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Biosorption of Chromium (VI) by Coconut Husk – Optimization of Adsorption Factors and Column Adsorption Studies

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Abstract

Hexavalent chromium is a major component of many industrial effluents and is toxic and carcinogenic even at very low concentrations. The present study aimed at evaluating the efficiency of coconut husk as an adsorbent for removal of Cr(VI)from solutions in a Packed Bed Adsorption Column. Batch adsorption studies were conducted to determine the effect of factors on removal of chromium from aqueous solutions by three forms of the biomass – untreated, acid-treated and alkali-treated. The acid-treated form of coconut husk was found to be the best with maximum chromium removal capacity of 84.06% at 2.35 pH and 34.3oC temperature, with highest initial metal concentration of 165.47 mg/L and lowest adsorbent usage of 4.89 g/100mL.Fixed bed column adsorption studies were conducted by varying flow rate of inlet stream (0.5 mL/min to 1.2 mL/min) while keeping the feed concentration at 250 mg/L, solution pH at 2.5 and bed height at 10 cm. Breakthrough curve was plotted and maximum value of adsorption capacity was obtained as 5.77 mg/g for flow rate of 1.2 mL/min. The observations were fit into well-established fixed-bed adsorption models namely, Adams-Bohart, Thomas and Yoon-Nelson models. Thomas and Yoon-Nelson models were found to fit the adsorption data to good extent, with correlation coefficient R2≥ 0.96.

***Keywords:** Chromium, Biosorption, Column Adsorption, Adams-Bohart Model, Thomas Model, Yoon-Nelson Model, Breakthrough Curve*

I. INTRODUCTION

One of the major cause of pollution of water bodies is discharge of industrial waste-water. Most of the industrial effluents contain heavy metals as contaminants, out of which, Chromium is the most abundant. It is widely found in effluents of industries involved in electroplating, metal fabrication, mining, paints & pigments & varnishes, leather tanning etc. [1-4].In solution forms, chromium exists in two valence states – trivalent chromium ions [Cr(III)] and hexavalent chromium ions [Cr(VI)]. Cr(III) has been reported to be relatively stable, unreactive & insoluble and an essential metal nutrient in trace quantities[5-6]. On the contrary, Cr(VI) is relatively unstable & a very strong oxidizing agent. It is known to have carcinogenic and toxic properties, thuscausing high degree of concern[7-9].

The permissible limits for Cr(VI) concentration in industrial effluents is 0.05 to 0.1 mg/L, whereas the effluents are commonly found to contain Cr(VI) to the extent of 0.5 to 270 mg/L[3, 10,11].It is, thus, essential to treat the effluents suitably in order to reduce the Cr(VI) concentrations, before discharging into the environment.The conventional methods available for treatment of waste-water are - Chemical/ Electrochemical Precipitation, Ion Exchange, Reduction, Solvent Extraction, Membrane Separation, Evaporation, Reverse Osmosis, Lime Coagulation and Adsorption [12-22].

The conventional methods of waste-water treatment have many demerits such as high chemical and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. However, researchers have determined that Adsorption is an effective method for removal of heavy metals & other contaminants from industrial effluents. Its advantages include easy sludge disposal and economic viability, especially when low-cost adsorbents are employed in conjunction with appropriate regenerative techniques[23].

In the recent years, several researchers have explored the possibility of employing low-cost, easily available biomass, such as agricultural byproducts & waste materials, for removal of chromium from aqueous effluents by adsorption.

Example of such biomass includes paper mill sludge, seaweed, sugar beet pulp, wheat bran, groundnut husk, coconut tree sawdust, shell & wood, spent tyre, cactus, wool, charcoal, rice husk, almond shell, cow dung etc.[24-34].

In the present study, the feasibility of using one such easily and cheaply available biomass viz. coconut husk has been explored. The study has been designed by utilizing Response Surface Methodology (RSM). It is especially useful when the process under study involves multiple independent variables & a wide range of values within, as is the case with adsorption[35-37].

The objective of the current study is to determine the factors affecting biosorption of Cr(VI) by coconut husk and to optimize the conditions for obtaining maximum removal of chromium in aqueous solutions. Further, the effect of pre-treatment processes on the performance of the biomass has been evaluated. Column Adsorption studies were conducted to analyze the feasibility of the biomass for continuous adsorption process. Not much work has been carried out in this direction in the context of coconut husk biomass.

2. MATERIALS & METHODS

2.1 Preparation of Biosorbent

coconut husk, which is agro waste of the coconut industry, was collected from coconut market yards. It was dried in sun, and then crushed and powdered. The powdered material was then sieved to obtain biomass of uniform particle size.

The biomass was split into three parts &they were subjected to different types of treatment, to obtain different forms of the biosorbent. One part was soaked in acid solution (0.2 N Hydrochloric acid) for 2 hours while the other part was soaked in an alkali solution (0.2 N Sodium hydroxide).

The left-over portion of the biomass was soaked in distilled water. The mixture was filtered through Whatman Filter paper. The retentate (treated biomass) was repeatedly washed with distilled water, followed by filtration, till the filterate obtained was colorless. The biomass so obtained was dried in hot-air oven at 60 oC for 24 hours and used as biosorbent for further studies.

2.2 Plotting Standard Calibration Chart

2.2.1 Principle

Cr (VI) concentration was identified by colorimetric estimation method using DiPhenyl Carbazide (DPC) as the coloring agent.

2.2.2 Estimation

Standard solutions of Cr(VI), with varying concentrations were obtained by dissolving known amount of Potassium dichromate($K_2Cr_2O_7$) in double distilled water and diluting appropriately.1 mL of the standard solution(s) wereestimated in Spectrophotometer and standard Calibration Chart was plotted for the absorbance of standard chromium solutions versus their respective Cr(VI) concentration.

2.3 Preliminary Study

Based on the preliminary studies, it was observed that following are the parameters and the range of values in which they predominantly affect Biosorption of Cr(VI): Biomass loading (1 – 10 g/100mL), pH (1 – 7), Temperature (30 – 60 oC) and initial metal ion concentration (10 – 200 mg/L). Further studies were focused in the above mentioned range of values for the respective factors.

2.4 Experiment Design by Central Composite Design Methodology

Central Composite Design (CCD) Methodology was employed for design of the experiment. A statistical software MINITAB v16 was used for this purpose. Each of the four variables had 5 levels of values in the range mentioned. With 24full-factorial experimental design for the above variables and levels, a total of 31 different combinations were obtained with 7 replicates at the center point. The design helps in analyzing the influence of the independent variables on chromium removal efficiency and, further, in obtaining the optimum conditions of these variables under which maximum removal of chromium can be achieved.

2.5 Batch Adsorption Study

Based on the Central Composite Design Matrix obtained, Batch studies were conducted to determine the percentage removal of Cr(VI) by the biosorbent. For conducting batch adsorption studies, 100 mL of synthetically prepared Cr(VI) solution with varying known concentration were taken in 250 mL conical flasks.

The conditions of temperature, pH, biosorbent loading & temperature were maintained as obtained from CCD. The flasks were shaken in a rotary shaker incubator. 1 mL of samples were obtained at regular intervals of time and analyzed by spectrophotometric method using DPC methodto determine the equilibrium concentration of chromium in the solution. From this, the percentage removal of chromium was calculated.

2.6 Optimization of Parameters Affecting Biosorption

The results obtained in batch adsorption studies were analyzed by using Response Surface Methodology. Regression analysis was performed on the response variable and the independent variables, which yielded a second degree polynomial equation. MINITAB v16 was employed for regression analysis of the data. Further, using the Response Optimizer in MINITAB v16, the second degree polynomial equation was solved to obtain the optimum values of the parameters.

2.7 Column Adsorption Studies

2.7.1 Design of Fixed Bed Adsorption Column

A glass column with an inner diameter of 1.1 cm and 50 cm in length was used for conducting column adsorption studies. Two centimeter layer of cotton was placed at the top and bottom of column. The biosorbent was packed in between these two cotton plugs, to emulate a packed bed adsorption column.

Standard solution of chromium metal ion was prepared by dissolving Potassium dichromate (AR grade) in double distilled water. This was allowed to flow through the packed bed column by loading into IVF (Intra-Venous Fluid) Bottle. The column was calibrated for the flow rate of the standard solution. The binding capacity of the columnwas calculated to check the adsorption capacity of the biosorbent. This column was further used for conduction of Column adsorption studies.

2.7.2 Adsorption Studies

The standard solution, with initial Cr(VI) concentration of 250 mg/L, was allowed to flow through the packed bed column under standard conditions of pH (2.5) and at 3 different flow rates viz. 0.5mL/min., 0.9 mL/min. & 1.2 mL/ min.

Fractions of the effluent were collected at regular intervals of time and the concentration of chromium was determined by subjecting the samples to colorimetric estimation using Diphenyl carbazide method. This was further used to determine the degree (%) of adsorption occurring in the packed bed column.

The analysis of Column Adsorption phenomenon was done by studying the breakthrough curve and by employing the following mathematical models:

- Adam-Bohart Model
- Thomas Model
- Yoon-Nelson Model

3. RESULTS & DISCUSSION

3.1 Batch Adsorption Study Results

From batch adsorption study, % removal of Cr(VI) was determined for each of the set of conditions obtained from CCD. The value of R2 obtained for C, CH and CN is 0.87, 0.90 and 0.84 respectively, clearly showing that the model is apt for the experimental data. The Regression coefficient (R2) determines the fitness of the model to the data, and value closer to 1 indicates that the statistical model fits the data well.

3.2 Regression Analysis by Response Surface Methodology

Regression analysis was performed on the experimental observations recorded during batch adsorption studies by Response Surface Methodology (RSM) using MINITAB v16. The value of the response variableY as a quadratic function of the independent variables for the three different forms of biosorbent CH, C and CN is given in equations (2), (3) and (4) respectively.

$$Y=69.51 - 13.23X_1 - 2.22X_2 + 6.34X_3 - 3.75X_4 - 3.34X_1^2 - 0.24X_2^2 - 2.42X_3^2 - 4.34X_4^2 + 0.19X_1X_2 - 1.92X_1X_3 + 1.31X_1X_4 - 0.26X_2 X_3 + 0.12X_2X_4 + 2.61X_3X_4 \quad \ldots\ldots\ldots.. (1)$$

$$Y = 67.43 - 12.83X_1 - 2.16X_2 + 6.15X_3 - 3.63X_4 - 3.24X_1^2 - 0.23X_2^2 - 2.34X_3^2 - 4.21X_4^2 + 0.19X_1X_2 - 1.86X_1X_3 + 1.27X_1X_4 - 0.25X_2 X_3 + 0.11X_2X_4 + 2.53X_3X_4 \quad \ldots\ldots\ldots.. (2)$$

$$Y = 65.41 - 12.55X_1 - 1.65X_2 + 6.07X_3 - 3.63X_4 - 3.17X_1^2 - 0.25X_2^2 - 2.30X_3^2 - 4.11X_4^2 + 0.83X_1X_2 - 1.65X_1X_3 + 1.07X_1X_4 + 0.09X_2 X_3 - 0.22X_2X_4 + 2.61X_3X_4 \quad \ldots\ldots\ldots.. (3)$$

where X_1 = Temperature (^oC), X_2 = pH, X_3 = Biomass loading (g/100 mL) &

X_4 = Initial concentration of metal ion (mg/L)

3.3 Optimization of Parameters Affecting Adsorption

The second degree polynomial equations (1, 2 and 3) were solved to determine the optimum value of the independent variables for extracting maximum response from the biomass.

From Table 1, it is clear that out of the three forms of coconut husk tested for chromium adsorption, the acid-treated form CH is the most desirable due to highest chromium removal efficiency. It can remove more chromium viz. 84.06% at lowest adsorbent dosage of 4.89 g/100mL of the effluent and highest initial metal ion concentration of 165.47 mg/L. Moreover, it is more suitable for large-scale operations compared to other forms, due to optimum temperature nearer to ambient temperature (34.3oC) and higher pH (2.35), which is lesser acidic compared to the other forms. Hence, this biosorbent was selected for Column Adsorption Studies.

Table 1 Optimized values of operational variables for obtaining maximum biosorption of Cr(VI) from the pre-treated forms of coconuthusk.

Biosorbent	Temperature (^oC)	pH	Biosorbentdosage (g/100mL)	Initial metal ion Concentration(mg/L)	Predicted Response(% Cr(VI) Removal)
C	32.8	1.87	7.23	117.46	83.12
CH	34.3	2.35	4.89	165.47	84.06
CN	31.4	1.32	8.75	83.25	80.20

3.4 Column Adsorption Studies

The analysis of results obtained in column adsorption studies is summarized below:

1. **Breakthrough Curve** - Breakthrough Curve indicates the time at which the adsorption column reaches saturation, a stage at which the concentrations of the inlet & outlet streams are same.

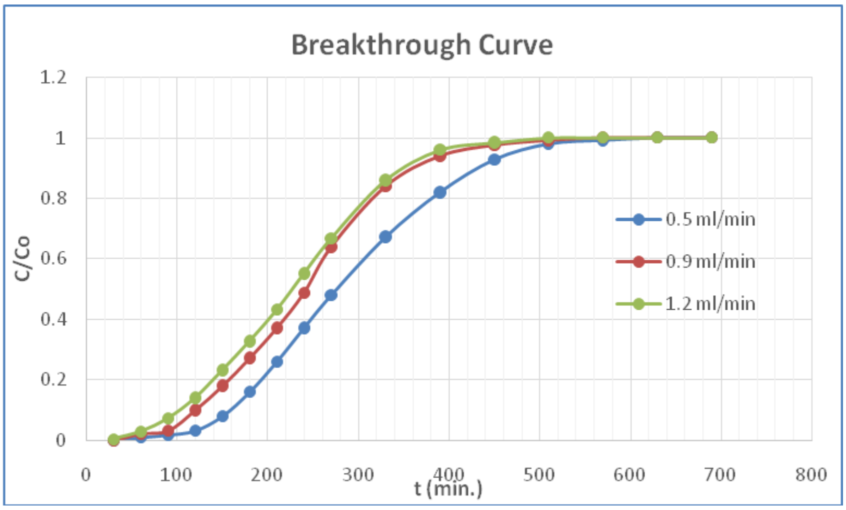

Fig. 1 Breakthrough Curve for Cr(VI) adsorption by HCl treated coconut husk (CH)

Based on the observations, the different constants related to Breakthrough Curve, such as Maximum Adsorption Capacity q_e etc. were calculated and are tabulated in below table:

Table 2 Parameters of Breakthrough Curve for different inlet flow rates for a bed height of 10 cm and metal ion concentration of 250 mg/L

Flow Rate (mL/min.)	**V_{eff} (mL)**	**q_{total} (mg)**	**q_e (mg/g)**	**M_{total} (mg)**	**%Cr(VI) Removal**	**t_b (min.)**	**t_e (min.)**
0.5	345	32.12	3.12	86.25	37.24	100	225
0.9	621	47.78	4.64	155.25	30.78	120	245
1.2	828	59.44	5.77	207	28.72	160	275

where V_{eff} = Effluent Volume collected (mL)

q_{total} = Maximum Column Bed Capacity (mg)

q_e = Maximum Adsorption Capacity (mg/g)

M_{total} = Amount of metal ion sent to the column (mg)

t_b = Breakthrough Time (min.) (Time at which metal ion concentration in effluent is 0.1*[inlet concentration])

t_e = Exhaustion Time (min.) (Time at which metal ion concentration in effluent is 0.5*[inlet concentration])

From Table 2, it is clear that as the inlet stream flow rate was increased, the breakthrough was achieved faster. This can be attributed to the higher rate of mass transfer at higher follow rates as reported by some researchers [38].However, the % removal of Cr(VI) decreased, with maximum % chromium removal observed for flow rate of 0.5 mL/min.At lower flow rates, there is sufficient time for the metal ion to get adsorbed on to the adsorbent [39].

2. Adams-Bohart Model - The following equation denotes the Adams-Bohart Model:

$$\frac{\ln C}{C_o} = K_{AB} C_o t - \frac{K_{AB} N_o Z}{U_O}$$

where C_o = Concentration of the heavy metal (mg/L) in the inlet stream

C = Concentration of the outlet stream after time't' (mg/L)

K_{AB} = Adams-Bohart kinetic constant (L/mg.min)

U_o = Superficial Velocity (cm/min)

N_o = Adsorption Capacity (mg/L)

Z = Height of the column (cm)

The values obtained from experiments were fit into the Adams-Bohart Model. The graph was in agreement with the observations of other research studies. The values of $K_{AB}$and $N_o$are listed in Table 3, along with the correlation coefficient values.

Adams-Bohart Model is useful in explaining the initial phase of adsorption in packed bed column. From the table, it can be observed that the value of kinetic constant (K_{AB}) decreased while the value of adsorption capacity (N_o) increased as the inlet stream flow rate was increased. Thus, it can be inferred that the adsorption kinetics in packed bed column is was dominated by external mass transfer. The relatively poor correlation coefficient values (0.59 – 0.72) indicates that the Adams-Bohart Model is less applicable for adsorption of chromium by coconut husk treated with acid in packed bed column. Similar observations have been reported in some research studies [40].

Table 3 Adams-Bohart Model parameters with correlation coefficient

Flow Rate (mL/ min.)	**N_o (mg/L)**	**K_{AB} (x10^{-5} L/mg.min)**	**R^2**
0.5	6971.69	2.64	0.72
0.9	13083.33	2.47	0.66
1.2	16048.73	2.36	0.59

3. Thomas Model The Thomas model is widely used in column performance modeling. Its derivation assumes Langmuir kinetics of adsorption-desorption and no axial dispersion. The linear form of Thomas model is expressed as:

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{k_{Th}q_e x}{Q}-k_{Th}C_0 t$$

where k_{Th} = Thomas model constant (mL/min.mg)

q_e = Equilibrium uptake of metal ion per gram of adsorbent or adsorption capacity (mg/g)

x = mass of adsorbent (g); Q = inlet stream flow rate (mL/min),

C_0 = initial solution concentration (mg/L) and

C_t = effluent solution concentration (mg/L)

Thomas model was fit to the experimental observations to evaluate the applicability of the model. Thomas model parameters were determined from the graph, and are listed in Table 4.

From Table 4, it can be observed that as the flow rate was increased, value of qe and kTh increased. The correlation coefficient values are between 0.96 & 0.99, indicating that the experimental results are in agreement with Thomas model. Thomas model is suitable for adsorption processes where external and internal diffusion phenomena are not the limiting step [41].

4. Yoon – Nelson Model Yoon and Nelson developed a model based on the assumption that the rate of decrease in the probability of adsorption of adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent. The linearized Yoon-Nelson model for a single component system is expressed as:

$$\ln\frac{C_t}{C_0 - C_t} = k_{YN}t - \tau k_{YN}$$

Where K_{YN} (1/min) is the rate velocity constant and τ (min) is the time required for 50% breakthrough. From a linear plot of ln[Ct/(Co-Ct)] against sampling time (t), values of K_{YN} and τ can be determined from the intercept and slope of the plot.

Table 4 Thomas model parameters with correlation coefficient values

Flow Rate (mL/min.)	q_e (mg/g)	k_{Th} (mL/min.mg)	R^2
0.5	8.1029	0.0716	0.98
0.9	12.2316	0.0735	0.99
1.2	16.1907	0.0748	0.96

Table 5 Yoon-Nelson Model parameters with regression coefficient values

Flow Rate (mL/ min)	K_{YN} (1/min)	τ (min)	R^2
0.5	0.0179	293.24	0.98
0.9	0.0188	245.92	0.99
1.2	0.0205	232.99	0.97

From Table 5, it is clear that as the flow rate was increased, the time required for 50% breakthrough decreased. This can be attributed to the lesser residence time of the solute in the column. With increase in flow rate, the rate velocity constant decreased. This is in concurrence with the observations of few researchers [39]. The regression coefficient values were in the range of 0.97 – 0.99, indicating good agreement between the experimental values and the mathematical model.

CONCLUSION

In the current study, adsorption of hexavalent Cr(VI)by coconut huskwas evaluated. Batch adsorption study was designed using Central Composite Design (CCD). Batch adsorption studies were conducted with three types of biomass derived from coconut husk – untreated coconut husk (C), acid-treated form (CH) and alkali-treated form (CN). Regression analysis of the obtained results was done using Response Surface Methodology and the optimum set of conditions for obtaining maximum % removal of Cr(VI) was determined. Results showed that the acid-treated form CH was the best among the adsorbents selected for the study with maximum Cr(VI) removal capacity of 84.06% at 2.35 pH and 34.3 oC temperature, with highest initial metal concentration of 165.47 mg/L and lowest adsorbent dosage of 4.89 g/100mL. Column Adsorption studies were conducted by varying flow rate of inlet stream while keeping other conditions as constant.

Breakthrough curve was plotted and maximum value of adsorption capacity was found to be 5.77 mg/g for a flow rate of 1.2 mL/min. Thomas and Yoon-Nelson models were found to fit the adsorption data to a good extent, with correlation coefficient R2 ≥ 0.96. The observations indicated that Fixed Bed Column Adsorption can be a feasible method for removal of hexavalent chromium from industrial effluents by using acid-treated coconut husk as the adsorbent.

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