



Modeling of Breakthrough Curves for Removal of Chromium from Waste Water

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Abstract: The development in technology and industrial activities has led to release of various metal ions to the environment. The present study aims to assess the efficiency of Rice Husk in treating chromium (VI) from simulated wastewater, with the help of fixed-bed adsorption column by performing continuous adsorption experiment. The results obtained through this study were confirmed by developing a model. A detailed analysis on the effects of extensive parameters on the adsorption experiment was done. The extensive parameters considered were Concentration, Flow-rate, and Bed-height. It was observed that as flowrate decreased from 60 ml/min to 30ml/min, the breakthrough time also decreased from 30 to 20 min. whereas as when the concentration was increased from 250 mg/L to 1000 mg/, the breakthrough time came down to 10 min from 40 min. The parameters which were calculated were total percentage removal of Cr (VI) and breakthrough time. It was observed that the exhaustion time decreases with increase in the concentration and flow rate and it increases with bed height. The data obtained during the entire experiment were fitted in Thomas and Yoon Nelson Model. The values of the model parameters were evaluated and analyzed.

Keywords: Adsorption, flow rate, concentration, break through curve, model parameters

1. INTRODUCTION

Water pollution has been a great concern worldwide due to the disposal of heavy metals. Waste effluent from numerous industries contains toxic elements such as heavy metals like Pb, Cr, Zn, Cu, Ni, and Fe. When these toxic heavy metals interact with the eco-system, there is a high possibility that they may also accumulate in the human body through direct intake or either through food chain. This accumulation even in micro quantity may lead to severe physiological and neurological damage. Hence measures must be taken to prevent these metals from entering the natural environment [2]. Taking into account the problems caused by these toxic metals to the humans as well as to the environment, their removal from waste water is a very serious concern [3]. Various methods for the removal of these heavy metals, both economical and non-economical are available. The non-economical methods and the conventional methods are Ion Exchange, Chemical Precipitation, Solvent Extraction, Membrane Process, Electrodialysis & Reverse Osmosis. There are many disadvantages of these methods including incomplete metal removal, high energy consumption. These methods generate toxic sludge that further requires proper disposal and treatment [4]. The Economical method is Biosorption. It is a physiochemical process that utilizes less low cost biosorbent. This process occurs naturally in some biomass [5]. Biosorption has many advantages over the conventional methods like low operating cost, short operation time, no chemical sludge, reusability of biomaterial. Vigorous attempts have been taken in order to use agricultural waste which is easy to obtain and also cheap such as Rice Husk, Groundnut Shell and many others as a bio-adsorbent for the removal of toxic metals from the waste water [1]. Recently there has been an increase in the use of biomass for the cleaning up of environment, Scientist and engineer are expecting that use of bio-adsorbent for the removal of toxic metals will be an economical option. Rice hulls are there to protect the seeds during growing season as they cover the seeds. Opaline, silica and lignin are present in rice husk. The agricultural waste which comprises of groundnut shell, peanut shell, rice hull comes under the species *Arachishypogaea*L. They have huge potential to isolate heavy metals from the water [6, 7]. The study is mainly based on identifying the potential of rice husk in removing heavy metals from the wastewater.

2. MATERIAL AND METHOD

2.1. Adsorbent Preparation

Rice husk is an agricultural waste and is used as low cost adsorbent. It was obtained from a local paddy mill [8]. The rice husk was heated to remove other impurities. After heating the rice husk was washed with Distilled Water and HCl. Further the rice husk was kept in an oven at 100°C for an hour; the water present in rice husk was removed

2.2. Adsorbate Preparation

The simulated stock solution was prepared by dissolving 1.414 g of Potassium Dichromate ($K_2Cr_2O_7$) in 1000ml of distilled water. In stock solution we had 1ml equivalent to 500µgm Cr. Further the solution of desired concentration (250-1000) mg/L was prepared by diluting the stock solution with distilled water.

2.3. Reagent Preparation

Diphenyl Carbazidereagent was prepared by dissolving 0.04 gm of 1,5-diphenyl Carbazide solution in 20ml Iso – propyl alcohol, along with it 8ml of conc. H_2SO_4 was added and the solution was diluted to 100ml by addition of 72ml of distilled water. This Diphenyl Reagent was then used for the detection process with the help of Spectrophotometer.

2.4. Experimental Studies

For the removal of toxic Cr (VI) from the aqueous solution a continuous fixed bed experiment was carried out, wherein activated rice husk was used as a low cost bio-adsorbent. The apparatus consisted of a fixed column of glass with 5cm internal diameter. The stock solution of Cr (VI) was made to pass through the column in a down flow mode. The flow was maintained by a valve. The parameters including flow rate, mass of adsorbent (bed-height), and inlet Cr (VI) concentration were varied during this study. The flow rate was maintained constant using a valve (30-60 mL min⁻¹). The method used for analyzing the quantity of Cr (VI) in the aqueous solution was Di-Phenyl carbazide. This method only indicates the quantity of Cr (VI) in the aqueous solution. At low pH this method has been used widely in various studies [9]. A purple-voilet color was developed when Di-Phenyl Carbazide reagent was added to the effluent collected from the experiment Further UV-Spectrophotometer was used for the analysis of the concentration of Cr (VI) ions in the effluent. Di-Phenyl Carbazide Reagent over here works as a complexing agent. The absorbance of the effluent after addition of the reagent was measured at a wavelength of 540 nm. With the help of calibration curve the deviation in the concentration of Cr (VI) was obtained.

3. MATHEMATICAL MODELING AND SIMULATION

3.1. Thomas Model

An expression for adsorption column by Thomas is given by following equation

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left[\frac{K_t}{Q(q_0M - C_0V)}\right]} \quad (1)$$

In the equation (1), C is the outlet concentration at any time t and Co is inlet concentration. V is throughput volume, Q volumetric flow rate, K_t is Thomas constant and q_0 is maximum adsorption capacity. [11]

The linear form of this equation is written as

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{K_t q_0 M}{Q} - k_t C_0 t \quad (2)$$

The plot of $\ln\left(\frac{C_0}{C} - 1\right)$ against t is a straight-line. The values of the parameters K_t , and q_0 are estimated from this plot.

3.2. Yoon and 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 [12].

This model is expressed by following equation

$$\frac{C}{C_0} = \frac{1}{1 + \exp[K(T-t)]} \tag{3}$$

$$\ln \frac{C}{C_0 - C} = kt - Tk \tag{4}$$

Here, k is the rate constant and T is time required for 50 percent adsorbate breakthrough and t is sampling time in the equation (3)&(4). The plot of $\ln \left(\frac{C}{C_0 - C}\right)$ against time is plotted. The parameters, T and k are obtained from the plot.

4. RESULT

4.1. Effect of Concentration

Detailed studies on the change of sorption capacity with time for different initial concentrations have been done in order to evaluate the sorption characteristics of Rice Husk for Cr ions. A series of experiments were undertaken by varying the initial Cr concentration in the range of 250 mg/L, 500 mg/L, 1000 mg/L on the removal of Cr from the simulated solution. It has been found that as the concentration increases the adsorption capacity also increases and the breakthrough point is obtained earlier. The optimum concentration was found to be 1000 mg/L. At this concentration the removal was 78.95% after 10 min, whereas for concentration of 250mg/l & 500mg/l it was found to be 55.65% & 20.97% respectively. So, the Rice Husk can be used in the industry effluent samples for higher concentrations of chromium. The values of K_t and q_0 were obtained from the graph and it was observed that as concentration was increased the value of R^2 also increased from 0.77 to 0.89.

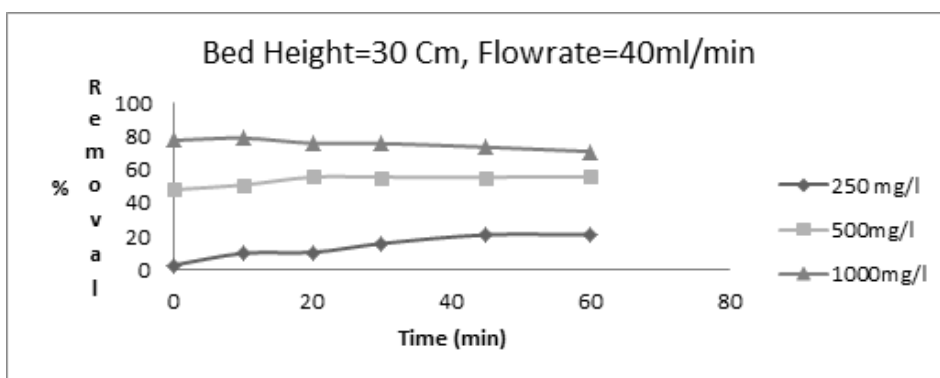


Fig4.1.1. Effect of Concentration on Cr Adsorption

Table1. Effect of Initial Concentration for Thomas Model

Parameters	Concentration at fixed bed height, pH and flow rate (mg/l)		
	250	500	1000
K_t (ml/min/mg)	-0.00013	-9.6E-06	6.5E-06
q_0 (mg/g)	7542.724	-4131653	67552.68
R^2	0.7795	0.6562	0.8922

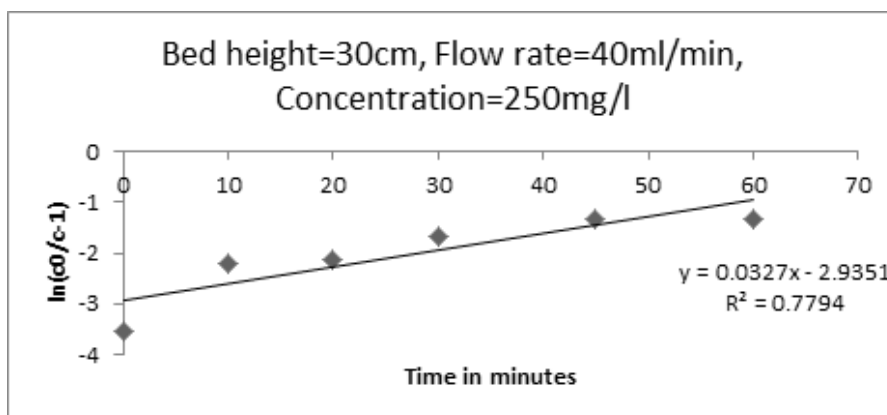


Fig4.1.2. Thomas Model at Initial Concentration of 250 mg/l

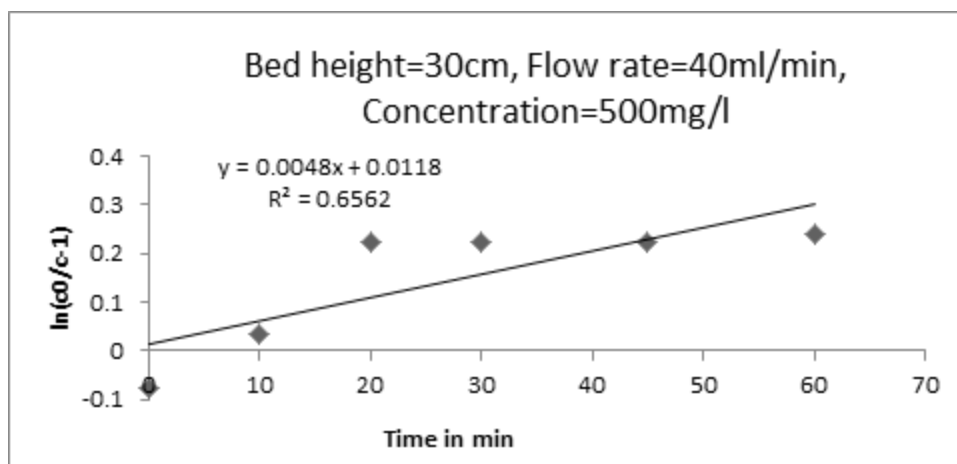


Fig4.1.3. Thomas Model at Initial Concentration of 500 mg/l

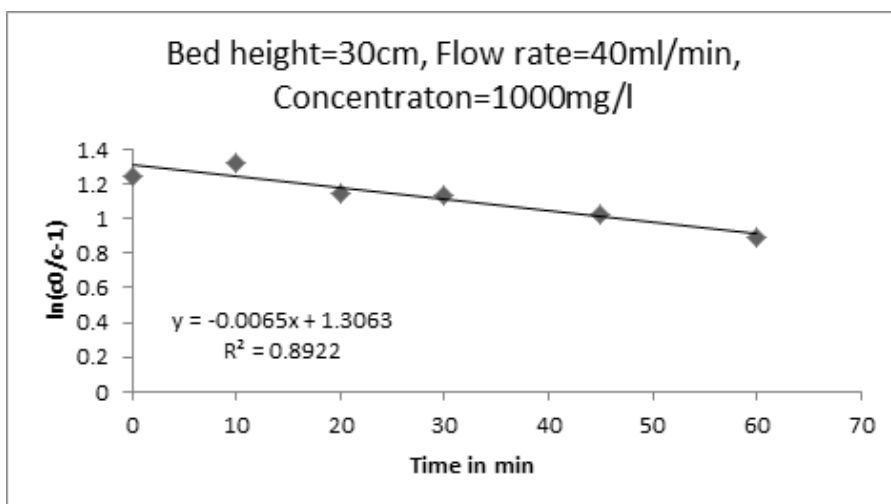


Fig4.1.4. Thomas Model at Initial Concentration of 1000 mg/l

Table2. Effect of Initial Concentration for Yoon Nelson Model

Parameters	Concentration at fixed bed height, pH and flow rate (mg/l)		
	250	500	1000
K(/min-1)	-0.0327	-0.0048	0.0065
T (min)	89.75841	-3.75	200.9692
R ²	0.7794	0.6562	0.8922

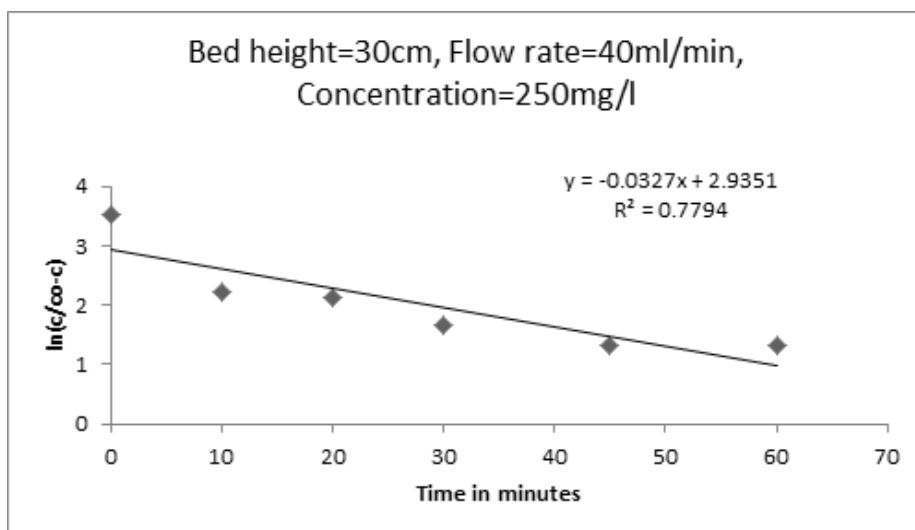


Fig4.1.5. Yoon Nelson Model at Initial Concentration of 250mg/l

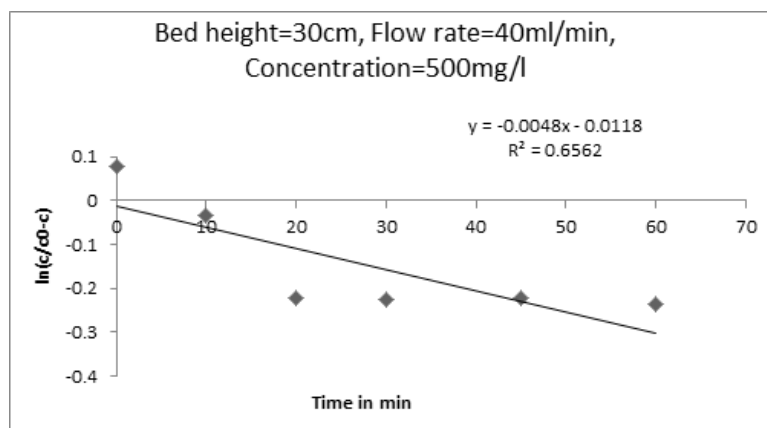


Fig4.1.5. Yoon Nelson Model at Initial Concentration of 500mg/l

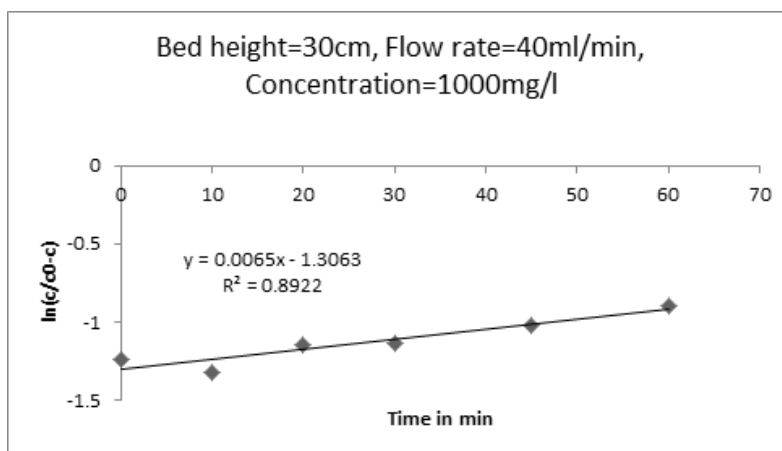


Fig4.1.7. Yoon Nelson Model at Initial Concentration of 1000mg/l

4.2. Effect of Concentration (C/C₀)

The study Cr concentration at different time intervals has been carried out. A series of experiments were undertaken by varying the initial Cr concentration in the range of (250 mg/L-1000 mg/L). For 1000 mg/L, initially the Cr concentration was low and once bed gets saturated it has increased. At zero time C/C₀ ratio was 0.223 and is decreased to 0.21 at time 10min. Further C/C₀ ratio was increased to 0.29 after one hour; this is due to the fact that the bed was exhausted. It can be concluded that at 1000 mg/L the removal was optimum and concentration of Cr was less.

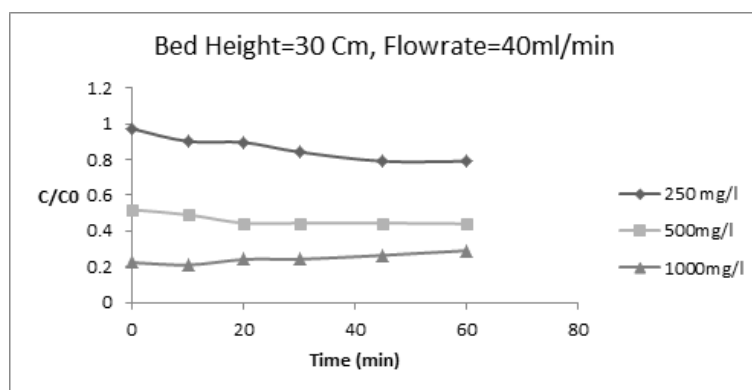


Fig4.2.1. Effect of Concentration (C/C₀)

4.3. Effect of Flow Rate (% removal vs. time)

An investigation was carried out on the effect of the flow rate on the adsorption of Cr by varying the flow rate, with a constant adsorbent bed height of 30 cm and the initial concentration of 250 mg/l. Series of experiments were undertaken by varying the flow rates in the range of (30ml/min -60ml/min) i.e. 30ml/min, 40 ml/min & 60 ml/min simulated solution. It has been found that as flow rate increases the

adsorption capacity also increases. The optimum flowrate was found to be 30ml/min. At this flow rate the removal of Cr was maximum i.e. 72% after 22min. Whereas with flow rates 40 ml/min & 60 ml/min the removal was 63% & 55% respectively. So, the Rice Husk can be used in the industry effluent samples with lower possible flowrates. It has been observed that as the flow rate increased the breakpoint time decreased, also the total adsorbed quantity of Cr also decreased simultaneously. The reason for this behavior is the insufficient residence time of solute (Cr) in the column. It can be concluded that residence time decreases with increase in the flow rate resulting in insufficient residence time for the diffusion of Cr. The values of K_t and q_0 were obtained from the graph for both the models. The value of R^2 for Thomas model was found to be maximum for the flow rate of 40 ml/min, whereas for Yoon & Nelson model it was found to be maximum for flowrate of 30ml/min

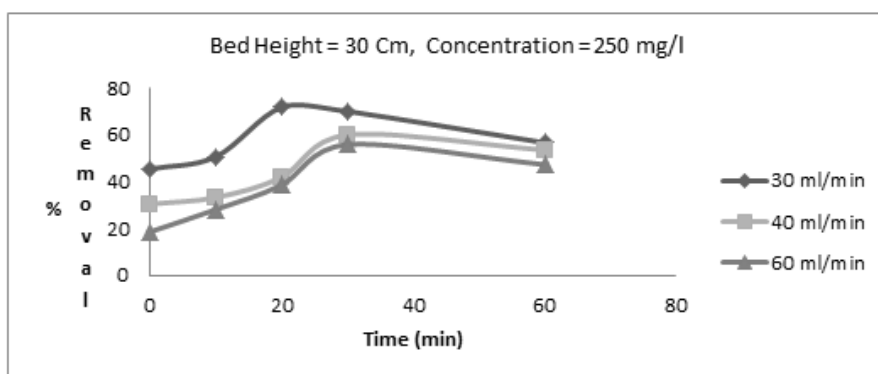


Fig4.3.1. Effect of Flow rate on Cr Adsorption

Table3. Effect of Flow Rate for Thomas Model

Parameters	Flow rate at fixed bed height & concentration (ml/min)		
	30	40	60
K_t (ml/min/mg)	-0.00014	-0.00011	-5.5E-05
q_0 (mg/g)	2339.927	2575.978	-885.113
R^2	0.7655	0.7675	0.2309

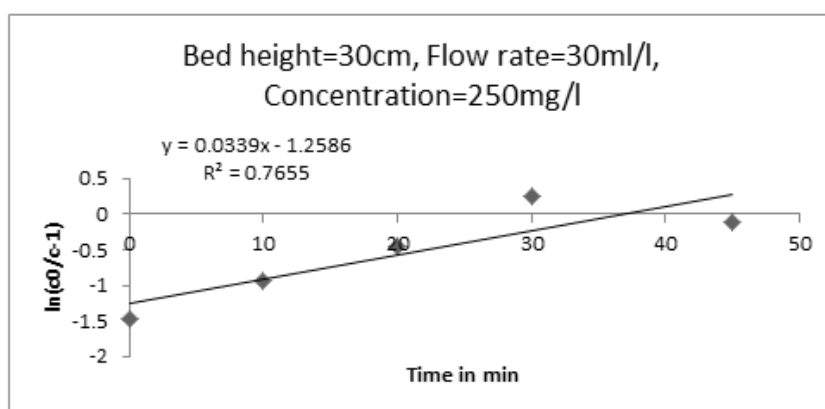


Fig4.3.2. Thomas Model at flow rate of 30 ml/min

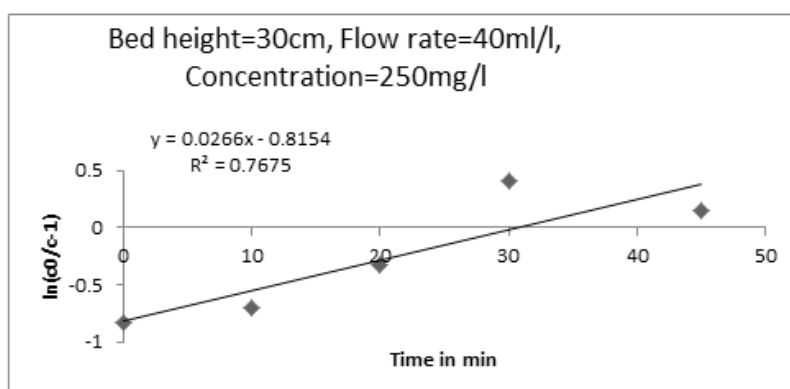


Fig4.3.3. Thomas Model at flow rate of 40 ml/min

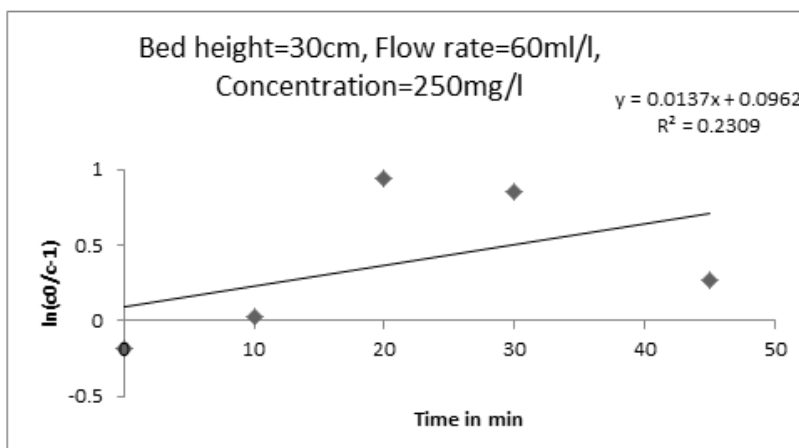


Fig4.3.4. Thomas Model at flow rate of 60 ml/min

Table4. Effect of Flow rate for Yoon Nelson Model

Parameters	Flow rate at fixed bed height & concentration (ml/min)		
	30	40	60
K(/min-1)	-0.034	-0.0264	-0.015
T (min)	37.72941	31.33333	-3.91333
R ²	0.7743	0.7572	0.2793

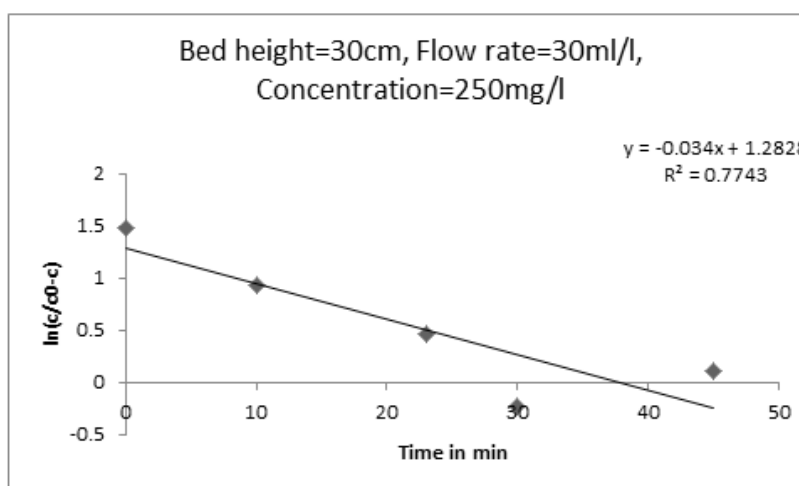


Fig4.3.5. Yoon & Nelson at flow rate of 30 ml/min

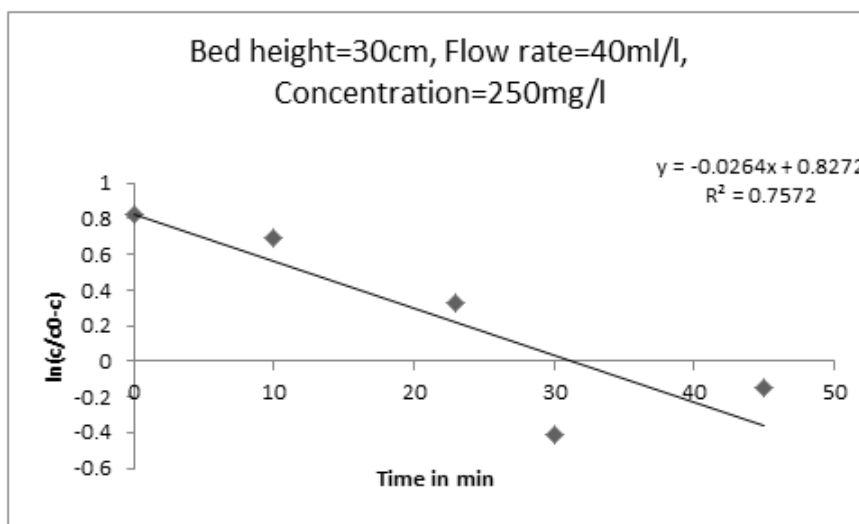


Fig4.3.6. Yoon & Nelson at flow rate of 40 ml/min

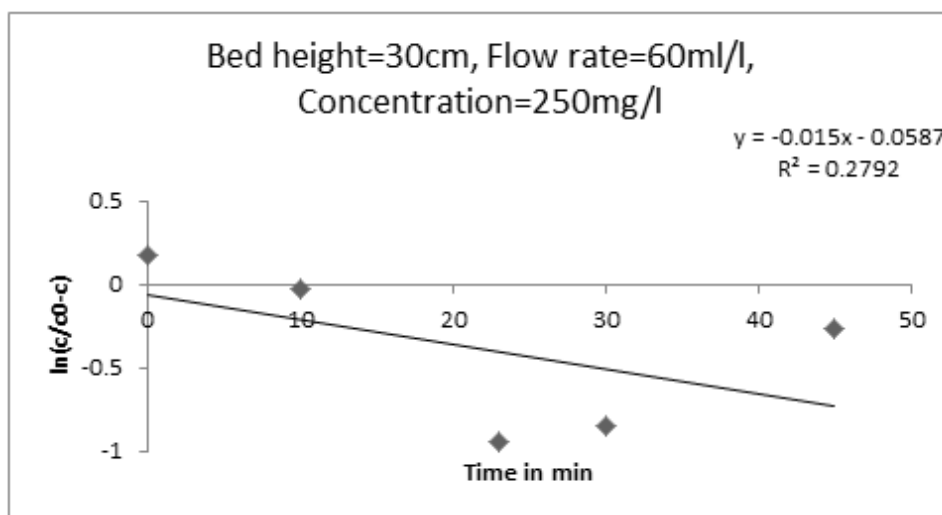


Fig4.3.7. Yoon & Nelson at flow rate of 60 ml/min

4.4. Effect of Flow Rate (C/C0 vs. Time)

The effect of the flow rate on change in concentration of Cr with initial value was investigated by varying the flow rate with a constant adsorbent bed height of 30 cm and the initial concentration of 250 mg/l. series of experiments were undertaken by varying the flow rates in the range of (30ml/min - 60ml/min) i.e. 30ml/min, 40 ml/min & 60 ml/min simulated solution. It has been found that as flow rate increases initially capacity of removal of Cr was very rapid further after saturation of bed it decreased. At flow rate 60ml/min initially c/c_0 ratio was 0.55 at zero time, then it decreased to 0.28 at 20min. as bed get saturated the value again increased. At 60 min it again reached to 0.46. We can conclude that with increase in flow rate, initially Cr concentration decreases and then it increases again after breakpoint time.

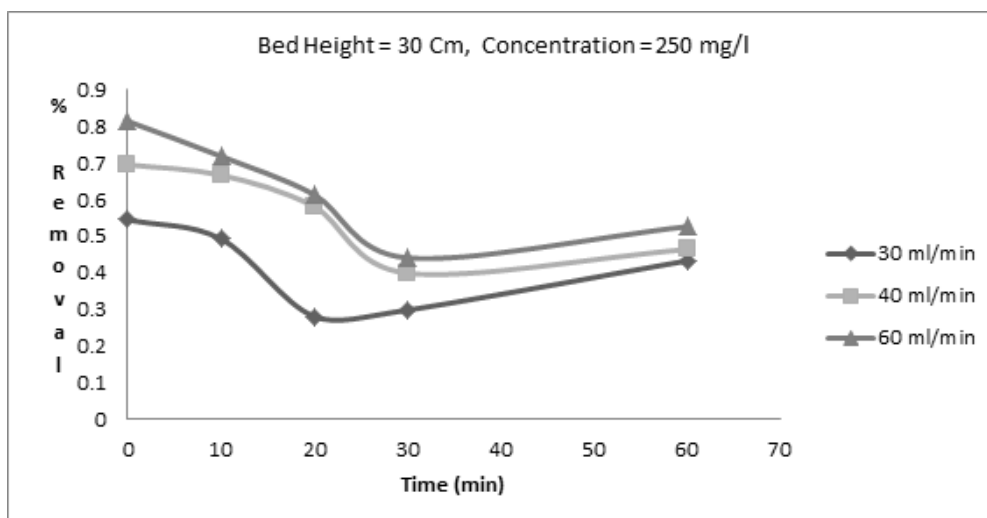


Fig4.4. Effect of Flow rate (C/C0)

4.5. Effect of Bed Height (% removal vs. time)

The bio-adsorbent used in packed bed influences the removal capacity of metal ions. Numbers of experiments were carried out for three different bed heights 25 cm, 30 cm and 35 cm using 92gm, 119gm, & 150gm of biomass respectively. Concentration and flow rate were fixed at 1000 mg/l and 40 ml/min respectively. Fig 4.5.1 and 4.6 represents the removal of Cr for various bed heights. It was observed that with increasing bed height removal of metal ions was higher until the bed gets saturated. As the bed height increases the contact time also increases and this results in increase in the % removal of chromium. Maximum removal obtained at 35 cm bed height. For 35 cm bed height initially the removal was about 70.12% which further increased to 78.22%, which was the maximum removal amongst various bed heights. The values of K_t and q_0 were obtained from the graph.

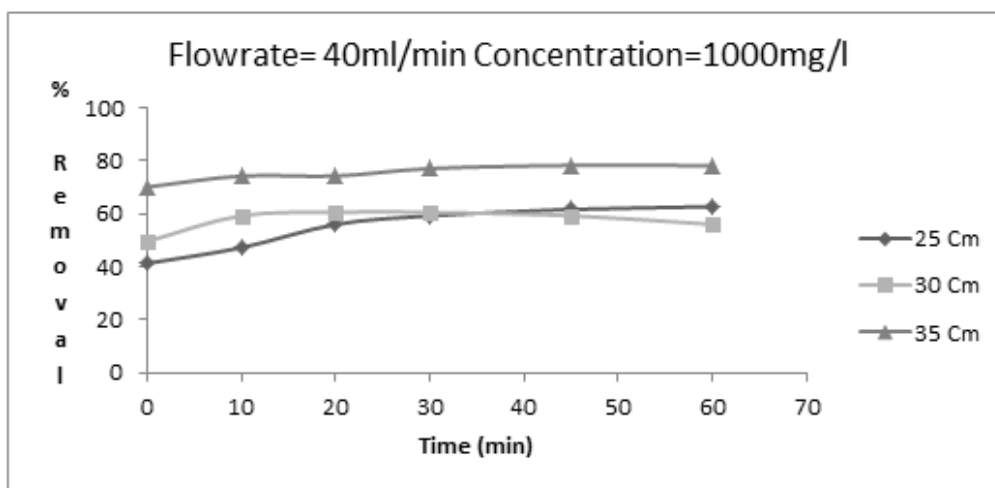


Fig4.5.1. Effect of Bed height on Cr Adsorption

Table5. Effect of Bed Height for Thomas Model

Parameters	Bed height at fixed Flow rate & concentration (ml/min)		
	25	30	35
K_t (ml/min/mg)	-0.0000145	-0.0000025	-0.0000041
q_0 (mg/g)	6227.88606	-31811.765	-70465.041
R2	0.852	0.1053	0.7313

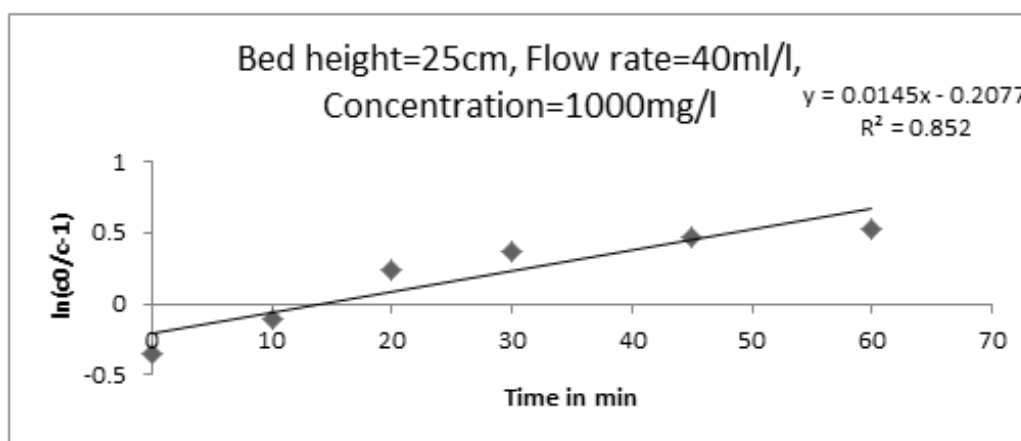


Fig4.5.2. Thomas Model for bed height of 25 cm

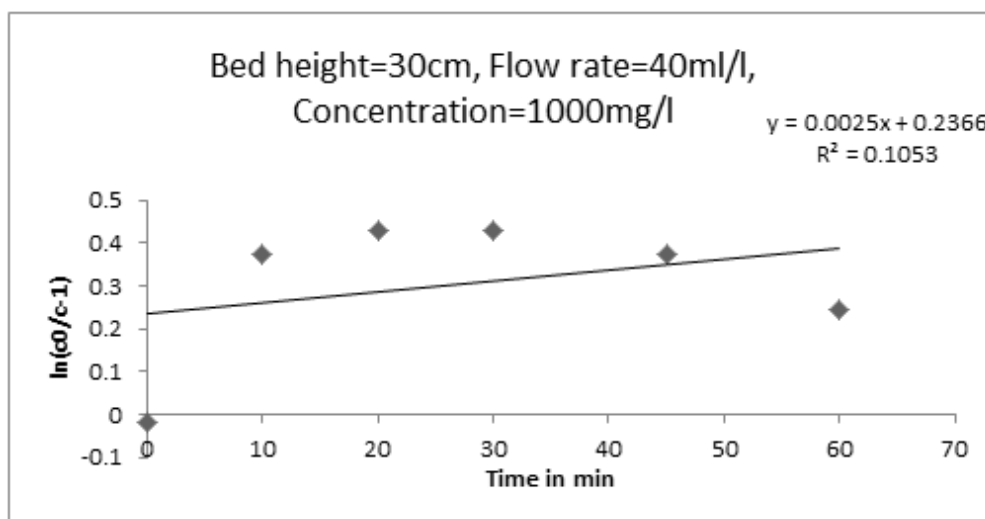


Fig4.5.3. Thomas Model for bed height of 30 cm

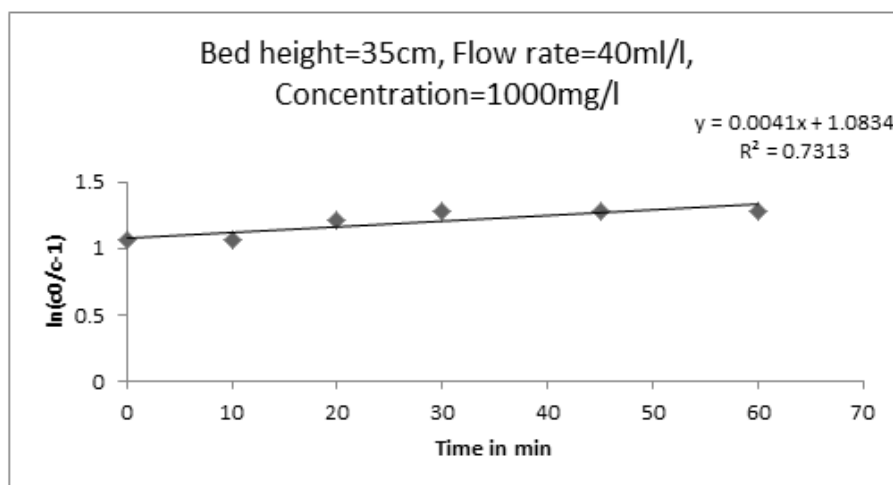


Fig4.5.4. Thomas Model for bed height of 35 cm

Table6. Effect of Bed Height for Yoon Nelson Model

Parameters	Bed height at fixed Flow rate & concentration (ml/min)		
	25	30	35
K(/min-1)	-0.0145	-0.0025	-0.0069
T (min)	14.32414	-94.64	-135.841
R ²	0.852	0.1053	0.8432

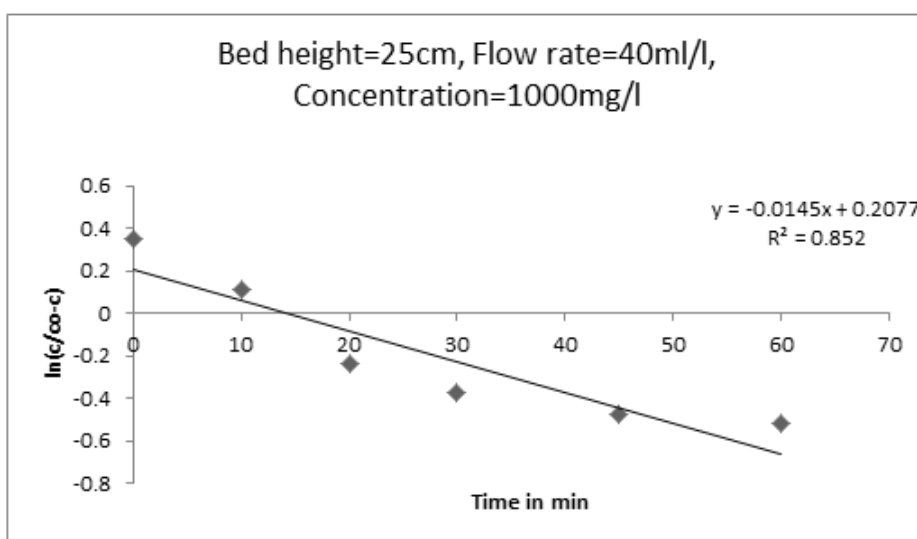


Fig4.5.5. Yoon & Nelson Model for bed height of 25 cm

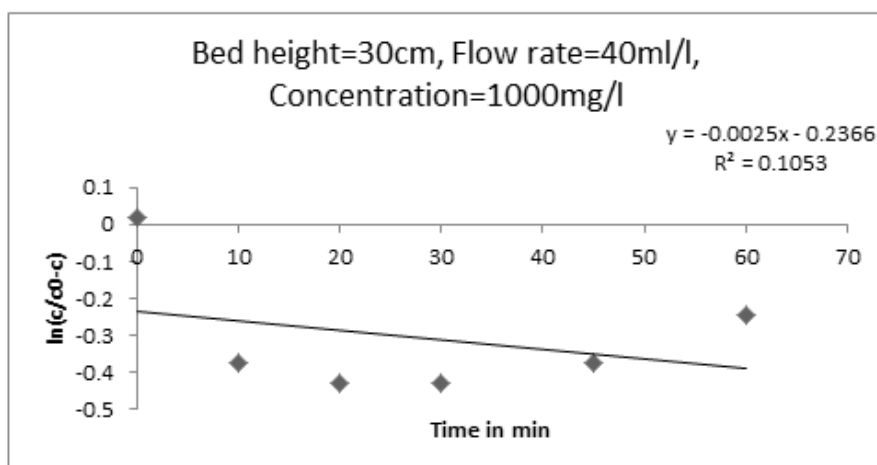


Fig4.5.6. Yoon & Nelson Model for bed height of 30 cm

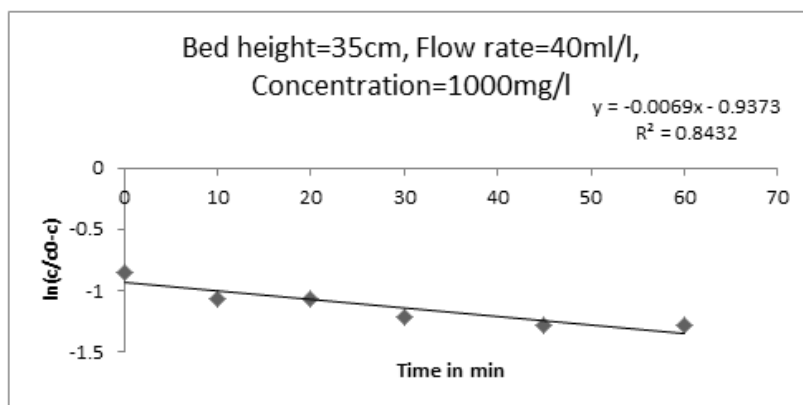


Fig4.5.7. Yoon & Nelson Model for bed height of 35 cm

4.6. Effect of Bed Height (C/C0 vs. time)

The effect of bed height on change in concentration of Cr with initial value was investigated by varying the bed height with a constant flow rate of 40ml/min. The initial bed height of column was kept 25 cm. Series of experiments were undertaken by varying the bed height in the range of (25-35 cm) i.e. 25cm, 30 cm and 35cm. It has been found that as bed height increases initially capacity of removal of Cr was rapid further after saturation of bed it decreased. At bed height 35cm initially, C/C₀ ratio was 0.298 at zero time, then it decreased to 0.256 at 20min, and reached point 0.217 at 60 min.

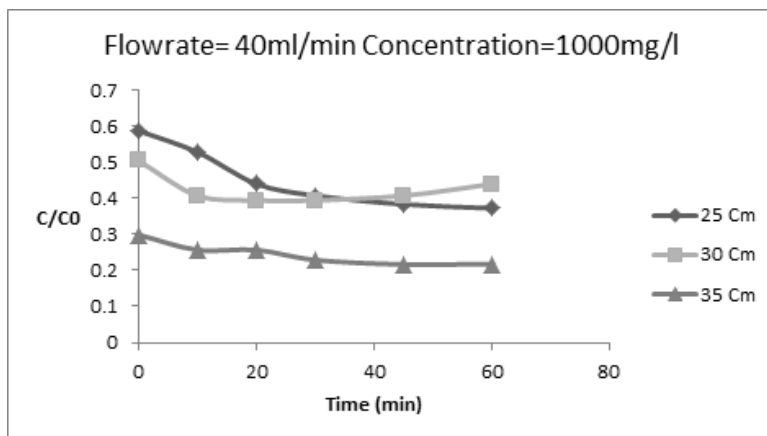


Fig4.6. Effect of Bed Height (C/C₀)

4.7. Effect of Regeneration

The rice husk used in packed bed was regenerated after it was saturated by treating it with HCl. The same experiments were carried out to see the changes in removal capacity. Fig shows graph of removal of Cr with regenerated rice husk. Flow rate was fixed at 60 ml/min and bed height was kept 35 cm and the maximum removal was 56.73%. Comparing with the removal of fresh batch of rice husk and regenerated rice husk, it has been found that the removal of Cr had reduced by 21.20%

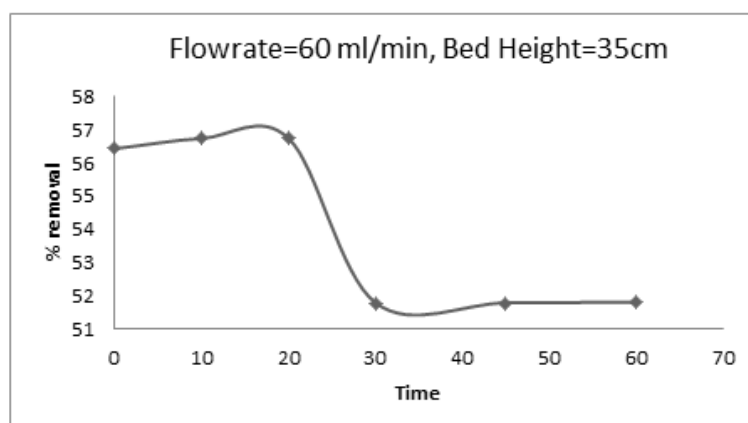


Fig4.7. Effect of use of regenerated rice husk on Cr adsorption

5. CONCLUSION

A potential alternative for the removal of Cr (VI) from the aqueous solution has been found in the form of Activated Rice Husk, which is a low cost adsorbent. The curves obtained by carrying out the experiment gives a clear understanding that the breakthrough curves are the function of adsorption exhaustion rate and the fraction of unused bed length. It can be observed that by increasing the bed height & concentration the breakthrough time was found earlier, whereas when the flowrate was decreased the breakthrough time was obtained earlier. The models were successfully checked with the theoretical & experimental data obtained during the entire experiment. The values of model parameters are in agreement with similar work carried out for various metal ions and adsorbents. The experimental data also fits in both the models for different concentrations. The data of different bed heights and different flow rates fits well in Yoon and Nelson model. The adsorption capacity increased with bed height and initial concentration and decreased with flow rate.

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