

# KINETIC AND STATIC STUDY ON BIOSORPTION OF HEXAVALENT CHROMIUM USING TAMARIND POD SHELL AND CARBON AS ADSORBENT

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**Abstract**— This study aims to employ low-cost agro waste biosorbent tamarind (*Tamarindus indica*) pod shells and activated carbon prepared by complete and partial pyrolysis of tamarind pod shell for the removal of hexavalent chromium ions from aqueous solution. The effect of parameters namely, initial metal ion concentration, pH, temperature, biomass loading on chromium removal efficiency were studied. More than 96.9% removal of Chromium was achieved using crude tamarind pod shells as biosorbent. The experimental data obtained were fitted with Langmuir, Freundlich, Temkin and Redlich-Peterson adsorption isotherm models. The experimental data fits well to Langmuir, Freundlich and Temkin isotherms with regression coefficient R<sup>2</sup> more than 0.9. For Redlich-Peterson adsorption isotherm the experimental data does not fit so well. The crude tamarind had maximum monolayer adsorption capacity of 40 mg/g and a separation factor of 0.0416 indicating it as best adsorbent among the three tested adsorbent. Further, an attempt is made to fit sorption kinetics with pseudo first order and pseudo second order reactions. Pseudo second order kinetics model fits well to the experimental data for all three adsorbents.

**Key words**— Chromium, Tamarind pod shell, pyrolysis, isotherms, kinetics.

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## I. INTRODUCTION

Industrialization has led to increased disposal of Chromium [Hexavalent Chromium] into the environment and hence effluent treatment is one of the most important targets for industry to remove chromium from waste water. Chromium found in wastewater is harmful to environment and their effects on biological systems are very severe. Unlike organic pollutants, the majority of which are susceptible to biological degradation, Chromium ions do not degrade into harmless end products [1]. Chromium have been extensively studied and their effects on human health are regularly reviewed by international bodies such as the WHO.

Chromium may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in manufacturing, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults [2]. Chromium is found naturally in the soil in trace amounts, which pose few problems. Exposure may occur from natural or industrial sources of chromium. Chromium (III) is much less toxic than chromium (VI). The average daily intake from air, water, and food is estimated to be less than 0.2 to 0.4 µg, 2.0 µg, and 60 µg, respectively [3].

Chromium is a heavy metal that is commonly found at low levels in drinking water. It can occur naturally but can also enter drinking water sources by historic leaks from industrial plant's hazardous waste sites. Various other sources also contribute to the amount of chromium in ground water. Chromium is known to be a potent carcinogen when inhaled [4]. It is very difficult for anyone to avoid exposure to

chromium that is so prevalent in our environment. Hence there is a strong need to reconsider our consumption patterns especially the concentration level and the way we use our water resources.

Chemical approaches are available for chromium remediation, but are often expensive to apply and lack the specificity required to treat target metals against a background of competing ions. In addition, such approaches are not applicable to a cost-effective remediation of large-scale subsurface contamination in situ. In view of this biological methods are becoming more popular [5].

Different alternatives for treating effluents are described in literature, including chemical precipitation, ion exchange and membrane separation process. These processes are either expensive or produce sludge [6]. Therefore the search for new technologies to remove chromium from wastewater has directed attention to biosorption especially using agro waste biomass, which is based on metal binding to various biological materials. Biosorption is a fast and reversible reaction of the chromium with biomass.

Many biosorbents were tried for chromium removal as seen in literature. Microorganisms including algae, fungi and bacteria were used and studied as biosorbents [7-8]. Among the agro waste used are Bengal gram husk (*Cicerarietinum*) [9], treated sawdust (*acacia Arabica*) [10], activated tamarind seed [11], walnut, hazelnut and almond shell [12], pods of Gulmohar (*delonixregia*) and activated carbon from Gulmohar pods [13] corn cob and coconut husks [14] and animal waste like crab shells [15]. Agro waste as biosorbent is promising because of low cost, abundance in availability and reasonably high efficiency.

In this study tamarind pod shell and activated carbon prepared from tamarind shell were used for chromium removal because of its proven efficiency for other metals and also abundance availability in India. Apart from this tamarind pod shell tamarind pod shell cheap low grade fuel, it is not used for any other useful work

The objective of the present work is to study the effect of pH, initial chromium concentration, adsorbent dosage and temperature were studied on chromium removal efficiency by conducting batch adsorption experiments. Further, experimental results were tested using Langmuir, Freundlich, Temkin and Redlich-Peterson adsorption isotherm models. In addition the experimental data were fitted to Pseudo-first order equation or Lagergren's kinetics equation and Pseudo-second order equation.

## II. MATERIALS AND METHODS

### A. Preparation of Biosorbent [16 -18]

#### i. Collection of tamarind pod shells

Natural agro waste biosorbent *Tamarindusindica* pod shells collected from Kolar area Karnataka were used for batch and kinetic studies for removal of chromium. Natural biosorbent along with two types of pyrolysis was employed

for comparative metal removal efficiency.

### ii. Crude (Untreated) tamarind pod shells (T)

Tamarind pod shells were sun dried, powdered, sieved using 60/80 mesh BSS Standard sieve to get uniform sized particles. Powder so obtained washed thoroughly with distilled water and dried in the hot air oven for 2 hours at 80 °C.

### iii. Preparation of Activated carbon by pyrolysis.

The activated carbons used in this study were prepared by Complete Pyrolysis and Partial Pyrolysis using Crude Tamarind pod shell in a muffle furnace. The complete pyrolysis tamarind (TCP) adsorbent is obtained by just keeping the crucible in the muffle furnace whereas partial pyrolysed tamarind (TPP) is obtained by keeping the lid on the crucible.

## B. Adsorbate

### i. Preparation of chromium stock solution

Synthetic chromium solution was prepared by dissolving potassium dichromate ( $K_2Cr_2O_7$ ) in double distilled water. 1000 ppm of stock chromium solution was prepared by dissolving 2.83 mg of potassium dichromate in one litre of double distilled water. Other required concentrations were prepared by diluting the stock solution. The pH of the solution was adjusted to the required value.

### ii. Preparation of diphenylcarbazide (DPC) solution

Diphenylcarbazide (DPC) solution was prepared by dissolving 250mg of DPC in 50ml of acetone in a 100 ml volumetric flask.

## C. Analysis of chromium [19]

0.25ml of phosphoric acid was added to 1ml of standard sample containing known concentration of chromium, pH was adjusted to  $1.0 \pm 0.3$  using 0.2N sulphuric acid. The solution was mixed well and then diluted to 100 ml in a volumetric flask using double distilled water. Further 2ml of DPC solution was added and mixed well. After full colour development for 10 min, 4ml of this solution was used in an absorption cell and the concentrations were measured spectrometrically at 540nm in UV-double beam spectrophotometer [Shimadzu- UV Visible 1700]. The calibration curve is prepared by measuring the absorbance of different known concentrations of chromium solutions and plotting a graph between concentrations versus absorbance. A straight line is obtained with  $R^2$  of 0.994.

## D. Batch Experiments-Adsorption isotherms

Batch adsorption studies were performed by Shaking 100 ml of solutions in 250 ml conical flasks fitted with cork lid kept in constant temperature shaker. Experiments are conducted by varying one of the parameter and keeping other parameters at constant values. All experiments were performed in triplicate and the results were averaged. The adsorption of chromium ions were calculated from the change in metal concentration in the aqueous solution before and after equilibrium sorption by using the following equation.

$$q_e = [V(C_o - C_e)] / W \quad (1)$$

where  $q_e$  is adsorbed metal (mg/g adsorbent),  $V$  is the solution volume (l),  $W$  is the amount of sorbent (g), and  $C_o$  and  $C_e$  (mg/l) are the initial and equilibrium chromium concentrations of the solution, respectively.

The chromium percent removal (%) was calculated using the following equation:

$$\text{Chromium Removal (\%)} = [(C_o - C_e) / C_o] * 100 \quad (2)$$

## E. Adsorption kinetics.

Adsorption experiments are conducted by taking 100 ml of known concentration of adsorbent and fixed amount of adsorbate doses in 250 conical flasks. As many as conical flasks are taken. All these flasks are maintained at fixed pH and the bottles were kept in the temperature controlled mechanical shaker at a constant temperature. Samples are collected for every 10 min until equilibrium is reached.

## III. RESULTS AND DISCUSSION

### A. Effect of pH

The solution pH has significant influence for the removal of chromium ions. Experiments were conducted over a range of pH values (1-7) keeping other conditions constant and the obtained values are shown in Figure 1. As seen from the figure 1 that biosorption capacity of chromium is maximum at around pH 1 for all the adsorbents. Paptri.Rao.et.al. [16] reported similar results for the biosorption of chromium using tamarind pod shell. Some functional groups, such as  $NH$ , are positively charged when protonated and may electrostatically bind with negatively charged metal complexes. At lower pH, the biosorbent is positively charged due to protonation and dichromate ion exists as anion leading to an electrostatic attraction between them [20]. As pH increases, deprotonation starts and thereby results in decrease of adsorption capacity. Maximum chromium removal of 99.86% was found for crude tamarind pod shell [20]. As pH increases, deprotonation starts and thereby results in decrease of adsorption capacity. Maximum chromium removal of 99.86% was found for crude tamarind pod shell

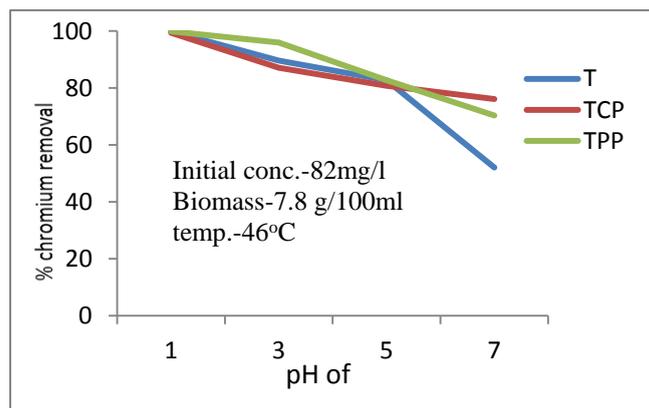


Figure 1: Effect of pH on removal of chromium

### B. Effect of initial concentration of chromium ions.

The equilibrium time required for the biosorption of chromium with three forms of tamarind pod shell was studied varying initial concentrations from 50-250 mg/l keeping other conditions at constant values. Figure 2. shows the effect of initial concentration on % chromium removal. As expected, adsorption capacity decreases with increase in initial concentration. It can be inferred from the figure that maximum removal is achieved at the initial concentration of 50 to 100 ppm. This is due to the fact that at lower initial concentration sufficient adsorption sites are available for adsorption of chromium ions and at higher concentrations the chromium ions will be more than the available adsorption sites [10]. It is observed that 99.9% of chromium removal is achieved at 50 ppm for crude tamarind pod shell. All the adsorbents showed the similar type of behaviour

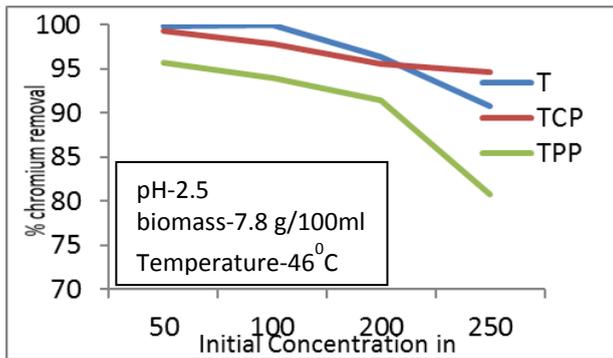


Figure 2: Effect of initial concentration of chromium on % removal

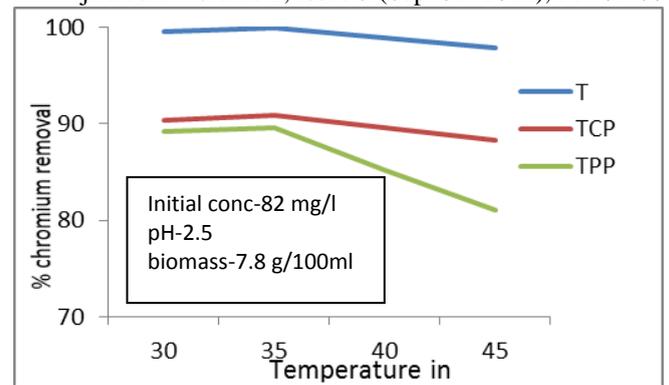


Figure 4: Effect of Temperature on removal of chromium

C. Effect of adsorbent dosage

To study the effect of adsorbent dosage on removal of chromium, adsorbent dosage is varied from 1 g/100ml to 10 g/100 ml keeping other conditions at constant values. The obtained results are shown in Figure 3.. There is an increase in removal of chromium ion with increase of adsorbent dosage as exhibited by all the adsorbent. It is apparent that the chromium ion removal increases with increase in adsorbent dosage due to the greater availability of the exchangeable active sites or the surface area for adsorption. Moreover the percentage of metal ion adsorption on adsorbent is determined by adsorption capacity of the adsorbent [10]. The maximum removal of 99.89% is observed at the dosage of 10 g/100ml for T among all three adsorbents.

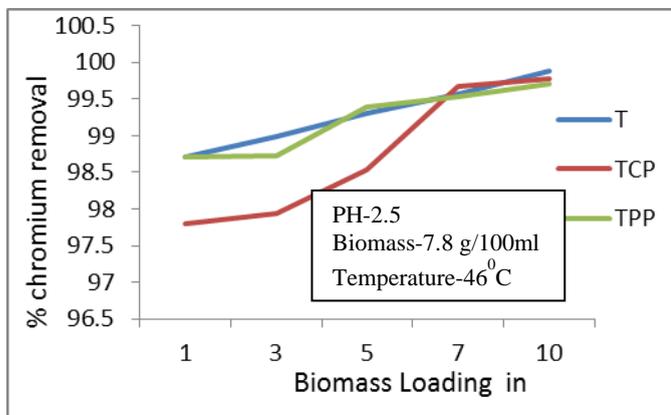


Figure 3: Effect of adsorbent dosage on removal of chromium

D. Effect of Temperature

Temperature effect on biosorption of chromium was studied by varying the temperature between 30°C to 45°C for all the three adsorbents. It is observed from Figure 4 that there is a slight increase in adsorption from 30°C to 35°C and there is a decrease in percentage removal of chromium with increase in temperature. This behavior may be due to the slight exothermic behavior of adsorption process.

E. Adsorption Isotherms.

Sorption equilibrium provides fundamental physicochemical data for evaluating the applicability of sorption process as a unit operation. Sorption equilibrium is usually described by an isotherm equation whose parameter expresses the surface properties and affinity of the sorbent at fixed temperature, pH and initial metal concentration. Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and solid phases, based on a set of assumptions that are related to the heterogeneity or homogeneity of the solid surface, the type of coverage, and the possibility of interaction between the adsorbate species. In this study, equilibrium data were analyzed using the Freundlich, Langmuir, Temkin and Redlich-Peterson isotherms expression.

i. The Langmuir isotherm [21]

The Langmuir model suggests, as a hypothesis, that uptake occurs on a homogeneous surface by monolayer adsorption without interaction between sorbed molecules. This model is described by the equation

$$q_{eq} = \frac{Q_0 b C_{eq}}{1 + b C_{eq}} \quad (3)$$

Where  $q_{eq}$  (mg/g) and  $C_{eq}$  (mg/l) in the above equation are the amount of adsorbed metal per unit weight of biosorbent and an adsorbed metal concentration in solution at equilibrium respectively.  $Q_0$  (mg/g) is the maximum amount of metal per unit weight of biomass to form a complete monolayer on the surface bound,  $b$  (l/mg) is the Langmuir constant related to the energy of adsorption. The equation (3) may be written as

$$\frac{1}{q_{eq}} = \frac{1}{Q_0 b C_{eq}} + \frac{1}{Q_0} \quad (4)$$

As per eq. (4) a plot of  $q_{eq}^{-1}$  and  $C_{eq}^{-1}$  provides  $Q_0$  and  $b$  are constants which are related to the affinity of the sites. The Langmuir constants obtained are presented in Table 1. They indicate that Langmuir isotherm model fits best for all the adsorbents as seen by high  $R^2$  value. T exhibits highest maximum monolayer adsorption capacity of 40 mg/g which is in agreement with work done by others in literature [20]

In addition, the effect of isotherm shape can also be used to predict whether an adsorption system is “favourable” or “unfavourable”. According to Hall K.Ret.al.,[22], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter  $K_R$ , which is defined by the following

adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies [25]. The Temkin isotherm is represented by the following equation in the linear form as

relationship

$$K_R = \frac{1}{1+bC_0} \quad (5)$$

Where  $K_R$  is a dimensionless separation factor,  $C_0$  is initial ion concentration (mg/l), and  $b$  is the Langmuir constant (l/mg). The calculated  $K_R$  values are also reported in the Table 1 and the value of  $K_R$  is in the range of  $0 < K_R < 1$  for all the adsorbents. Further, the value of  $K_R$  also indicates the shape of the isotherm. According to Table 2 the adsorption of chromium is favorable for all three adsorbents.

**Table 1. Langmuir Isotherm Constants**

| Biosorbent | Langmuir isotherm constants |            | $R^2$ | Separation factor $K_R$ |
|------------|-----------------------------|------------|-------|-------------------------|
|            | $Q_0$ (mg/g)                | $b$ (l/mg) |       |                         |
| T          | 40.0                        | 0.012      | 0.994 | 0.0417                  |
| TCP        | 18.2                        | 0.015      | 0.990 | 0.0666                  |
| TPP        | 20.1                        | 0.022      | 0.981 | 0.6902                  |

**Table 2. Isotherm Separation Factor [22]**

| Values of $K_R$ | Type of isotherm |
|-----------------|------------------|
| $K_R > 1$       | Unfavourable     |
| $K_R = 1$       | Linear           |
| $0 < K_R < 1$   | Favourable       |
| $K_R = 0$       | Irreversible     |

ii. The Freundlich isotherm [23]

The Freundlich model proposes a monolayer adsorption with a heterogeneous energetic distribution of active sites, and with interactions between sorbed molecules, as described by the equation (5)

$$q_{eq} = K_F C_{eq}^{\frac{1}{n}} \quad (6)$$

Where  $C_{eq}$  (mg/l) is the equilibrium concentration and  $q_{eq}$  (mg/g) is the amount of adsorbed metal ion per unit mass of the adsorbent. The constant  $n$  is the Freundlich equation exponent that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface [24]. Freundlich constants  $K_F$  and  $n$  are the indicators of adsorption capacity and adsorption intensity, respectively. Equation (5) can be linearized in logarithmic form which is presented in eq (6)

$$\ln q_{eq} = \ln K_F + \frac{1}{n} \ln C_{eq} \quad (7)$$

A plot is made between  $\ln q_{eq}$  and  $\ln C_{eq}$  provides the Freundlich isotherm constants and calculated values are presented in Table 3. The high  $R^2$  value indicates that Freundlich isotherm model also fits well with all the three adsorbents. The high value of  $K_F$  of 0.882 and  $n$  of 0.855 for crude tamarind shell indicates it is best adsorbent among the all three adsorbents.

**Table 3. Freundlich Isotherm Constants**

| Biosorbent | Freundlich constants |      | $R^2$ |
|------------|----------------------|------|-------|
|            | $K_F$ (L/g)          | $n$  |       |
| T          | 0.882                | 0.85 | 0.957 |
| TCP        | 0.360                | 1.41 | 0.971 |
| TPP        | 0.513                | 1.65 | 0.988 |

iii. Temkin Isotherm Equation.

The Temkin isotherm equation assumes that the heat of

$$q_{eq} = A + BC_{eq} \quad (8)$$

Where  $C_e$  is the equilibrium concentration of the adsorbate in mg/l,  $q_e$  is the amount of adsorbate adsorbed at equilibrium (mg/g),  $A$  (mg/g) =  $RT/b \ln a$  and  $B$  (l/mg) =  $RT/b$  where  $T$  is the temperature (K),  $R$  is the ideal gas constant,  $A$  and  $B$  are constants. A plot of  $q_e$  against  $\ln C_e$  enables the determination of constants  $A$  and  $B$ . The constant  $B$  is related to the heat of adsorption and  $A$  is the equilibrium binding constant corresponding to the maximum binding energy. From Table 4 it is evident that the adsorption also follows Temkin model as regression coefficient ( $R^2$ ) is high and it is highest for TPP at 0.99. It has been reported [26] that the typical range of bonding energy (value of  $A$ ) for ion-exchange mechanism is 8-16 kJ/mol. The low values in this study indicate a weak interaction between sorbate and sorbent

**Table 4. Temkin isotherm constants**

| Biosorbent | Temkin constants |            | $R^2$ |
|------------|------------------|------------|-------|
|            | $A$ (mg/g),      | $B$ (l/mg) |       |
| T          | 0.637            | 2.5106     | 0.951 |
| TCP        | 1.551            | 0.5559     | 0.976 |
| TPP        | 1.446            | 0.8693     | 0.990 |

iv. Redlich–Peterson model.

Redlich–Peterson model is used as a compromise between Langmuir and Freundlich models, which can be written as [27].

$$q_{eq} = \frac{K_R C_{eq}}{1 + \alpha C_{eq}^\beta} \quad (9)$$

Equation 9. can be expressed in its linear form as:

$$\ln \left( \frac{K_R C_{eq}}{q_{eq}} - 1 \right) = \ln \alpha_R + \beta C_{eq} \quad (10)$$

Where  $K_R$  (l/g),  $\alpha_R$  (l/m.mol) and  $\beta$  are Redlich-Peterson constants. The value of  $\beta$  lies between 0 and 1. The Redlich–Peterson isotherm constants can be predicted from the plot between  $C_e/q_e$  versus  $C_e$ . However, this is not possible as the linear form of Redlich–Peterson isotherm equation contains three unknown parameters  $\alpha_R$ ,  $K_R$  and  $\beta$ . Therefore, a minimization procedure is adopted to maximize the coefficient of determination  $R^2$ , between the isotherm equation and the experimental data. The Redlich–Peterson isotherm constants for the chromium ions are presented in Table 5. It is seen from the Table 5 that  $R^2$  value are low indicating this model does not fit the as accurately as other models.

**Table 5: Redlich-Peterson isotherm constants**

| Biosorbent | $A$    | $\beta$ | $R^2$ |
|------------|--------|---------|-------|
| T          | 87.619 | -0.066  | 0.746 |
| TCP        | 38.78  | 0.512   | 0.801 |
| TPP        | 38.015 | 0.399   | 0.873 |

F. Adsorption kinetics.

Equilibrium study is important in determining the efficacy of adsorption. It is also necessary to identify the adsorption mechanism for a given system. Kinetic models have been exploited to test the experimental data and to find the mechanism of adsorption and its potential rate-controlling step that include mass transport and chemical reaction. In addition, information on the kinetics of metal uptake is required to select the optimum conditions for full scale batch or continuous metal removal processes

In order to analyze the rate of adsorption and possible adsorption mechanism of chromium onto biomass, the pseudo first order and pseudo second order kinetic models were applied to adsorption data.

Pseudo-first order equation or Lagergren's kinetics equation [28] is widely used for the adsorption of an adsorbate from an aqueous solution.

$$\frac{dq_t}{dt} = K_{p1}(q_e - q_t) \tag{11}$$

After integration and applying boundary conditions to above equation,  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the integrated form of above equation 11, becomes

$$\ln(q_e - q_t) = \ln q_e - \frac{K_{p1}}{2.303} t \tag{12}$$

Where  $q_t$  is the amount of metal adsorbed per unit of adsorbent (mg/g) at time  $t$ ,  $k_{p1}$  is the pseudo-first order rate constant (l/min), and  $t$  is the contact time (min). The adsorption rate constant ( $k_{p1}$ ) was calculated from the plot of  $\ln(q_e - q_t)$  against  $t$ . The obtained rate constant value  $K_1$ ,  $q_e$  and  $R^2$  values are reported in the Table 6. The low values of  $R^2$  indicating that the adsorption data does not follow Pseudo first order kinetics.

Pseudo- second order model [29] presented the pseudo-second order kinetic. The pseudo-second- order kinetic model which is based on the assumption that chemisorption is the rate-determining step we have the equation as follows [30].

| Biosorbent | qe(exp) mg/g | Pseudo first order |                |                 | Pseudo second order |                |        |                 |
|------------|--------------|--------------------|----------------|-----------------|---------------------|----------------|--------|-----------------|
|            |              | K1 min-1           | qe (theo) mg/g | R1 <sup>2</sup> | K2 g/mg.min         | qe (theo) mg/g | h      | R2 <sup>2</sup> |
| T          | 2.716        | 0.0197             | 3.684          | 0.934           | 0.0247              | 3.099          | 0.3729 | 0.995           |
| TCP        | 1.648        | 0.0077             | 1.579          | 0.885           | 0.0055              | 4.719          | 0.0169 | 0.989           |
| TPP        | 1.354        | 0.004              | 1.156          | 0.92            | 0.004               | 1.538          | 0.012  | 0.972           |

Table 6: Parameters of the kinetic models for the adsorption of Chromium on different adsorbents

V. NOMENCLATURE

- T-tamarind crude.
- TCP-tamarind crude completely pyrolysed.
- TPP- tamarind crude partially pyrolysed.

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$$\frac{dq_t}{dt} = (q_e - q_t)^2 \tag{13}$$

This on integration for boundary conditions when  $t=0$  to  $>0$  and  $q=0$  to  $>0$  and further simplifications of equation 13 gives

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{14}$$

Or the equation 14 can be written as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t = \frac{1}{h} + \frac{1}{q_e} t \tag{15}$$

Where  $h = k_2 q_e^2$  and is known as initial sorption rate. Where  $k_2$  is the rate constant of second order adsorption (g/mg/min). Values of  $K_2$  and  $q_e$  were calculated from the linear plots of  $t/q_t$  versus  $t$ . The obtained rate constant value  $K_2$ ,  $q_e$  and  $R^2$  values are also reported in the Table 6.

It is seen from Table 6 that the adsorption of chromium with all the adsorbent is following pseudo second order kinetics (high  $R^2$ ). This indicates adsorption may be chemisorption.

IV. CONCLUSION

The agro waste biomass, tamarind and carbon from tamarind demonstrated a good capacity of chromium biosorption, highlighting its potential for effluent treatment processes. High chromium removal is possible at low pH, high adsorbent dosage and low initial concentrations. Further, highest chromium removal was possible at moderate temperature of 35°C. Among all the adsorbents crude form of tamarind pod shell is the best with a highest removal capacity. Langmuir, Freundlich and Temkin isotherm models were in good agreement with experimental results. The biosorption of chromium obeyed the pseudo second-order biosorption kinetic model as it fitted the experimental data with a high correlation coefficient,  $R^2$  of 0.995

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