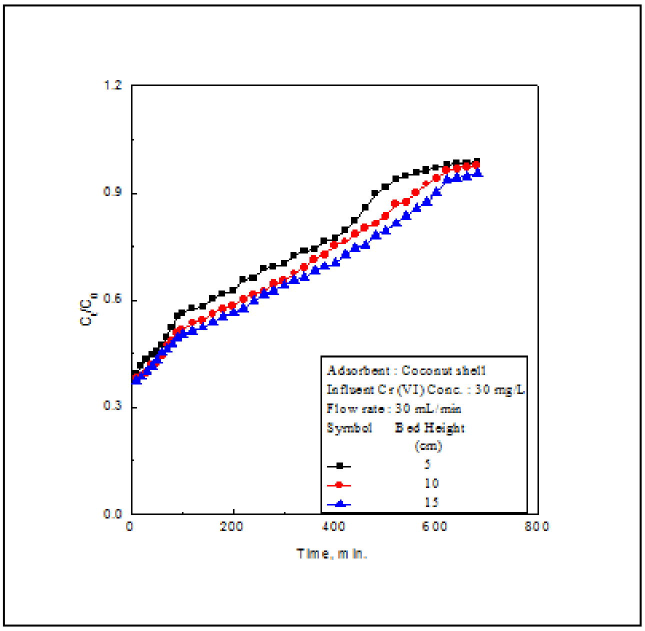

Figure 6 Effect of bed height of column for removal of Cr(VI) on coconut shell at constant flow rate and influent metal ion concentration

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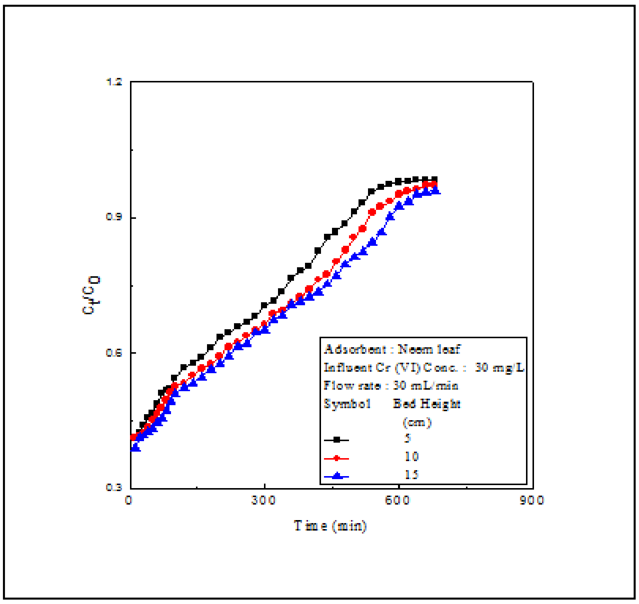

Figure 7 Effect of bed height of column for removal of Cr(VI) on neem leaf at constant flow rate and influent metal ion concentration

IV. MODELLING OF COLUMN STUDY

Maximum adsorption capacity of the adsorbent in a fixed bed column is calculated by following equations

$$q_e = \frac{v}{1000w}\int_0^{t_{total}} (C_0 - C_t)\,dt \qquad (1)$$

$$q_{e_{\max}} = \frac{q_{total}}{w} \qquad (2)$$

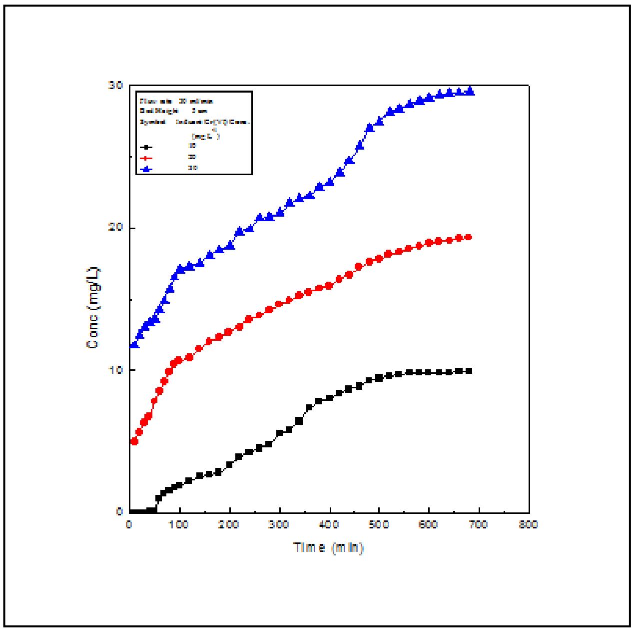

Figure 8 Effect of influent metal ions concentration for the removal of Cr(VI) on coconut shell at constant bed height and flow rate

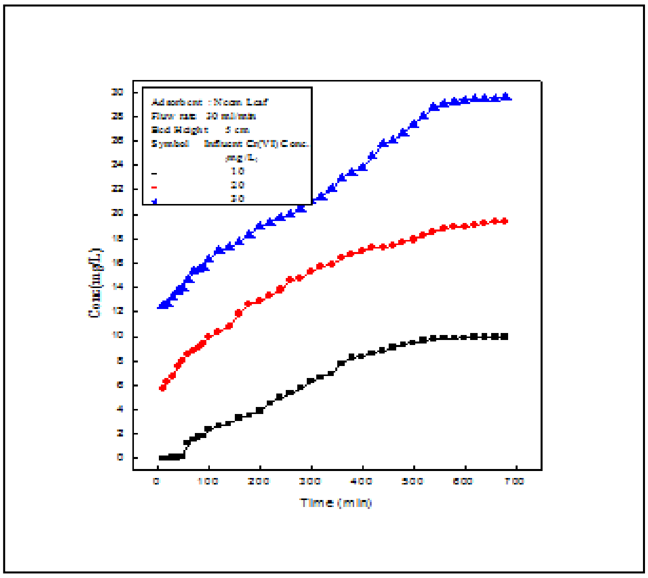

Figure 9 Effect of influent metal ions concentration for the removal of Cr(VI) on neem leaf at constant bed height and flow rate

Bohart-Adams (1920) model

Bohart and Adams developed to find the adsorption capacity and adsorption rate constant of the continuous column operation (Bohart and Adams, 1920).The expression given by Bohart and Adams for an adsorption column is given as follows (Aksu and Gönen, 2004),

$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB}C_0 t - k_{AB}N_0\left(\frac{z}{v}\right) \qquad (3)$$

The intercept and slope of the linear plot of $\ln(C_t/C_0)$ versus time were used to determine the value of adsorption capacity N_0 and kinetic constant $k_{AB.}$ The values of k_{AB}, N_0 and statistical parameters are tabulated in Table 2. It is observed that the rate constant (k_{AB}) and saturation concentration (N_0) is dependent on flow rate and metal ion concentration. It is also observed that the value of rate constant (k_{AB}) increases with the increasing flow rate.

Table 2 Bohart -Adams model parameters

Flow rate v (ml/min)	Influent concentration C_0 (mg/L)	Bed height (cm)	Rate constant, k_{AB} X 10^4 ml/(min. mg)	Saturation concentration, N_0 (g/L)	R^2
Adsorbent : Coconut shell					
10	10	5	5.68	11.48	0.7999
20	10	5	5.55	14.03	0.7869
30	10	5	13.92	13.91	0.6586
10	20	5	2.4	18.665	0.8155
20	20	5	2.4	40.65	0.8825
30	20	5	3.75	21.963	0.9280
10	30	5	0.433	70.27	0.9368
20	30	5	0.933	58.20	0.9096
30	30	5	1.26	45.73	0.9810
10	30	10	0.933	37.74	0.9285
20	30	10	0.8	48.64	0.9077
30	30	10	1.233	24.90	0.9750
10	30	15	0.8	32.7108	0.9637
20	30	15	19.4	40.16	0.8630
30	30	15	0.4033	48.28	0.9555
Adsorbent : Neem leaf					
10	10	5	3.5	12.97	0.8796
20	10	5	3.8	21.10	0.8228
30	10	5	10.3	13.10	0.6409
10	20	5	2.2	15.95	0.8770
20	20	5	2.1	34.24	0.8737
30	20	5	2.7	21.95	0.9387
10	30	5	0.4	48.97	0.9421
20	30	5	0.8	50.32	0.9017
30	30	5	0.9	43.14	0.9815
10	30	10	1.2	24.41	0.9688
20	30	10	0.7	38.37	0.9300
30	30	10	0.9	23.84	0.9848
10	30	15	1.1	20.27	0.9618
20	30	15	0.7	28.63	0.8920
30	30	15	0.5	28.55	0.9636

Yoon-Nelson (1984) model

The basic assumption of this model is the rate of decrease in the probability of adsorption for each adsorbate molecule depends on the adsorbate adsorption. The Yoon-Nelson equation is as follows (Zeinali and et al., 2010),

$$\frac{C_t}{C_0 - C_t} = \exp(k_{YNt} - k_{YN\tau}) \qquad (4)$$

The intercept and slope of the linear plot of $\ln(C_t/C_0\text{-}C_t)$ versus time were used to determine the value of breakthrough parameters τ and k_{YN}. Parameters and the values of R^2 are tabulated in Table 3. From the tabulated data it is observed that time required for 50% breakthrough decreases as the flow rate increases but the value of rate constant k_{YN} increases with the increasing flow for Cr(VI) removal on coconut shell and neem leaf respectively. From the R^2 values it can be concluded that Yoon-Nelson model is appropriate to describe the column operation of Cr(VI) removal on coconut shell and neem leaf respectively. Similar result obtained by other researcher (Saadi et al., 2013).

Table 3 Yoon-Nelson model parameters

Flow rate v (ml/min)	Influent concentration C_0 (mg /L)	Bed height (cm)	Time, τ (min)	Rate constant k_{YN} (1/min)	R^2
Adsorbent : Coconut shell					
10	10	5	475.0072	0.0069	0.8623
20	10	5	359.4598	0.0072	0.8581
30	30	5	191.2437	0.0170	0.7370
10	20	5	332.679	0.0065	0.8791
20	20	5	377.849	0.0063	0.9304
30	20	5	89.48	0.0126	0.9520
10	30	5	633.398	0.0020	0.9826
20	30	5	237.68	0.0046	0.9403
30	30	5	66.497	0.0061	0.9672
10	30	10	1027.048	0.00349	0.9604
20	30	10	524.57	0.0035	0.9475
30	30	10	149.84	0.0031	0.9230
10	30	15	1419.0813	0.0028	0.9773
20	30	15	691.978	0.0027	0.9192
30	30	15	257.4705	0.0020	0.9708
Adsorbent : Neem leaf					
10	10	5	654.9772	0.0044	0.9284
20	10	5	663.2368	0.0038	0.8277
30	10	5	216.7615	0.0130	0.7286
10	20	5	340.952	0.0063	0.9238
20	20	5	391.551	0.0058	0.9240
30	20	5	102.75	0.0091	0.9620
10	30	5	543.63	0.0022	0.9675
20	30	5	258	0.0040	0.9330
30	30	5	61.96	0.0056	0.9830
10	30	10	864.66	0.0045	0.9746
20	30	10	507.64	0.0034	0.9630
30	30	10	84.34	0.0053	0.9790
10	30	15	1134.7027	0.0037	0.9580
20	30	15	625.1	0.0030	0.9358
30	30	15	161.533	0.0030	0.9721

Thomas (1948) model

Thomas model has been widely used for heavy metal removal in fixed bed column studies (Thomas, 1948). The mathematical form of Thomas model is expressed as follows (Malkoc et al., 2006),

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp[(\frac{k_{Th} q_e x}{Q}) - k_{Th} C_0 t]} \qquad (5)$$

Linearized form of Thomas model is expressed as follows,

$$\ln(\frac{Ct}{C_0} - 1) = \left(\frac{k_{TH} q_e x}{Q}\right) - k_{TH} C_0 t \qquad (6)$$

The model parameters and the values of R^2 are tabulated in Table 4. From the table it is observed that the value of calculated q_e from Thomas model is greater than the value of experimental q_e. The value of q_e increases as the adsorbent dose increases but the value of K_{Th} decreases for the same. It is also observed that value of q_e decreases as the flow rate of aqueous solution increases.

Table 4 Thomas model parameters

Flow rate, v (ml/min)	Influent concentration C_0 (mg/L)	Bed height (cm)	k_{Th} ml/(min.mg)	$q_{e,max(cal)}$ (mg/g)	$q_{e,max(exp)}$ (mg/g)	R^2
Adsorbent : Coconut shell						
10	10	5	0.690	7.63	4.28	0.8623
20	10	5	0.72	11.47	6.06	0.8561
30	10	5	1.7	9.31	5.35	0.7370
10	20	5	0.325	10.61	5.97	0.8791
20	20	5	0.32	23.8	13.2	0.9304
30	20	5	0.633	8.52	5.19	0.9502
10	30	5	0.068	30.45	16.009	0.9828
20	30	5	0.15	22.63	13.16	0.9403
30	30	5	0.203	9.5	4.86	0.9672
10	30	10	0.116	25	13.77	0.9603
20	30	10	0.1167	24.97	14.18	0.9475
30	30	10	0.104	10.71	6.35	0.9327
10	30	15	0.093	22.75	11.84	0.9773
20	30	15	0.913	21.49	11.99	0.9131
30	30	15	0.07	11.50	6.14	0.9666
Adsobent : Neem leaf						
10	10	5	0.44	10.39	5.75	0.9284
20	10	5	0.49	16.14	9.23	0.8837
30	10	5	1.3	10.32	6.32	0.7286
10	20	5	0.3	10.36	6.58	0.9238
20	20	5	0.29	24.86	13.82	0.9247
30	20	5	0.45	9.78	5.52	0.9620
10	30	5	0.07	42.65	13.61	0.9675
20	30	5	0.13	24.58	14.08	0.9335
30	30	5	0.18	8.87	5.45	0.9839
10	30	10	0.15	20.58	11.13	0.9746
20	30	10	0.11	24.18	13.21	0.9632
30	30	10	0.17	6.028	3.12	0.9792
10	30	15	0.12	18.01	9.10	0.9580
20	30	15	0.10	19.84	10.72	0.9358
30	30	15	0.10	7.69	4.23	0.9721

Table 5 Yan et al. model parameters

Flow rate v (ml/min)	Influent concentration on C_0 (mg/L)	Bed height (cm)	Rate constant k_Y ml/(mg.min)	q_Y (mg/g)	R^2
Adsorbent : Coconut shell					
10	10	5	1564.19	5.6743	0.9740
20	10	5	2405.80	11.32	0.9534
30	30	5	5099.70	5.67	0.9486
10	20	5	413.10	16.70	0.9899
20	20	5	843.17	41.51	0.9642
30	20	5	1111.05	13.18	0.9675
10	30	5	129.76	142.73	0.8974
20	30	5	635.1	1.27	0.9468
30	30	5	259.12	46.87	0.8911
10	30	10	360.6	38.61	0.8988
20	30	10	412.67	59.42	0.9465
30	30	10	244.07	55.11	0.9692
10	30	15	351.70	48.71	0.8322
20	30	15	453.46	44.40	0.9836
30	30	15	216.37	74.35	0.9528
Adsorbent : Neem leaf					
10	10	5	1124.50	11.89	0.9867
20	10	5	1455.80	61.34	0.9890
30	10	5	3889.80	0.95	0.9786
10	20	5	401.80	18.20	0.9599
20	20	5	812.40	42.31	0.9707
30	20	5	632.10	27.33	0.9560
10	30	5	128.13	104.61	0.9255
20	30	5	268.26	77.10	0.9525
30	30	5	190.80	45.94	0.9143
10	30	10	360.73	38.04	0.7967
20	30	10	375.40	67.27	0.9351
30	30	10	185.05	42.78	0.7992
10	30	15	354.26	41.60	0.7539
20	30	15	409.80	48.58	0.9588
30	30	15	185.40	58.09	0.8948

Yan et al. (2011) model

Mass transfer model is used to describe the breakthrough curve of the fixed bed column study (Yan et al. 2011). This model proposed a better approach to describe the breakthrough curve than the Thomas model. Linearized form of Yan et al. model is given as follows,

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = \frac{K_Y}{Q} C_0 \ln\left(\frac{Q^2}{K_Y q_Y m}\right) + \frac{K_Y C_0}{Q} \ln t \qquad (7)$$

The value of rate constant (K_Y), adsorption capacity (q_Y) and R^2 are tabulated in Table 5. From the table it is observed that the adsorption capacity (q_Y) increases with the increase in flow rate and bed height. The rate constant (K_Y) value increases with the increase in flow rate.

Wolborska (1989) model

The mathematical expression of Wolborska model is similar to Adams-Bohart model. The linearised form of Wolborska model is given as follows (Wolborska, 1989),

$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB} C_0 t - k_{AB} N_0 \left(\frac{z}{v}\right) \qquad (8)$$

The model parameter values are tabulated in Table 6. These values depend on the flow rate and bed height. The value of b increases with the increase in flow rate but decreases with the increases in bed height.

Table 6 Wolborska model parameters

Flow rate, v (ml/min)	Influent concentration C_0 (mg/L)	Bed height (cm)	B (L/min)	Saturation concentration, N_0 (g/L)	R^2
Adsorbent : Coconut shell					
10	10	5	0.6520	11.48	0.7999
20	10	5	1.0367	14.03	0.7869
30	30	5	1.9360	13.91	0.6586
10	20	5	0.4479	18.665	0.8155
20	20	5	0.9750	40.65	0.8825
30	20	5	0.8230	21.963	0.9280
10	30	5	0.3042	70.27	0.9368
20	30	5	0.5430	58.20	0.9096
30	30	5	0.5463	45.73	0.9810
10	30	10	0.3521	37.74	0.9285
20	30	10	0.3890	48.64	0.9077
30	30	10	0.2852	24.90	0.9750
10	30	15	0.2616	32.7108	0.9637
20	30	15	0.2590	40.16	0.8630
30	30	15	0.1947	48.28	0.9555
Adsorbent : Neem leaf					
10	10	5	0.5721	12.97	0.8796
20	10	5	1.0103	21.10	0.8228
30	10	5	1.7007	13.10	0.6409
10	20	5	0.4421	15.95	0.8770
20	20	5	0.9270	34.24	0.8737
30	20	5	0.7470	21.95	0.9387
10	30	5	0.2880	48.97	0.9421
20	30	5	0.5281	50.32	0.9017
30	30	5	0.5250	43.14	0.9815
10	30	10	0.3791	24.41	0.9688
20	30	10	0.3708	38.37	0.9300
30	30	10	0.2802	23.84	0.9848
10	30	15	0.2725	20.27	0.9618
20	30	15	0.2645	28.63	0.8920
30	30	15	0.1918	28.55	0.9636

IV. SAFE DISPOSAL OF USED ADSORBENTS

The leaching possibility of the Chromium ions from the used adsorbents restricts its dumping in the open environment. The Cr(VI) loaded adsorbents were incinerated at 700° C to form ash and then 5 mg of the ash samples were mixed with 25 ml of deionized water to give a liquid - solid ratio of 5:1 (Nag et al., 2015). After continuous gentle stirring for 24 h the filtrate was analyzed for Cr(VI) ions. It was observed that Cr(VI) did not leach from the ash sample. Hence, this ash may be used for road filling particularly in the nearby rural areas or to be placed in the agricultural field.

V. CONCLUSIONS

Fixed-bed column studies have been carried out for the removal of Cr(VI) ions using coconut shell and neem leaf .

1. An effective removal of Cr(VI) is observed by a fixed bed column using coconut shell and neem leaf as an low-costadsorbent.
2. The removal efficiency of the adsorbent depends on the pH and flow rate of the metal solution, influent metal ion concentration and the bed height of the packed column. The removal process is effective at pH 2 for Cr(VI) removal on coconut shell and neem leaf respectively.
3. Maximum amount of metal removal is observed at lower flow rate. But at higher flow rate breakthrough time decreases which finally produces insufficient amount of metal removal.
4. At higher bed height maximum amount of heavy metal is removed than the lower bed height at a constant flow rate.
5. At low metal ion concentration adsorption capacity of the packed column increases. At higher metal ion concentration lower amount of metal removal is observed.
6. Bohart-Adams model, Yoon-Nelson model, Thomas model, Yan et al. model and Wolborska model are used to describe the performance of the fixed be column study. Thomas model and Yoon-Nelson model fit well with the experimental data for predicting the breakthrough curves for Cr(VI) removal compare to the other models.
7. Incineration of the used adsorbents to form non-leachable ash is the safe disposal suggested method.

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NOMENCLATURE

C_0 initial Cr(VI) concentration (mg/L)
C_t Cr(VI) concentration at time t (mg/L)
k_{AB} kinetic constant (ml/min.mg)
k_{Th} rate constant (ml/min.mg)
k_{YN} rate constant (1/min)
K_Y rate constant (ml/mg.min)
N_0 adsorption capacity (g/L)
$q_{e,max}$ maximum adsorption capacity (mg/g)
q_Y maximum adsorption capacity (mg/g)
x mass of the adsorbent (g)
t breakthrough time (min)
z bed depth (cm)
Greek letters
β Wolborska model constant (L/min)
τ time required for 50% adsorbate breakthrough (min)
v flow rate of metal solution (ml/min)

REFERENCES

[1] Aksu, Z. and F. Gönen (2004), Biosorption of phenol by immobilized activated sludge in acontinuous packed bed: prediction of breakthrough curves. Proc. Biochem. 39 599–613.
[2] APHA, AWWA (1998). Standard methods for examination of water and wastewater, 20th Ed., Washington, DC, New York.
[3] Bohart G., E. N. Adams (1920). Some aspects of the behavior of charcoal with respect to chlorine. J. Am. Chem. Soc. 42 523–544.
[4] Casarett, L. J. and J. Doul (1980). Toxicology, the basic science of poisons, Macmillan, New York.
[5] Deepali (2011). Bioremediation of Chromium (VI) from Textile Industry's Effluent and Contaminated Soil Using *Pseudomonas putida*. Iranica J. Energy and Environ. 2(1) 24-31.

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[6] Gurgel, L. V . A., J. C. P. de Melo, J. C. de Lena and L. F. Gil (2009). Adsorption of chromium (VI) ion from aqueous solution by succinylatedmercerized cellulose functionalized with quaternary ammonium groups. Biores. Technol. 100 3214–3220.
[7] Hanen, N. and O. Abdelmottaleb (2013). Modeling of the dynamics adsorption of phenol from an aqueous solution on activated carbon produced from olive stones. J. Chem. Engg. Process Technol. 4(3) 153 doi:10.4172/2157-7048.1000153.
[8] Hasfalina, C. M., R. Z. Maryam, C. A. Luqman and M. Rashid (2012). Adsorption of copper (II) from aqueous medium in fixed-bed column by kenaf fibres. APCBEE Procedia 3 255-263.
[9] Malkoc, E., Y. Nuhoglu and Y. Abali (2006). Cr(VI) adsorption by waste acron of quercusithaburensis in fixed beds: prediction oh breakthrough curves. Chem. Engg. J. 119 61-68.
[10] MINAS, Pollution control acts, rules, and notification there under Central Pollution Control Board, Ministry of Environment and Forests, Government of India, New Delhi, 2001.
[11] Nag, S., A. Mondal, U. Mishra, N. Bar, S. K. Das (2016). Removal of chromium(VI) from aqueous solutions using rubber leaf powder: batch, column studies and ANN modeling. Desalination Water Treat., 57(36) 16927-16942.
[12] Nwabanne, J. T. and P. K. Igbokwe (2012). Adsorption Performance of packed bed column for the removal of Lead (II) using oil Palm Fibre. Int. J.App. Sci. Technol. 2(5) 106-115.
[13] Raji, C. and T. S. Anirudhan (1998). Batch Cr(VI) removal by polyacrylamide-grafted sawdust:kinetics and thermodynamics. Water Res. 32(12) 3772–3780.
[14] Saadi, Z., R. Saadi and R. Fazaeli (2013). Fixed-bed adsorption dynamics of Pb (II) adsorption from aqueous solution using nanostructured γ-alumina. J. Nanostructure chem., http://www.jnanochem.com/content/3/1/48.
[15] Singha, B. and S. K. Das (2011). Biosorption of Cr(VI) ions from aqueous solutions : kinetics, equilibrium, thermodynamics and desorption studies. Coll. Surfaces B: Biointerfaces, 84 221 – 232.
[16] Singha, B., T. K.Naiya, A. K. Bhattacharya and S. K.Das (2011). Cr(VI) Ions removal from aqueous solutions using natural adsorbents—FTIR studies. J. Environ. Protection, 2 729-735.
[17] Sivaprakash, B., N. Rajamohan and A. Mohamed Sadhik (2010). Batch and column sorption of heavy metal from aqueous solution using a marine alga *Sargassumtenerrimum*. Int. J. Chem. Tech. Res. 2(1) 155-162.
[18] Srivastava V.C, I. D.Mall, I. M. Mishra (2006). Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. J. Hazard. Mater. B134 257–267.
[19] Thomas H.G. (1948). Chromatography: A problem in kinetics. Ann. N.Y. Acad. Sci. 49 161–182.
[20] Wolborska, A. (1989). Adsorption on activated carbon of p-nitrophenol from aqueous solution. Water Res. 23 85–91.
[21] Yan, G.Y., T. Viraraghavan and M. Chem (2001). A new model for heavy metal removal in a biosorption column. Ads. Sci. Technol. 19 25-43.
[22] Yoon Y.H., J.H. Nelson(1984). Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life. Am. Ind. Hyg. Assoc. J. 45 509–516.
[23] Zeinali, F., A. A. Ghoreyshi and G. D. Najafpour (2010). Adsorption of dichloromethane from aqueous phase using granular activated carbon : isotherm and breakthrough curve measurements. J. Scientific Res. 5(4) 191–198.