

# Bio-adsorptive Removal of Cr (VI) from Stimulated Tannery Waste Water using Different Adsorbents and Compare with GAC

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## ABSTRACT

*The present study has been taken up for the removal of chromium from stimulated tannery waste water prepared in lab, by using adsorbents like Sawdust, acid treated banana peel, rice husk carbonized and compared with GAC. Optimization parameter like pH, dosage, contact time and initial concentration is studied for all adsorbents. Maximum adsorption of Cr (VI) is generally found at pH 2 and initial concentration about 100 ppm. Kinetic modeling is also studied from which result generally found that the pseudo second order model best fitted with these adsorbents. Isotherm modeling (Langmuir and freundlich model) are also investigated for these adsorbents in which freundlich model is best fitted for all four adsorbents as R square value is greater than the other model. From all the result obtained from these experiments, it is clearly shows that acid treated banana peel has the maximum removal efficiency as removal efficiency of the GAC.*

**Keywords:** Adsorbents, Potassium dichromate ( $K_2Cr_2O_7$ ), 1, 5-diphenylcarbazide, phosphoric acid, sulphuric acid, acetone, hydrochloric acid and Ultra-pure de-ionized water.

## 1. INTRODUCTION

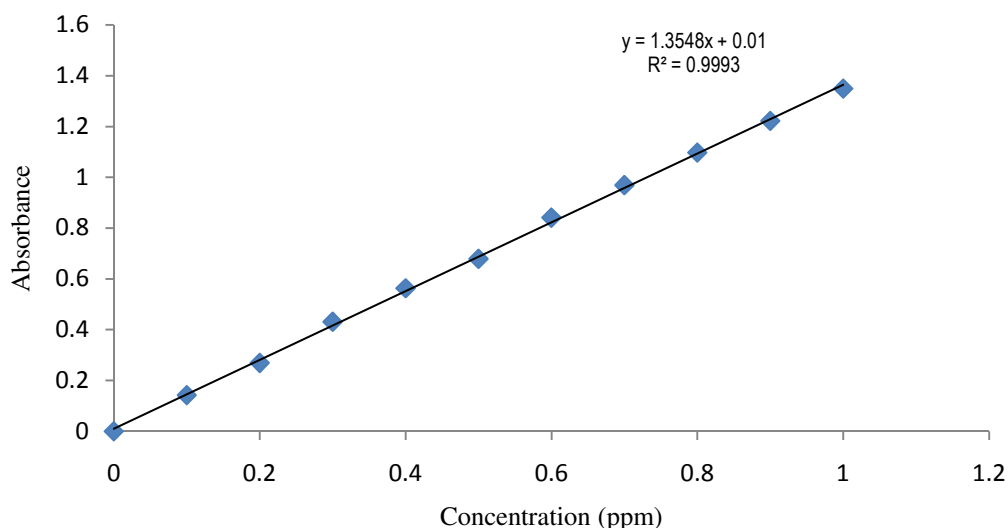
Increase in industries, the agricultural population and the world has degraded the property of the environment and disrupts the global ecosystem. Continuously increasing in small and large industries and population growth, agriculture, so there is reduced water resources occur in very high speed [1]. Pollutants in water are constantly increasing which create a major problem. so, it is necessary to evaluation and revision of the current policy resources at all stages water. It is important to treat the wastewater to reduce pollutants in the water for future reference. Because of the number of harmful and toxic substances increase in water and become a problem of the extent in which heavy metal chromium is the most dangerous pollutants and more serious. Mining, leather tanning [2] textile dyeing, cement, paper, power plants, steel manufacturing, processing wood preservatives, fertilizers and photography industries are the major industries which discharge heavy metals Cr(VI). Chromium presents in many valence states like Cr(0), Cr(II), Cr(III) and Cr(VI) but

from the point of view of pollution, Cr(III) and Cr(VI) are important in which Cr(VI) is 500 times more toxic than Cr(III). Because this metal is toxic, dangerous collects easily in the living organism, also non biodegradation, due to the strong oxidizing agent; it is easily absorbed by the skin, thus causing various diseases and disorders. The objective of this study is to explore the adsorption process for removal of Cr (VI) from stimulated tannery waste water solutions using “Rice Husk Carbonized, Acid treated Banana peel, SAW dust and compare with GAC and to optimize the important parameters that affect adsorption with a purpose to achieve complete removal and to provide optimum consumption of adsorbents. The effects of pH, initial Cr (VI) concentration, adsorbent dose, and contact time on adsorption are investigated subsequently. A comparative study of various adsorption kinetic models and isotherms has been made.

## 2. EXPERIMENTAL DESCRIPTIONS

### 2.1 Materials

Materials used for the experiments were potassium dichromate ( $K_2Cr_2O_7$ ), “Rice Husk Carbonized, Acid treated Banana peel, Sawdust and GAC”. Other chemicals used in the study also included 1, 5-diphenylcarbazide (DPC), sulphuric acid, hydrochloric acid, acetone and Ultra-pure de-ionized water [3].



**Figure 1: Calibration Curve**

**2.2 Experimental procedure:** Stock solution of the 500 ppm solution was prepared by dissolving 1.41 g of  $K_2Cr_2O_7$  in 1 l distilled water. The reagent solution was prepared by dissolving 250 mg of 1, 5-diphenylcarbazide in 50 ml of acetone and stored in a brown bottle. Solution is discarded when he lost his color. Sulfuric acid was used to maintain pH. This solution was diluted to obtain the concentration ranges of the standard solution from 0.1 to 1.0 ppm. By adding the required amount of reagent solution, the color of the solution turned to pink. The calibration curve is drawn from the absorbance and different dilution of the known concentration of chromium is shown in fig 1. The line equations and  $R^2$  values have been useful to take to calculate the unknown concentration of chromium in the treated wastewater. Adsorbing Cr (VI) in the feedstock was processed out with different doses of adsorbent at pH 1 to 6, and the concentration of 50 to 450 ppm. The solutions were stirred for periods of time in an incubator with shaking at 150 rpm. Samples were collected, filtered and the absorbance was measured against time using a UV spectrophotometer at 540 nm wavelength. The pink color has formed by adding 1, 5-Diphenylcarbazid.

The amounts of Cr (VI) adsorbed and percent removal were calculated from the concentrations in solutions before and after adsorption using

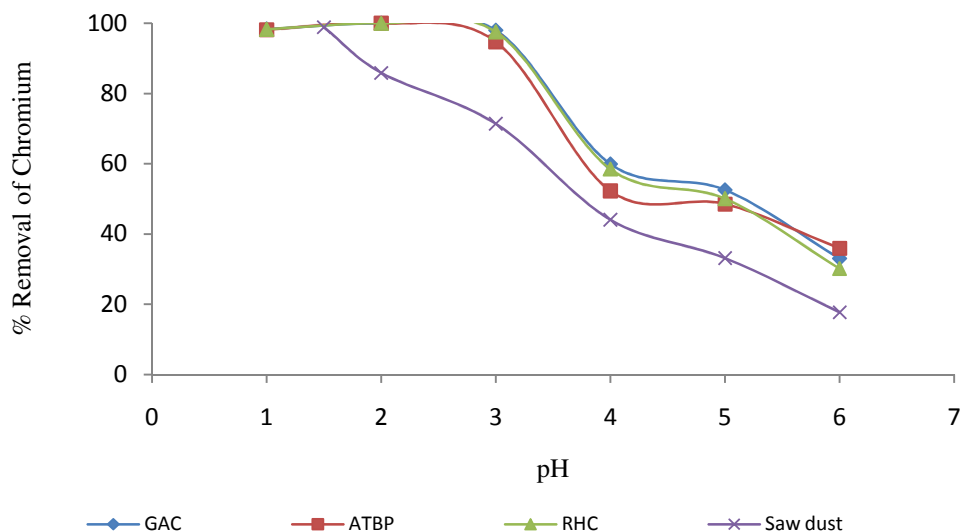
$$q_e = \frac{(C_0 - C_e)V}{w} \quad \text{And } \%R = \frac{(C_0 - C_e) \times 100}{C_0}$$

Where, w mass of adsorbent (g), V volume of the solution (L),  $C_0$  initial concentration of metal ( $mgL^{-1}$ ),  $C_e$  final equilibrium concentration ( $mgL^{-1}$ ) and  $q_e$  is the amount of metal adsorbed at equilibrium ( $mgg^{-1}$ ).

### 3. RESULTS AND DISCUSSION

#### 3.1 Parameters optimization

**Effects of pH:** For Cr (VI) stability pH is essential factor which controls the surface properties of adsorbents, functional groups and ionic state of metal's species. Adsorption tests were passed out over the pH range of 1– 6 for all the adsorbents, by keeping other factor constant. Experimental outcomes show that the adsorption was giving the positive result at acidic condition, which is maintained by 0.1 N HCl. Maximum Cr (VI) uptake was observed at pH 2-3 shown in fig 2. The percentage of Cr (VI) adsorbed by raw material shown in table 1. So pH near about 2 was the optimum pH for extreme deduction of Cr (VI) for all adsorbents. This was done because of at pH between 1 to 6 chromium type co-exist in countless forms, such as  $Cr_2O_7^{2-}$ ,  $HCrO_4^-$ ,  $Cr_3O_{10}^{2-}$ , and  $Cr_4O_{13}^{2-}$ , of which  $HCrO_4^-$  predominates.

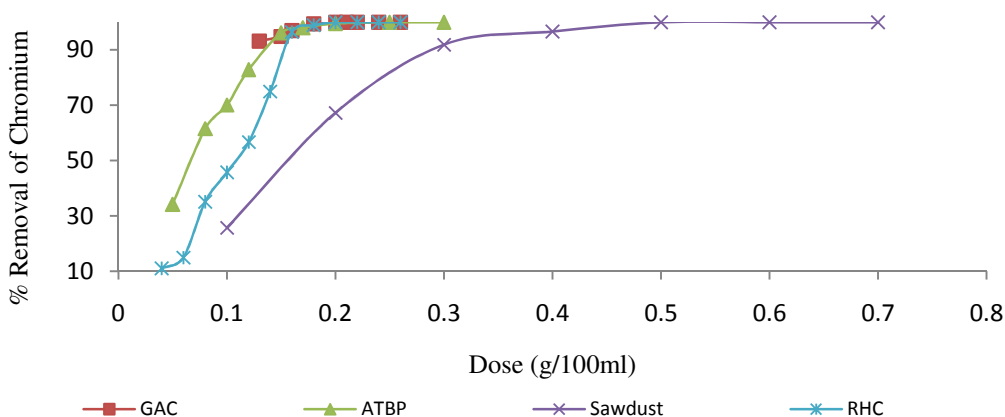


**Fig 2: % removal vs pH for different adsorbents.**

**Table 1: The percentage of Cr (VI) adsorbed by adsorbents at Optimum pH**

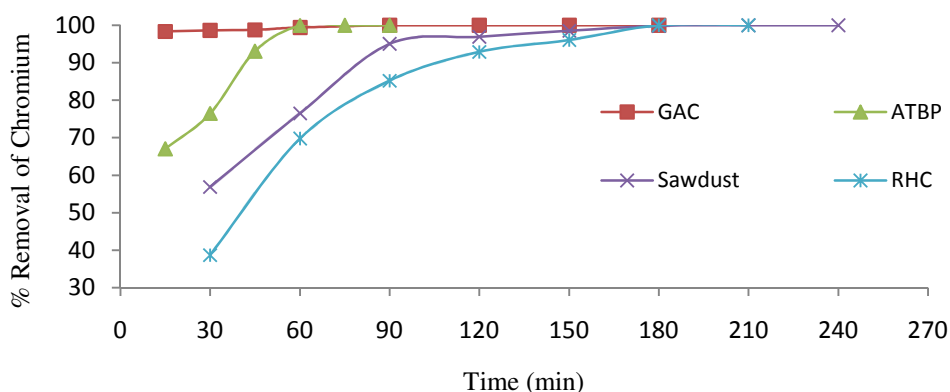
adsorbents	pH	% Removal
GAC	2	99.98
Acid treated banana peel	2	99.99
Saw dust	1.5	98.96
RHC	2	99.57

**Effect of adsorbent dosage:** Adsorbent dosage is an important parameter since it determines the ability of an adsorbent for removal of Cr (VI) at a given initial concentration and separation cost. In this report, results shows that the removal of Cr (VI) increased rapidly from lower to higher removal when adsorbent dosage was increased at concentration of 50 ppm. Fig 3 shows optimum adsorbent dose for each adsorbents were obtained 0.2 g/100ml of RHC which showed 99.98 % removal, 0.2 g/100ml of ATBP which shows the 99.99% removal, 0.5 g/100ml of sawdust which shows the 99.99 % removal and 0.2 g/100ml which shows the 99.99% removal. Further investigation shows that an increase in adsorbent dose increases the percentage removal of Cr (VI) as more surface area is available for adsorption. At lower dose, the adsorbent surface becomes saturated as the Cr (VI) concentration is high.



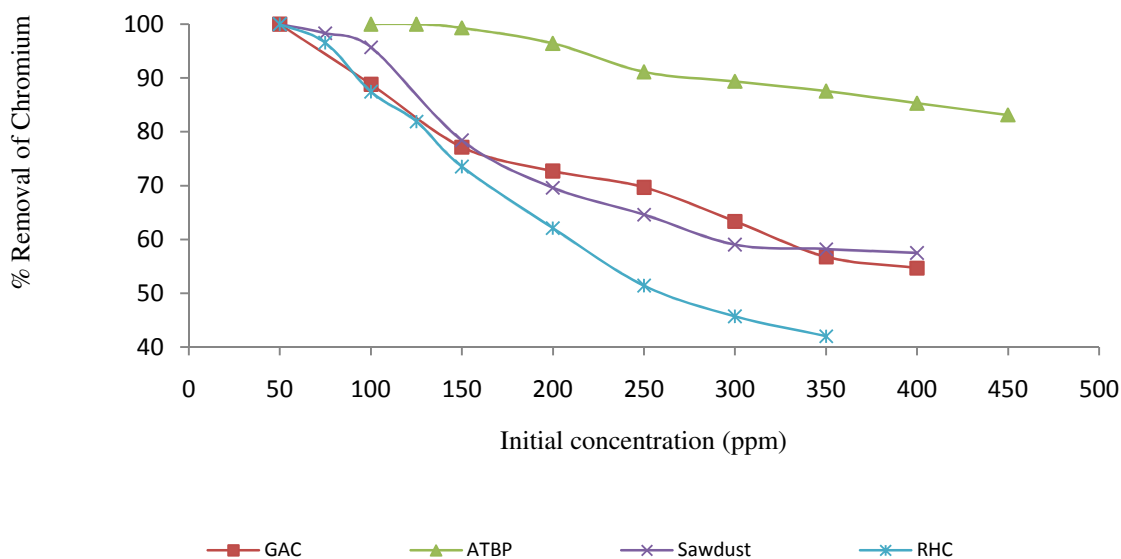
**Figure 3: % Removal of Cr (VI) on GAC, banana peel, saw dust and RHC dose at initial concentrations 50 mg/L and pH 2**

**Effect of Contact Time:** Fig 4 shows the result of contact time on the amount of adsorption of Cr (VI) on the adsorbents at 50 mg/l original chromium concentration at pH 2.0 and temperature 303 K and 100 mg/l for acid treated banana peel. Result obtained after the experiments that the rate of adsorption of chromium metal is very high at the starting stage and then gradually declines very slowly till fullness levels reached at the equilibration point. At the start, large number of empty spots accessible which was considered as active compulsory sites available throughout the original period of time and huge quantity of Cr (VI) were bound quickly on adsorbent surface at a quicker adsorption rate.



**Figure 4: % Removal of Cr (VI) vs contact time for GAC, Acid treated banana peel, Saw dust and RHC at 30 ° C, pH 2 and optimum dose**

**Effect of initial concentration:** The effect of initial metal concentration Cr (VI) on adsorbents were investigated at different chromium concentrated solutions shown in fig 5 which tells that maximum removal takes place at lower ion concentration at optimum pH and adsorbent dose. Increasing Cr (VI) concentration decreased the per cent removal at optimum pH 2.0. The growth in initial concentration of chromium, domino effect obtained in the decrease in the removal capacity as well as gradually rises in adsorption uptake capacity. Table 2 shows the result of initial Cr (VI) concentration on adsorption for all adsorbents.



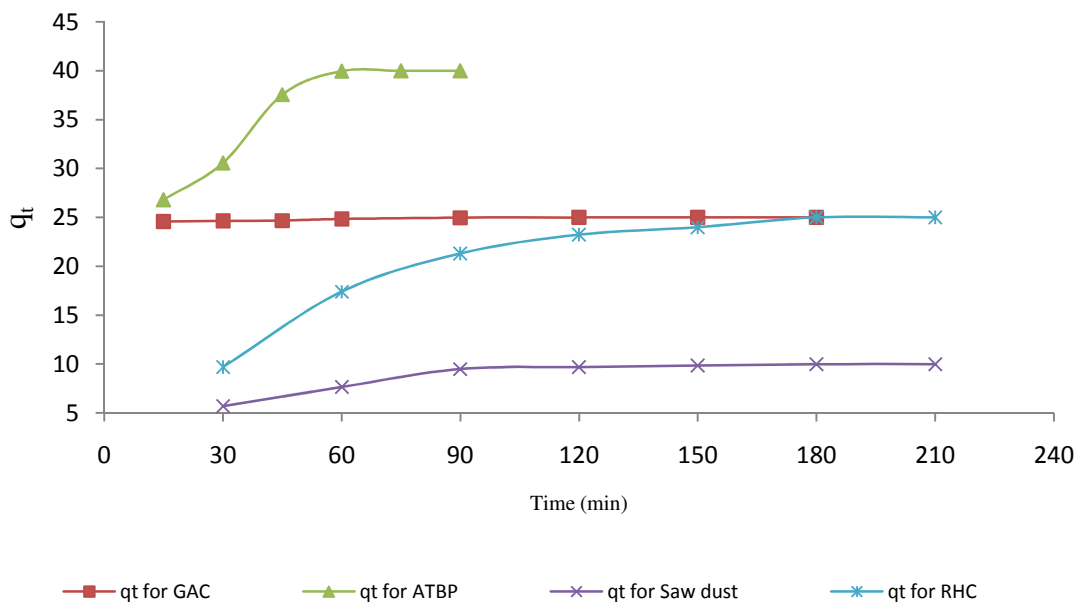
**Figure 5: % removal of Cr (VI) at different concentration for different adsorbents**

**Table 2: The percentage of Cr (VI) adsorbed by adsorbents at different concentrations**

adsorbents	Concentration (ppm)	% removal
GAC	50 - 400	99.98 - 54.7
Acid Treated banana peel	100 - 450	99.99 - 83.12
Saw dust	50 - 400	99.99 - 57.46
RHC	50 - 400	99.97 - 40.87

### 3.2 Kinetic Models

The effects of contact time on adsorption of Cr (VI) [4] onto adsorbents are shown in figure 6, the adsorption abilities of adsorbents rises quickly in the early periods of interaction time and reach steadiness time.

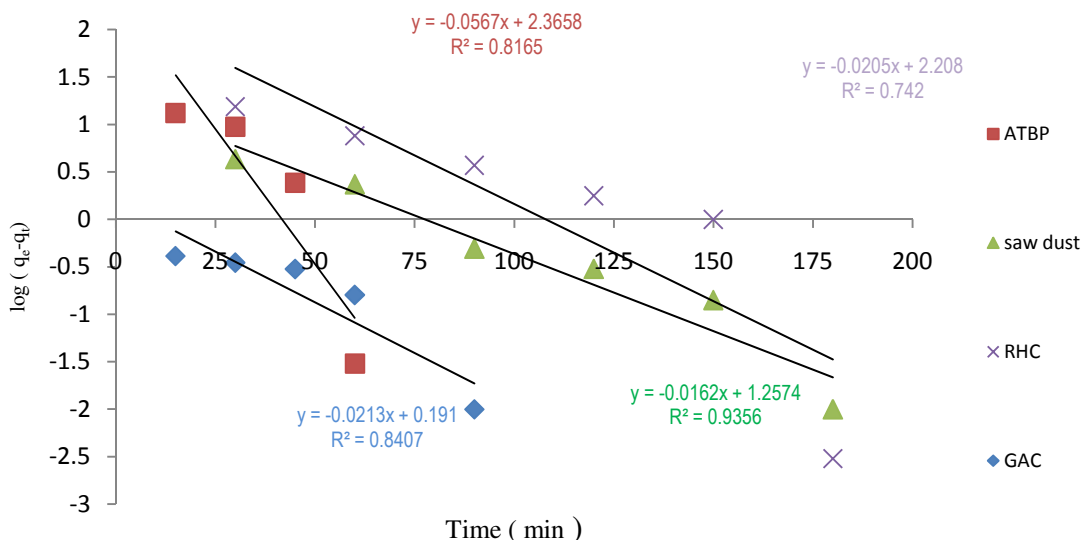


**Figure 6: Adsorption capacity vs time for GAC, Acid treated banana peel, saw dust and RHC at optimum condition**

The pseudo first order kinetic model: This order kinetic model is stated by the subsequent expression. [5, 6]

$$\frac{dq}{dt} = k_1(q_e - q_t) \dots \text{By solving this equation} \dots \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

Where,  $k_1$  Rate constant ( $\text{min}^{-1}$ ) of pseudo- first order kinetic equation,  $q_e$  and  $q_t$ , quantities of adsorbate adsorbed at equilibrium and at some time ( $\text{mg g}^{-1}$ ). Hence a linear hint predictable among the two limits  $\log(q_e - q_t)$  and  $t$  which gives the result about kinetics model, shown in fig 7. The values of  $k_1$  and  $q_e$  can be determined from the slope and intercept and value of  $k_1$ ,  $q_e$  and  $R^2$  is given in table 3.



**Figure 7: Pseudo-first order kinetic plots for the adsorption of Cr (VI) onto GAC, acid treated banana peel, saw dust and RHC at optimum condition**

Pseudo-second order kinetic model: The adsorption may also be described by pseudo-second order kinetic model if the adsorption does not follow the first order kinetics. Two assumption carried out by second order model first one is that rate limiting step is chemical adsorption and second one is process is second order.[7]

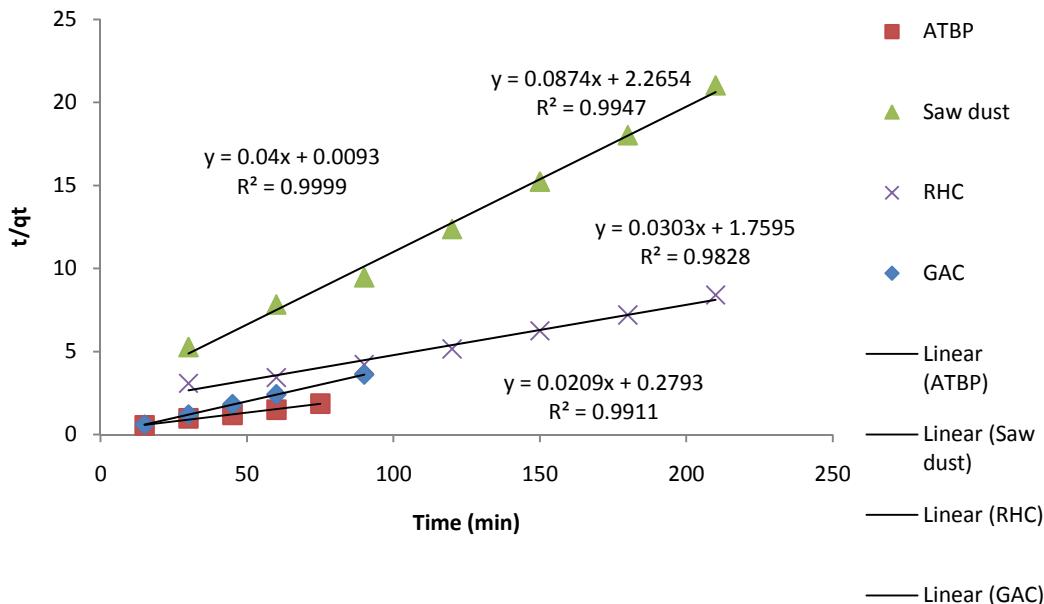
**Table 3: Value of  $k_1$ ,  $q_e$  and  $R^2$  for pseudo first order kinetic model**

Pseudo First order kinetic model				
Adsorbents	$k_{ad}(\text{min}^{-1})$	$q_{e(cal)}(\text{m}g\text{g}^{-1})$	$q_{e(expl)}(\text{m}g\text{g}^{-1})$	$R^2$
GAC	0.049	1.55	25	0.8407
Acid treated Banana peel	0.1305	232	39.99	0.8165
Saw dust	0.0373	18.08	9.99	0.9356
RHC	0.0472	161.43	24.99	0.742

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \dots \dots \dots \text{linearized form} \dots \dots \dots \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$



Where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant of pseudo-second order kinetic equation. A plot of  $\frac{t}{q_t}$  and  $t$  should show a linear correlation if the adsorption follows second order,  $q_e$  and  $k_2$  can be calculated from the slope and intercept of the plot shown in figure 8. The values of pseudo second order rate constants  $k_2$  and the corresponding linear regression correlation coefficients  $R^2$  are given in table 4



**Figure 8 : Pseudo-second order kinetic plots for the adsorption of Cr (VI) onto GAC, acid treated banana peel, saw dust and RHC at optimum condition**

**Table 4: Value of  $k_{ad}$ ,  $q_{e(cal)}$  and  $R^2$  for pseudo first order kinetic model**

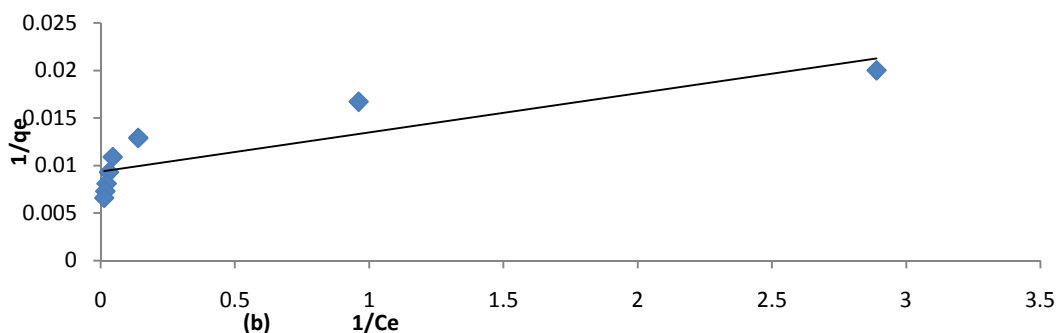
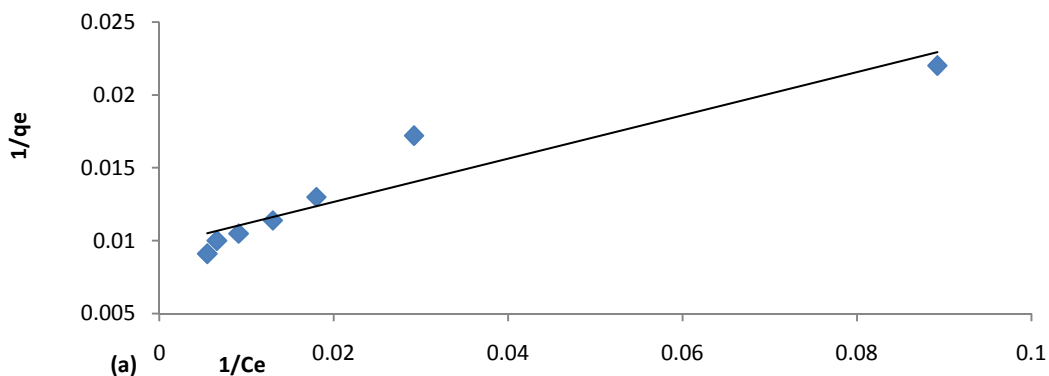
Pseudo second order kinmetic model				
Adsorbents	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$q_{e(cal)}$ ( $\text{mgg}^{-1}$ )	$q_{e(expl)}$ ( $\text{mgg}^{-1}$ )	$R^2$
GAC	5.81	24.99	25	0.9999
Acid treated Banana peel	0.0015	47.8	39.99	0.9911
Saw dust	0.0033	11.44	9.99	0.9947
RHC	0.0052	33.003	24.99	0.9828

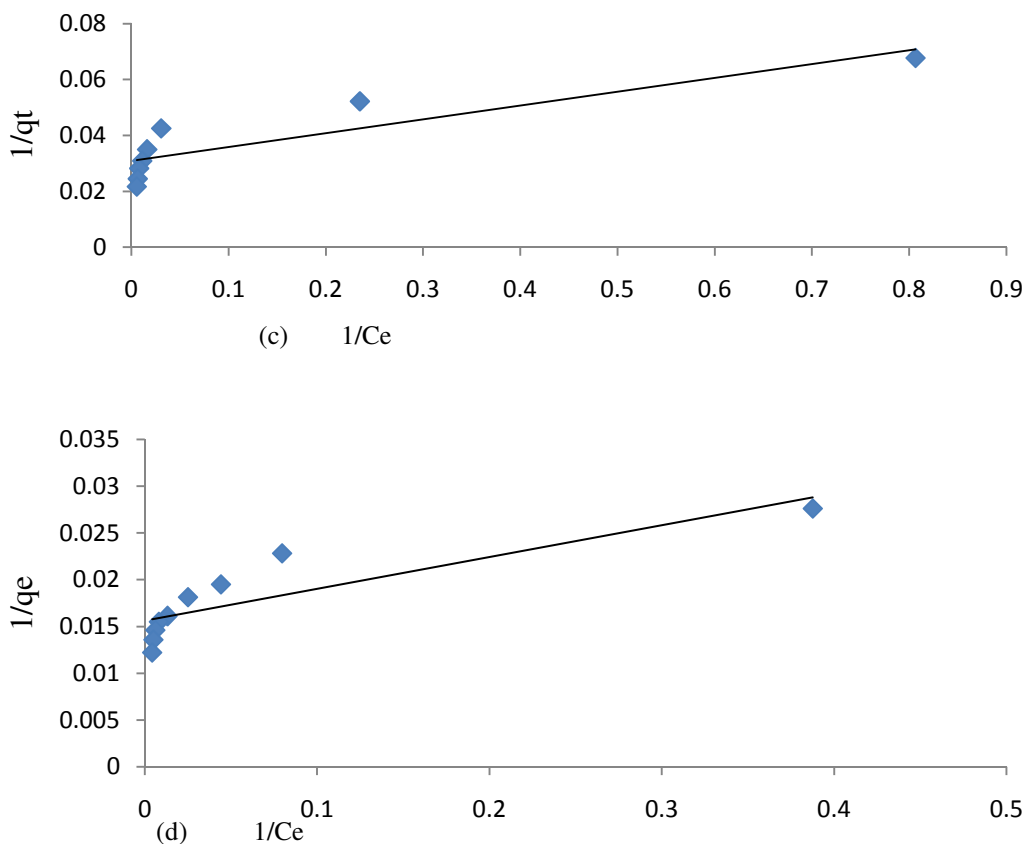
### 3.3 ADSORPTION ISOTHERMS

The Langmuir isotherm is applied to the present study to estimate the adsorption capacity of adsorbents. [8] It is valid for monolayer adsorption onto a homogenous surface containing a finite number of identical sites without any interaction between adsorbed molecules.

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}, \quad R_L = \frac{1}{1 + k_L C_0}$$

Where  $C_e$  equilibrium concentration of Cr (VI) ions (mg/L),  $C_0$  original solute concentration (mgL<sup>-1</sup>),  $k_L$  constant of adsorption equilibrium (L mg<sup>-1</sup>),  $q_e$  amount of Cr (VI) ions adsorbed (mg/g),  $q_m$  maximum adsorption capacity of Cr (VI) ions, (mg/g)  $k_L$  Langmuir isotherm coefficient (L/mg) [9].  $R_L$  is dimensionless separation factor.  $R_L$  tells us the adsorption is favorable or not. When the value of  $R_L > 1$ , isotherm unfavorable, linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). The linear plots of  $1/q_e$  vs  $1/C_e$  for Cr (VI) show in figure 9 for the Langmuir adsorption model.  $q_m$  and  $k_L$  is determined from the slope and the intercept of the plot and value of dimensionless separation factor which summarized in table 5





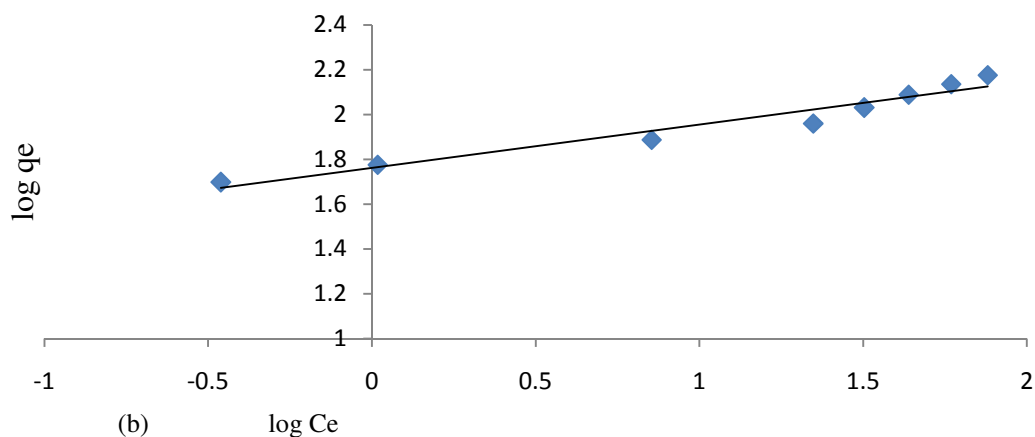
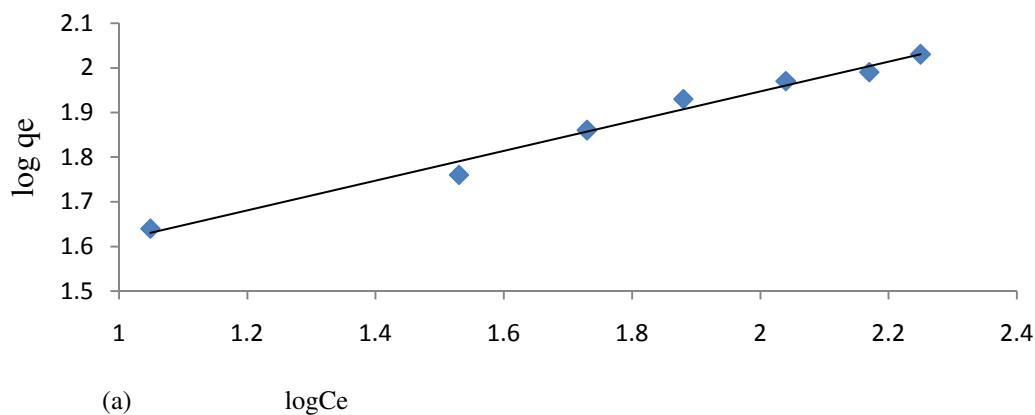
**Figure 9: Langmuir isotherm model plots for the adsorption of Cr (VI) onto (a) GAC, (b) banana peel, (c) saw dust and (d) RHC**

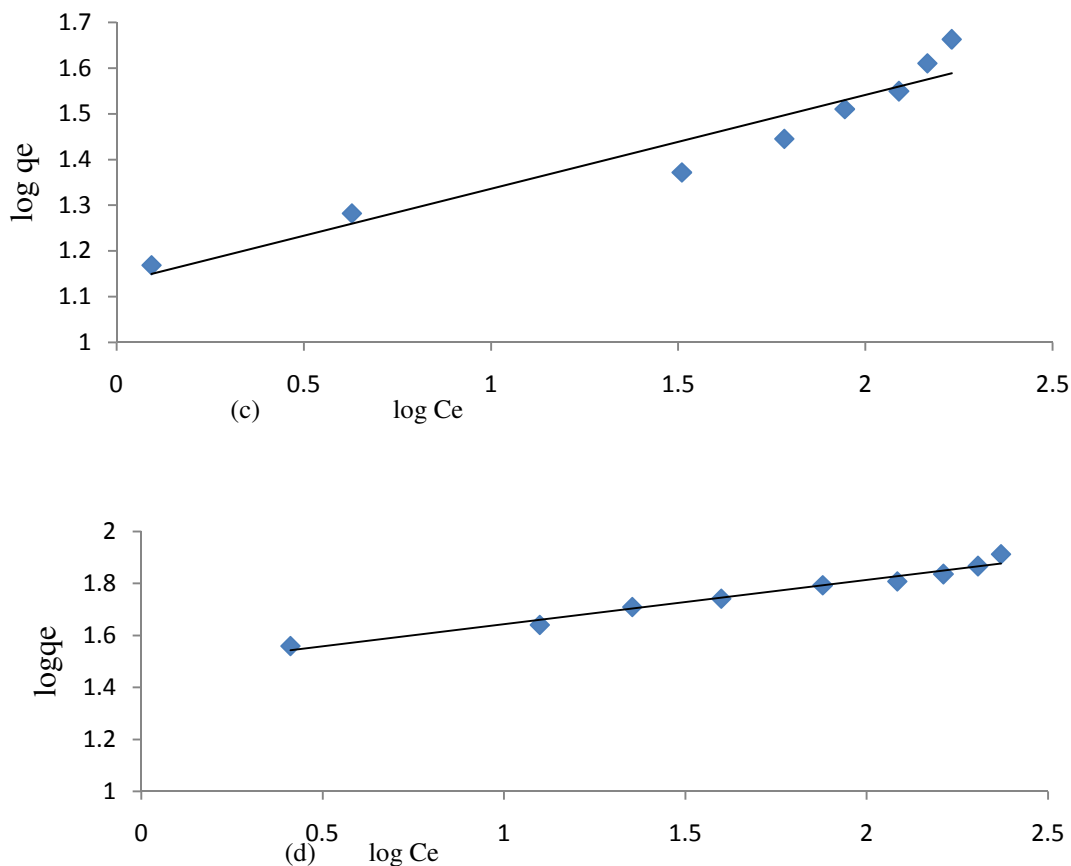
**Table 5 : The values of  $q_m$ ,  $k_L$ ,  $R_L$  and  $R^2$  for langmiur isotherm model**

Langmuir isotherm model				
Adsorbents	$q_m$ (mg/g)	$k_L$ (L/mg)	$R_L$	$R^2$
GAC	106.38	0.0632	0.24	0.8922
Acid treated Banana peel	106.38	2.29	0.0043	0.7621
Saw dust	32.26	0.6242	0.0310	0.7887
RHC	64.102	0.4574	0.0418	0.744

To define the sorption on heterogeneous surface and also a multilayer sorption, Freundlich model can be used. Freundlich equation shows the adsorptive capability or loading factor on the adsorbent surface. The uptake of adsorbate ions follows on a heterogeneous adsorbent surface Freundlich model is describe as follows [10]  $q_e = k_F C_e^{\frac{1}{n}}$  ... By simply it becomes ..... $\log q_e = \log k_F + \frac{1}{n} \log C_e$

Where  $k_F$  is roughly an indicator of the adsorption capacity and  $1/n$  of the adsorption intensity  $k_F$  and  $1/n$  can be determined from the linear plot of  $\log(q_e)$  versus  $\log(C_e)$  shown in figure 10. Table 5 lists the calculated results. The magnitude of the exponent  $1/n$  gives an indication of the favorability of adsorption. Values,  $n > 1$  represent favorable adsorption condition.





**Figure 10: Freundlich isotherm model plots for the adsorption of Cr (VI) onto (a) GAC, (b) banana peel, (c) saw dust and (d) RHC**

**Table 5: The values of n, 1/n,  $k_F$  (mg/g) and  $R^2$  for freundlich isotherm model**

Freundlich isotherm model				
Adsorbents	n	1/n	$k_F$ (mg/g)	$R^2$
GAC	3	0.333	9.64	0.9844
Acid treated Banana peel	5.1706	0.1934	57.78	0.95
Saw dust	4.8866	0.2055	13.49	0.9214
RHC	5.875	0.1702	29.73	0.9746

#### 4. . CONCLUSION

From the present study, it is concluded that, the acid treated banana peel has complete ability to remove the chromium and capacity of bio sorption, very near about GAC. It is more effective and economical as compare to any other combination of biomass. Pseudo second order model was followed by all the adsorbent. This also indicated that diffusion is not only the controlling step and chemisorption processes might also be taking place. Comparison was done on isotherm model of Langmuir, and freundlich isotherm models for all adsorbents. It follows Langmuir and Freundlich isotherm model depending upon the concentration and value of dose. Isotherm models for Cr (VI) adsorption onto bio sorbents, R- squared value is more in case of freundlich isotherm models so it is fit as per experimental data as compare to Langmuir isotherm models.

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