

## ADSORPTIVE REMOVAL OF CR (VI) ION FROM WASTEWATER BY ACTIVATED COFFEE HUSK AND BANANA PEEL: COMPARATIVE STUDY

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### ABSTRACT

This study reports the biosorption of Cr (VI) on surface of acid activated coffee husk (CH) and banana peel (BP). The common functional groups identified at the surface of the CH and BP were OH -COOH, and -NH. A contact time of 240 and 60 minutes assured attainment of equilibrium for CH and BP, respectively. The maximum adsorption capacity of CH was  $59.54 \pm 0.63$  and for BP was  $18.60 \pm 0.01 \text{ mgg}^{-1}$ . As the dose increased, removal efficiency increased with statistical significance for both cases ( $p < 0.05$ ) despite CH removal efficiency is better than BP for same dose used. The optimum pH for CH was  $2.1 \pm 0.01$  and for BP was  $4.50 \pm 0.01$ . The optimum

temperature for removal of Cr (VI) with both adsorbents was  $30^\circ\text{C}$ . The sorption model followed Langmuir for the two adsorbents ( $R^2=0.955$  for CH;  $R^2=0.975$  for BP). The experimental data fitted pseudo second order kinetic model ( $R^2=0.994$  and  $R^2=0.975$  for BP). The reaction was spontaneous in nature as  $\Delta G^\circ = -4.63$  for CH;  $-2.47 \text{ kJ/mol}$  for BP. This showed CH and BP are suitable candidates for use as biosorbents in the removal of heavy metals from aqueous solutions.

**KEYWORDS:** Banana peel, Biosorption, Isotherms, Kinetics.

### I. INTRODUCTION

Heavy metals are present in the soil, natural water, and air in various forms. They may become contaminants in food and drinking water. <sup>[1-4]</sup> Removal of heavy metals from wastewater is achieved principally by the application of several processes such as adsorption, sedimentation, electrochemical processes and, ion exchange, biological operations,

cementation, coagulation/flocculation, filtration and membrane processes and chemical precipitation. [5-8]

Activated carbons are more effective in the removal of heavy metals due to some specific characteristics that enhance the use of activated carbon for the removal of contaminants including heavy metals from water supplies and wastewater. [9-12] Adsorption of hexavalent chromium on activated carbon was reported to be considerable at pH 2–5. The point of pH of zero charge ( $pH_{PZC}$ ) values of the banana peel in the range of 3.5-4 and coffee husk was 2-3. Therefore, pH values should be maintained above 4 to ensure a predominant negatively charged surface on banana peel for effective adsorption. [13-14]

Scholars found FTIR spectra displayed a number of peaks indicating the complex nature of the banana peel. Bands appearing at 3313.4, 2920.3, 2850.6, 1734, 1613.6, 1317.4, 1035.2 and  $884.6\text{cm}^{-1}$  were assigned to OH stretching, C-H stretching of alkane, C-H and -C=O stretching of carboxylic acid or ester, COO<sup>-</sup> anion stretching, OH bending, C-O stretching of ester or ether and N-H deformation of amines, respectively. [15-16]

Cr (VI) adsorption onto banana peel was relatively quicker than those reported for some other bio-adsorbents. They observed a rapid adsorption during the first 30 min, followed by a constant rate of removal for further 30 min before reaching equilibrium. There was no significant increase in adsorption of chromium ion on surface of banana peel after about 60 minutes as cited in [17] and effects of temperature is maximum at 30°C. [18] The present research described the utilization of cleaned, oven dried; powdered and acid treated coffee husk and banana peel for the biosorption of Cr (VI) from wastewater.

## II. MATERIALS AND METHOD

### Adsorbent Collection, Preparation and Characterization

Adsorbents were acquired from Gammo Gofa Zone, Arba Minch town, Ethiopia. Then, they were washed with distilled water to remove dirt, powdered, acid treated and oven dried at 105°C for 6 h. The pH of point of zero charge ( $pH_{PZC}$ ) determination was estimated according to the titration procedures cited in. [18]

### Adsorbate Preparation

1000mg/L of stock solution of Cr (VI) was freshly prepared from 2.827g of  $K_2Cr_2O_7$  dissolved in distilled water. The test solution was prepared by diluting stock solution of metal

ion. 20 to 100mg/L of series of working standard was prepared in volumetric flask. 100mL of 100mg/L metal ion concentrations were taken in different Erlenmeyer flask.

### Effect of Contact Time

Batch experiments of biosorption were performed from 30 to 240 mins. In all sets of experiments, 4g of adsorbents were thoroughly mixed with 100mL solution of the specific ion being sorbed. The solution pH was adjusted to 2 for CH and 4.5 for BP with HCl (0.1M) and NaOH(0.1M).

### Effect of Adsorbent Dose

All parameters were kept constant at their optimum level and only various doses of 0.5-5.0 g of adsorbents were used.<sup>[19]</sup> The uptake is calculated using:  $q = V [L] (C_o - C_e)[mg/L] / S[g]$  [in weight units mg/g]. Where, V is the volume of the metal-bearing solution contacted (batch) with the sorbent [L];  $C_o$  and  $C_e$  are the initial and equilibrium (residual) concentrations of the metal in the solution, respectively. S is the amount of the added (bio) sorbent on the dry basis [g].

### Effects of pH

The choice of pH range should be 2–8. The pH of point of zero (pHpzp) charge of was determined by Boehm titration.

### Effects of Temperature

Experiments were conducted at 25, 35, 45 and 55°C keeping all the other parameters constant at their optimum levels.

### Metals Analysis by FAAS

Water samples were analyzed for metals using Flame Atomic Absorption Spectroscopy (BUCK SCIENTIFIC MODEL 220V).

### Sorption Isotherms

Both Langmuir<sup>[20]</sup> and Freundlich<sup>[21]</sup> models were tested for equilibrium description. Langmuir equation, based on a theoretical model, assumes monolayer adsorption over an energetically homogeneous adsorbent surface. It does not take into consideration interactions between adsorbed molecules. It can be represented by the equation 1.

$$qe = \frac{q_{max}bCe}{1+bCe} \text{----- Equation 1}$$

Where,  $q_e$  corresponds to the amount adsorbed per gram of adsorbent at equilibrium (mg/g),  $C_e$  is the solute concentration (mg/L) in the aqueous solution at equilibrium, and  $q_{\max}$  and  $b$  are constants related to the maximum adsorption capacity (mg/g) and the adsorption energy (L/mg), respectively. Freundlich's equation is an empirical model based on heterogeneous adsorption over independent sites and is given by equation 2.

$$q_e = (K_F C_e)^{1/n} \text{-----Equation 2}$$

Where,  $K_F$  is related to binding energy and adsorption capacity and  $n$  is related to the intensity of adsorption-incorporating all the factors affecting adsorption capacity and intensity.

### Sorption kinetics

The controlling mechanism of the metal biosorption process was investigated by fitting first and second-order kinetic models to the experimental data. [22] The linearized first-order kinetic model is given as in equation 3.

$$\log(q_e - q_t) = \log q_e - 0.4342 k_1 t \text{-----Equation 3}$$

Where  $q_e$  and  $q_t$  are the amounts of metal ions adsorbed per unit mass of biosorbent (mg/g) at equilibrium and at time  $t$ , respectively, and  $k_1$  is the rate constant for first-order adsorption ( $\text{min}^{-1}$ ). The linearized second-order kinetic model is given as in equation 4.

$$\frac{t}{at} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \text{-----Equation 4}$$

Where,  $k_2$  is the rate constant for the second-order adsorption kinetics ( $\text{g mg}^{-1} \text{min}^{-1}$ ). The straight-line plots of  $\log(q_e - q_t)$  against  $t$  and of  $t/q_t$  against  $t$  were used to determine the rate constants for first and second, respectively.

### Adsorption Thermodynamics

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless separation factor, which describes the type of isotherm and is defined by the equation 5. [23]

$$RL = \frac{1}{1 + b C_0} \text{-----Equation 5}$$

Where,  $b$  is a Langmuir constant, which indicates the nature of adsorption and indicates the shape of the isotherm accordingly.  $C_0$  is the initial concentration of metal ion. In such cases value of  $R_L > 1$  shows the adsorption of these metals on banana peels is weak enough and is

called as unfavorable. But, value of  $R_L = 1$  indicates the experimental points are directly on straight-line and is called as linear. This is practically impossible to achieve. If the value of  $R_L$  lies in the range between  $0 < R_L < 1$ , the adsorption is possible and is known as favorable. This is the most common one. Finally, if value of  $R_L = 0$  it is said to be irreversible. This mean that after metals get bound on the surface of adsorbents the physicochemical bound between them become very strong enough and seem impractical to recover both if the need arises.

### III. RESULTS AND DISCUSSION

#### Characterization of the Biosorbent

The major and common functional groups at the surface of CH and BP as characterized by *SHIMADZUFTIR8400S* (Kyoto Japan) were free  $\text{OH}^-$  (phenolic or alcohol) between 3547.60-3450.57,  $\text{OH}^-$  stretch between 2957.97-2850.91,  $-\text{COOH}$  between 1700-1650,  $-\text{NH}$  (primary ammine) between 1411.95, (Fig.1 ). This study is in agreement with. [24-25]

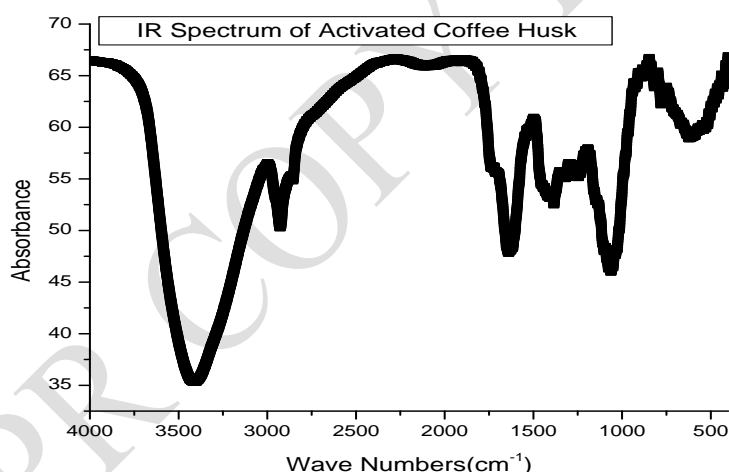
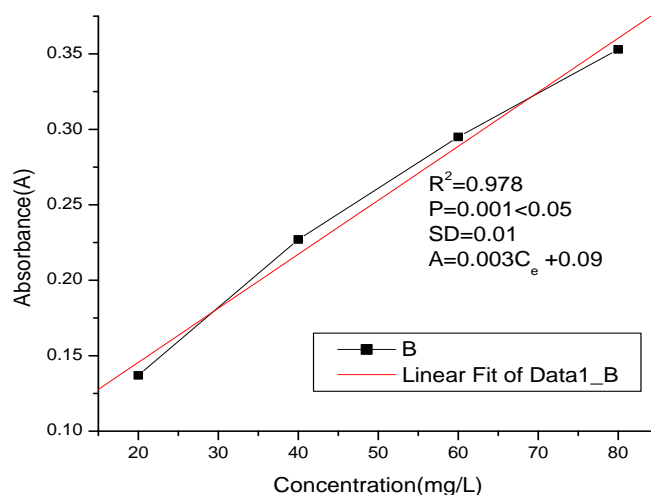


Fig.1. FTIR spectrum acid treated activated coffee husk.

#### Calibration Curve

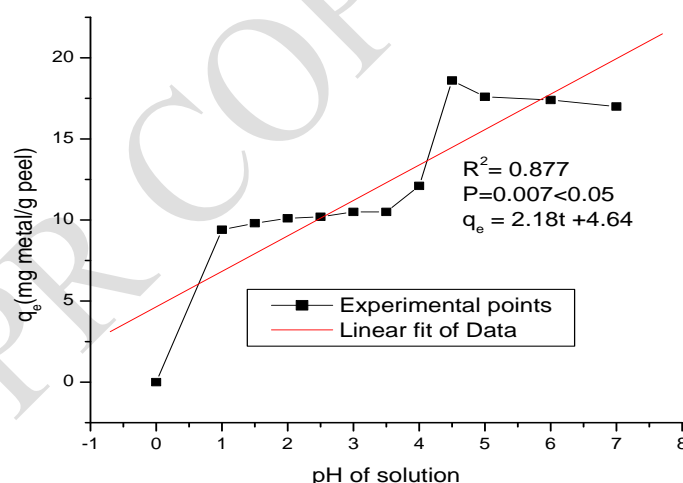
Fig.2. presented calibration graph of series of working standards. It showed as concentration increases and absorbance linearly increases and positively correlated ( $R^2 = 0.978$ ). The increase in absorbance is statistically significant, too ( $P < 0.05$ ).



**Fig.2. Calibration graph of five series of working standards.**

### Effects of pH

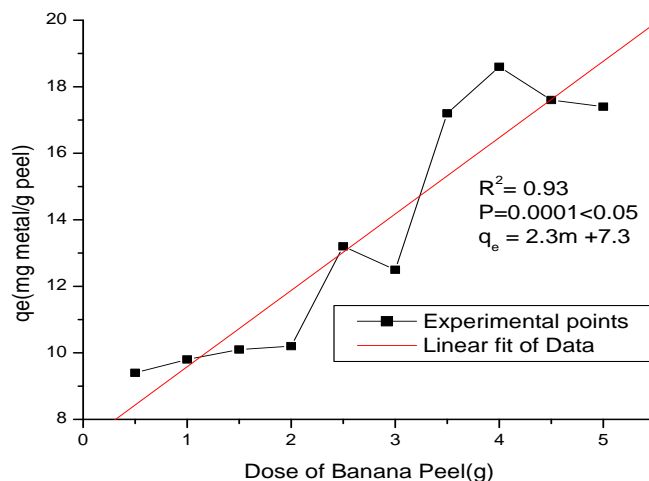
The experimental titration provided an average pH of zero point charge ( $\text{pH}_{\text{PZC}}$ ) values in the range 1.5-1.9 for CH and for BP 3.5-4 and therefore pH values was maintained above 2 and 4 to ensure a predominant negatively charged surface on CH and BP. The effect of pH (in the range 2-8) on uptake of metal is statistically significant ( $p < 0.05$ ) (Fig.3). The optimum pH for Cr(VI) removal was 2 and 4.50. This is nearly in line with. [25, 26]



**Fig.3. Effects of pH of solution on adsorption of  $\text{Cr}^{6+}$  on acid treated banana at  $30^\circ\text{C}$ ; solution volume =0.01 L; contact time = 60mins; metals concentration =100mg/L, adsorbent dose= 4g.**

### Effects of Adsorbent Mass

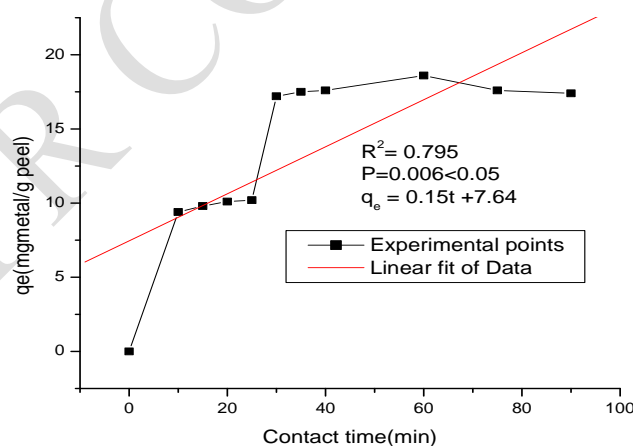
The removal efficiency increased as adsorbent mass increased from 0.5 to 5 g and is statistically significant ( $p < 0.05$ ) (Fig.4). This is due to increases the number of binding sites for the ions also increases. This is in agreement with. [27]



**Fig.4. Effects of adsorbent mass adsorption of Cr(VI) on to acid treated activated banana peel at 30°C; pH =4.5; solution volume =0.01L; contact time = 60mits, initial metals concentration=100mg/L.**

#### Effects of Contact Time

Cr (VI) ions had maximum removal efficiency at the end of 240 for CH and 60mits for BP (Fig.5). This is because the rate of adsorption increased as time goes as reaction rate increases with time. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system. This finding is similar with other researcher.<sup>[28]</sup>



**Fig.5. Effects of contact time on adsorption of Cr (VI) on to acid treated activated banana peel.**

#### Biosorption Equilibrium: Thermodynamics of Sorption

The effect of temperature on the sorption of Cr(VI) ions onto the adsorbents was studied in the range of 25–45°C at the optimized conditions.  $\ln K_c = F_e / (1 - F_e)$ . Where  $F_e$  is the fraction

sorbed at equilibrium, was plotted against  $1/T$  (Fig. 6). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were estimated using the relationships from the slope and intercept of the linear plot.

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ \text{-----Equation 6}$$

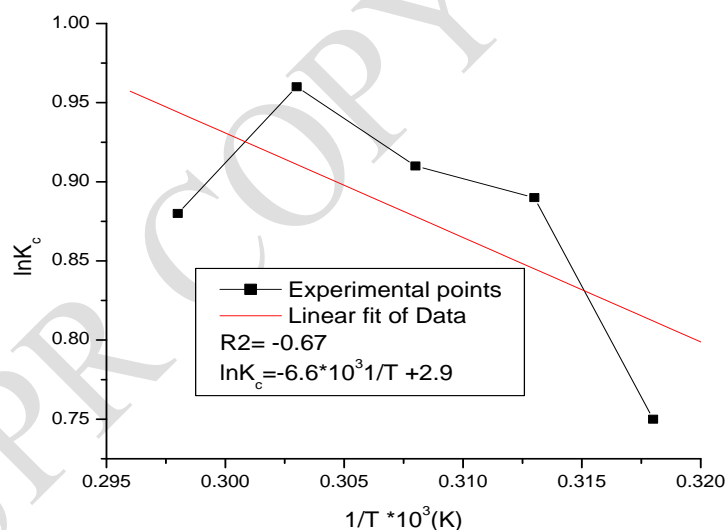
Using equation 7, linear form is as follows

$$\ln K_c = -\Delta H^\circ/RT + \Delta S^\circ/R$$

The magnitude of  $\Delta G^\circ$  (KJ/mol) at equilibrium was calculated using equation 7

$$\Delta G^\circ = -RT \ln K_a \text{-----Equation 7}$$

Where, R is universal gas constant, 0.008314 kJ/mol.K; T is absolute temperature (K) and  $K_c$  the sorption equilibrium constant. The value of  $\Delta G^\circ$  at temperature of 30°C was -4.63 kJ/mol for CH and for BP -2.47 kJ/mol (Fig.6.) confirmed spontaneity of the reaction. The positive value of  $\Delta H^\circ = 0.06$  for CH and 6.6 kJ/mol for BP indicated that the adsorption reaction was endothermic and enthalpy driven. In addition, the value of  $\Delta S^\circ = -20$  for CH and 2.9 kJ/mol.K for BP also suggested that the adsorption was less random. This is in agreement with. [27]



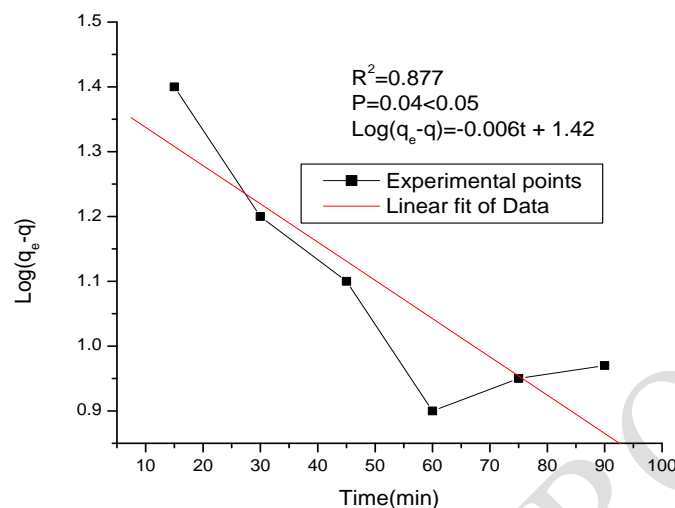
**Fig.6.Effects of temperature on adsorption of Cr (VI) on acid treated activated banana peels at 30°C; pH=4.5; solution volume =0.01L; contact time=60mits, metal concentration=100mg/L, adsorbent dose=4g.**

### Adsorption kinetics

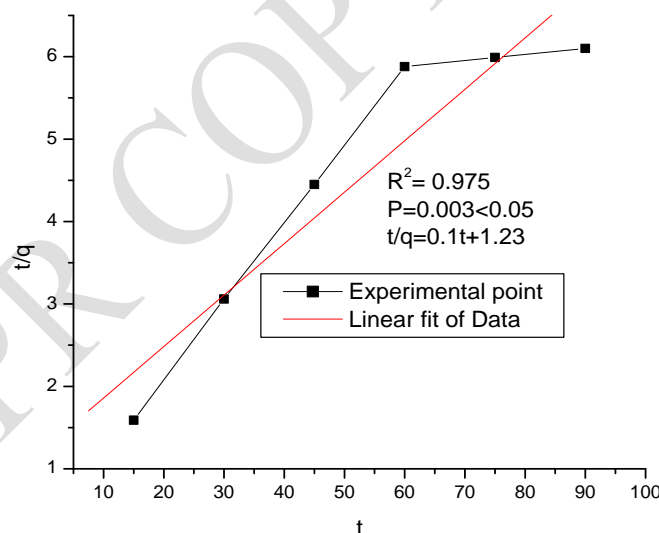
A straight line of  $\log(q_{eq}-q_t)$  versus  $t$  suggested the applicability of this pseudo first order as it is linearly and negatively correlated with time and statistically significant ( $R^2=0.877$ ;  $p<0.05$ ) (Fig.7) for BP. This is in agreement with. [30, 31] Similarly, the plot of  $t/q$



against  $t$  provided linear relationship ( $R^2 = 0.975$ ) BP. It is in line with the findings of. <sup>[32]</sup> It confirmed that the adsorption followed more of pseudo-second order reaction (Fig.8.).



**Fig.7. Pseudo first order sorption kinetics of Cr (VI) onto banana peel. Temperature: 30 °C; biomass concentration: 4; pH=4.5;metal concentration=100mg/L.**



**Fig. 8. Pseudo second-order sorption kinetics of Cr (VI) on banana peels. Temperature: 30 °C; biomass concentration=4 g; pH=4.5;metal conc=100mg/L.**

### Adsorption Isotherms

The equilibrium sorption data for all metal ions produced upward curves, which are indicative of strong sorption (Table 1, Fig 9 and Fig 10).The experimental data fitted to both

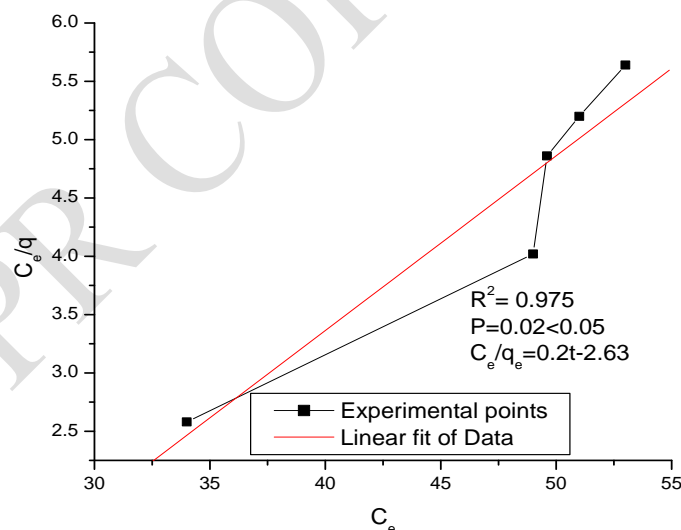
Langmuir and Freundlich models (Table 1). Metal uptake capacity, represented by  $q_{\max}$ =mg metal/g adsorbents in Langmuir equation was relatively higher for CH over BP. This finding is similar with other scholar. [33] The essential characteristics of Langmuir isotherm can be explained in terms of dimensionless constant separation factor ( $R_L$ ) defined by

$$RL = \frac{1}{1 + bq_{\max}}$$

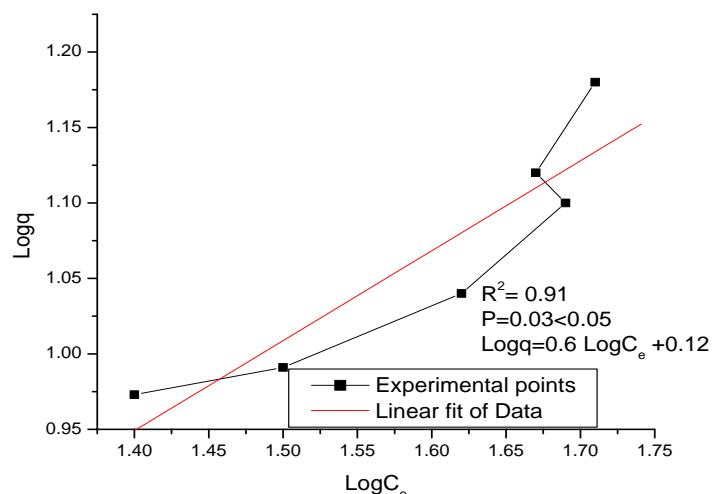
Where,  $b$  is a Langmuir constant, which indicates the nature of adsorption and indicates the shape of the isotherm accordingly.  $q_{\max}$  is the maximum adsorption constant. The reaction was favorable as  $0 < R_L < 1$  (Table 1). The Langmuir constant  $b$  is small that confirmed high affinity/intensity of sorbent for sorbate. Similarly, the lesser value of Freundlich constants  $n$  and larger value of  $K_F$  confirmed adsorption capacity was high (Table 1).

**Table 1. Langmuir and Freundlich constants for sorption of metals on Adsorbents.**

Langmuir	$b=0.025$	$q_{\max}= 18.60\text{mg/g}$	$R^2=0.975$	BP
Freundlic	$K_F=9.960$	$n=1.31$	$R^2=0.91$	BP
Langmuir	$b=0.02$	$q_{\max}= 59.54\text{mg/g}$	$R^2=0.944$	CH
Freundlic	$K_F=9.971$	$n=1.256$	$R^2=0.994$	CH



**Fig.9. The linearized Langmuir adsorption isotherms of Cr(VI) ion by banana peel**  
Temperature: 30°C; biomass concentration: 4g; pH= 4.5 metal concentration=100mg/L.



**Fig. 10. The linearized Freundlich adsorption isotherms of Cr(VI) ion by banana peel Temperature: 30°C; biomass concentration: 4g; pH= 4.5 metal concentration=100mg/L.**

#### IV. CONCLUSION

A study of the feasibility of using CH and BP as acid treated biosorbents for the removal of heavy metal ions from aqueous solutions was successfully carried out. The biosorption efficiency was high for chromium ions at pH 2 and 4.5 using CH and BP, respectively. Biosorption kinetics was described by both a pseudo-first-order model and a pseudo-second-order model, but betterment is to pseudo-second-order model. Equilibrium was attained after 240 and 60 minutes for CH and BP, respectively. Sorption isotherms were described by both Langmuir and Freundlich models but more is by Langmuir. The experimental data demonstrated CH and BP to be a suitable candidate for use as biosorbents in the removal of heavy metals from aqueous solution. Finally, this lab scale should be repeated in environment on wastewater to validate and verify this study.

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