



# Adsorption of Chromium from Aqueous Solution by Lignocellulosic Biomass (*Pinus palustris*): Studies on Equilibrium Isotherm, and Kinetics

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## Abstract

Different methods to convert biomass into useful materials and products without generating pollutants will be useful for global environmental protection. The present study deals with the preparation of adsorbent from a suitable lignocellulosic biomass, *Pinus palustris* seeds. The adsorbent thus prepared will be used for the removal of heavy metals from aqueous solutions. Factors influencing the adsorption characteristics under batch conditions were studied for chromium concentrations in range of 30 – 150 ppm. The studies were conducted to optimize the size of the adsorbent, temperature and contact time. The maximum adsorption is attained at a pH of 6.5 and a dosage of 3g. The effective temperature for the reaction was at 37°C. The removal percentage increase when the optimized condition of different parameters such as size, temperature, contact time, concentration, pH and dosage. The adsorption isotherms showed that the Freundlich Isotherm is a better adsorption model and the characteristic parameters were determined. The results of the kinetic models showed that the pseudo second order kinetics was found to correlate with the experimental data. The present analysis, the adsorbent that is produced from *Pinus palustris* seed has an efficient adsorption for chromium.

**Keywords:** Lignocellulose, adsorption, isotherms, kinetics

## 1 Introduction

Lignocellulosic biomass sources range from forestry to agricultural residues. Banana plant, cotton stalk, bamboo and cotton gin waste are agricultural residues that are not currently used as industrial raw materials on a larger scale (1, 2). They contain cellulose, and hemicellulose, which could be used as a source of monomeric sugars for fermentation to produce high-value products. Long ago, these materials were used as firewood, building materials and animal feed. Nowadays, lignocellulosic materials have expanded its application from pulp and paper products to second-generation biofuel (3). The development of industrial methods to convert biomass into useful materials and products without generating pollutants such as waste gas, wastewater and solid waste material will be useful for global environmental protection (4-5). The adsorbent which we have made is economically feasible and also locally available and has an ability to absorb chromium in higher concentration (6). Once the absorption is completed, it is easy to dispose of the adsorbent by composting, compaction, incineration, ashing, pyrolysis, direct disposal, liquid extraction (7,8). The adsorbent was obtained from pine plant seeds that were powdered and activated. Currently, the removal of heavy metal contaminants from

aqueous wastewater is one of the most important environmental issues (9). Even though this issue has been studied for several years, effective and precise treatment methods are still scanty due to its low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials (10). Excessive toxic heavy metals are often discharged by several industries, like battery manufacturing and tanneries and they are not biodegradable and can lead to accumulation in living organisms, causing various diseases such as cancer, dermatological issues and disorders like itai-itai disease. Monitoring and subsequent removal of toxic heavy metals from industrial wastewater have been made mandatory before their discharge into the environment (11). Chromium, one of the heavy metals, is a widely used industrial metal for electroplating, tannery, leather industry and wood processing industries and the permissible amount chromium is 0.1 mg/l (12).

Conventional methods applied to remove toxic heavy metals from effluents include chemical precipitation (13), ion exchange (14), carbon adsorption (15) and membrane separation process (16). Among all kinds of adsorption materials, activated carbon

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adsorption has been regarded as an efficient and major technology, but the process is expensive (17). Some main limitations are existent in these alternatives, such as expensive cost, labor – intensive operation, and low efficiency. Therefore, more approaches have been investigated for the development of low-cost adsorbates with a good sorption capacity to remove heavy metal ions from wastewater (18). In recent years, considerable attention has been devoted to the study of application of lignocellulosic biomass as adsorbents (19). Natural materials have an advantage of availability in large quantities, low cost, and good sorption capacity. These are unutilized materials, but they have high potential to be used as adsorbents for heavy metals removal. Adsorption is a versatile treatment technique practiced widely in fine chemical and process industries for wastewater and waste gas treatment (20). The usefulness of the adsorption process lies in the operational simplicity and reuse potential of adsorbents during long term applications (21).

At present, adsorption is widely accepted in environmental treatment applications throughout the world compared with the other methods. The aim of this paper is to use adsorbent obtained by processing of *Pinus palustris* seeds, and to evaluate its effective removal of chromium from industrial effluents.

## 2 Materials Required

### 2.1 Chemicals and materials

Potassium dichromate ( $K_2Cr_2O_7$ ), Potassium iodide (KI) (1 M), Sodium thio-sulphate ( $Na_2S_2O_3$ ) (1M), 1N and 0.1N Hydrochloric acid (HCl), starch solution, Sodium hydroxide NaOH (1M), *Pinus palustris* seeds

### 2.2 Methodology

The sample *Pinus palustris* seeds (Figure 1) was collected from Chennai and thoroughly washed using tap water. It was then dried in the sun. The further drying of the seeds was done in the dryer at a temperature of 70°C. When the seeds are completely dried, it was crushed in the blender. This was done until the seeds are crushed into fine particles. The crushed seeds are then sieved into three sizes namely mesh numbers 25 and 52, and pan (22, 23).



Figure 1: Seeds of *Pinus palustris*

### 2.3 Estimation of chromium

A stock solution of chromium (IV) solution ( $1000 \mu\text{g ml}^{-1}$ ) was prepared by dissolving 0.2829 g of  $K_2Cr_2O_7$  in 100 ml of deionised double distilled water. The stock solution was further diluted as needed. A stock solution of chromium (III) ( $1000 \mu\text{g ml}^{-1}$ ) was prepared by dissolving 0.2829 g of  $K_2Cr_2O_7$  in 50 ml of deionised double distilled water, adding 1 ml of saturated

sodium sulphite solution followed by acidifying with 1 ml of 2.5 M sulphuric acid, and then boiling for 2 min to remove excess  $SO_2$  and diluting with water to 100 ml. A suitable volume of this solution was diluted to obtain the working standard. To find the concentration of chromium, the solutions were spectrophotometrically analysed and from the absorbance value concentrations of the solutions were calculated (24).

### 2.4 Optimization of Chromium concentration with adsorbent, adsorbent size and contact time

A sample of volume 10 ml of 30, 60, 90, 120 and 150 ppm of the chromium solutions were taken and 0.5g of the powder ranging from .075–0.150 mm was mixed with the solutions. The solutions were kept for 10min and then the solutions were filtered. The filtrate was given for spectrophotometry analysis. 30ml of the solution with the optimized concentration was taken in different beakers and to it 1.5g of the adsorbent of sizes pan and mesh no 25 and 52 are added, respectively. These solutions were mixed thoroughly for 30 minutes and filtered and then given for spectrophotometry analysis. 30ml of the solution containing the optimized concentration and 1.5g of the optimized sizes were taken in different beakers. They were kept for time durations of 30, 60, 90 and 120 minutes. The solutions were filtered and spectrophotometry analysis was performed (25)

### 2.5 Optimization of temperature

To optimize the temperature 1.5g of the optimum sized adsorbent was taken and heated in an incubator for 2 hours at different temperatures, 32°C, 37°C and 45°C. The adsorbent was added to 30ml of the solution of optimum concentration and kept for an optimum time (26).

### 2.6 Optimization of pH

To optimize the pH, 30ml of the solution with optimum concentration is maintained with different pH, namely 2, 4, 6, 8 and 10. To maintain the acidic pH of 2, 4 and 6 0.01N HCl was added and to maintain the alkaline pH of 8 and 10 1M NaOH was used. 1.5g of the optimized size adsorbent was taken and heated at the optimized temperature and added to the solutions and kept for the optimum contact time (27).

### 2.7 Optimization of dosage

To optimize the dosage, 1.5, 3.0 and 4.5 g to 30 ml of the solution with optimized concentration was maintained at optimum pH. The adsorbent with optimum size was heated at optimum temperature and added to the solution. These solutions were mixed thoroughly and kept for an optimum contact time (28).

### 2.8 Models for adsorption isotherms

#### • Langmuir isotherm (Model 1)

The theory for Langmuir isotherms assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. Therefore at equilibrium, a saturation point is reached where no further adsorption can occur adsorption takes place at specific homogeneous sites within the adsorbent by the following equation (21).

$$\frac{C_0}{m} = \frac{abC_e}{1+aC_e} \quad (1)$$

Alternate equation

$$\frac{m}{C_o} = \frac{1}{ab} \times \frac{1}{C} + \frac{1}{b} \quad (2)$$

where  $C_o/m$  is adsorbed per unit mass of the adsorbent and the concentration of color remaining in the in the solution after adsorption is complete ( $C_e$ ) by a relation. where  $a$  and  $b$  are constants representing bond energy and adsorption capacity, respectively.

- **Freundlich isotherm (Model 2)**

The theory for Freundlich isotherms describes a monolayer and multilayer coverage of adsorption over a heterogeneous surface area adsorbent (22). An adsorption isotherm is an empirical relation between the concentrations of solute on to the surface of an adsorbent to the concentration of the solute in the liquid with which it is contact. In following equation

$$\frac{x}{m} = KC^{1/n} \quad (3)$$

Alternate equation

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C \quad (4)$$

where  $X/M$  is loading, is the amount of impurity adsorbed ( $X$ ) per unit weight of carbon ( $M$ );  $C$  is equilibrium concentration after adsorption; and  $k$ ,  $n$  are constants.

- **BET (Brunauer- Emmett -Teller) isotherm (Model 3)**

This isotherm describes the physical adsorption of adsorbent on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material (29). In following equation.

$$q_e = \frac{q_m \times K_B \times C_e \times Q_o}{(C_s - C_e) \{1 + (K_B - 1) (C_e / C_s)\}} \quad (5)$$

Alternate equation

$$\frac{C_e}{(C_s - C_e) q_e} = \frac{K_B - 1}{K_B \times Q_o} \times \frac{C_e}{C_s} + \frac{1}{K_B \times Q_o} \quad (6)$$

where  $q_e$  is the amount adsorbed at equilibrium (mg/g) which can be found by  $q_e = \{(C_s - C_e)V\}/W$  where  $C_s$  and  $C_e$  are initial and final concentration, respectively;  $q_m$  is maximum adsorption; and  $K_B$  is BET coefficient or equilibrium distribution coefficient and presenting adsorption intensity.

- **Tempkin Isotherm (Model 4)**

This isotherm describes the effects of some indirect 1 adsorbate/adsorbate interactions on adsorption isotherms suggested that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to these interactions. In the following equation:

$$q_e = \frac{RT}{bT} \times \ln(K_T C_e) \quad (7)$$

Alternate equation

$$q_e = bT \ln K_T + bT \ln C_e \quad (8)$$

where  $K_T$  (L/g) is the Temkin isotherm constant,  $bT$  (J/mol) is a constant related to heat of sorption,  $R$  is the ideal gas constant (8.314 J/mol K), and  $T$  is absolute temperature (K).

## 2.9 Models of sorption kinetics

- **Pseudo First Order Kinetics**

The pseudo first order equation (Lagergren's Equation) describes adsorption in solid liquid system based on the sorption capacity of solid. In the following equation:

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad (9)$$

Alternate equation

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (10)$$

where  $q_e$  and  $q_t$  refer to the adsorption capacities at equilibrium and time  $t$ , respectively, in mg/g and  $k_1$  is the pseudo-first-order rate constant. Plotting the  $\log(q_e - q_t)$  against  $t$  provides the slope and the intercept as  $-k_1/2.303$  and  $\log(q_e)$ , respectively.

- **Pseudo Second Order Kinetics**

The pseudo second order rate expression has been applied for analyzing chemisorptions kinetics from liquid solutions. In the following equation:

$$\frac{dq_t}{dt} = K_1 (q_e - q_t)^2 \quad (11)$$

Alternate equation

$$\frac{t}{q_t} = \frac{1}{K_2} + \frac{1}{q_e} t \quad (12)$$

where  $k_2$  is the pseudo-second-order rate constant. Plotting the  $t/q_t$  against  $t$  provides the slope and the intercept as  $(1/q_e)$  and  $1/k_2 q_e$ , respectively

## 3 Results and Discussion

### 3.1 Influence of concentration

The experiment was carried out with 0.5 g of the adsorbent which is added to 10 ml of different concentrations (30, 60, 90, 120 and 150 ppm) and the filtered solutions were given for spectrophotometry analysis. The result showed that percentage adsorption increases with lower concentration. Therefore, the optimum concentration is 30ppm (Figure -2a). The adsorption of chromium on bioadsorbent, was given by Khazaei et al., 2011, (27) they also shows a similar kind of adsorption pattern on the basis of initial concentration and 0.5ppm shows the maximum adsorption.

### 3.2 Influence of size

Three different sizes of adsorbent have been taken, i.e. pan and mesh nos. 52 and 25. 0.5g of the adsorbent of different sizes was kept in 10 ml of the optimized concentration (30ppm) for 10 min. The filtered solutions were given for spectrophotometry analysis. The adsorption concentration of chromium increases as the size of the adsorbent decreases. This is because as the size

becomes smaller the surface area increases. Therefore, it was concluded that pan size of adsorbent is the optimum size since it shows the highest adsorption percentage (Figure-2b). The adsorption of chromium on almond and apricot shells occurs at the smallest size (100 to 150  $\mu\text{m}$ ), given by the Khazaei et al., 2011 (27) which is similar to this experiment.

### 3.3 Influence of contact time

The experiment was carried out with the different time periods, i.e. 30, 60, 90 and 120 minutes. 0.5g of the pan size adsorbent is added to 10ml of optimum concentration; 30ppm of chromium solution. These solutions are kept at different time intervals and filtered and stirred in magnetic stirrer. Then the obtained filtrate was then analyzed by spectrophotometric method and the adsorption percentage was calculated. It was found that as the time increases adsorption percentage increases but after a certain time there is no change in the adsorption percentage. Because after a certain time the adsorption capacity of adsorbent

is not increasing and its remain same. Therefore, after 90 min the absorption ceases. Therefore, the 90 minutes is the optimum contact time at determined optimum loading of the adsorbent (Figure -2c). A comparative study, done by the Hamdi et al.,2001 (31), of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  adsorption onto chitin and chitosan biopolymers was performed. To attain equilibrium  $\text{Cu}^{2+}$  has taken 480 min,  $\text{Pb}^{2+}$  has taken 360min,  $\text{Cd}^{2+}$  has taken 240 min and  $\text{Ni}^{2+}$  has taken 480 min., but the chromium adsorption on *Pinus palsturis* seeds has only taken 90 min, which is very much lesser. The almond shells took 40 min to reach equilibrium and the apricot shells takes 30 min to reach equilibrium, which was optimized by Khazaei et al., 2011 (27), but it has only lower removal of Cr (60%). The  $\text{Cr}^{6+}$  adsorption on *Pinus palsturis* seeds takes 90 min which is more than the almond and apricot shells, but *Pinus palsturis* seeds have a removal capacity of 90% which is more than the former.

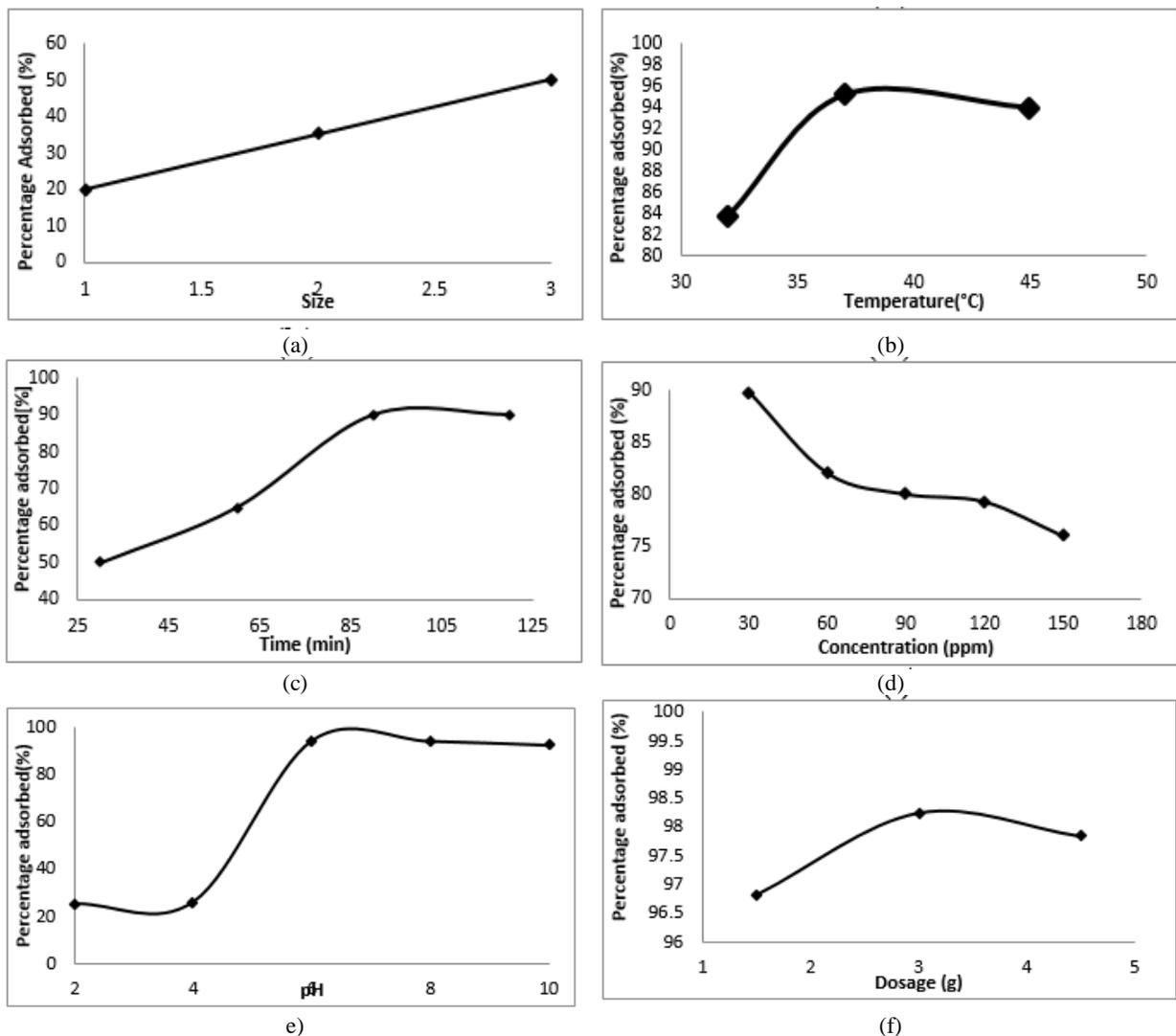


Fig. 2: (a) Influence of size on Cr(VI) removal; (b) Influence of temperature on Cr (VI) removal; (c) Influence of contact time on Cr(VI) removal; (d) Influence of concentration on the adsorption; (e) Influence of pH on Cr(VI) removal; and (f) Influence of dosage on Cr (VI) removal

### 3.4 Influence of temperature

The experiment was carried out at three different temperature i.e. 32, 37 and 45 °C. 1.5g of the pan size of adsorbent was dried in an incubator for 2 hours at different temperatures to remove the moisture. The heated adsorbent was kept in 30ml solution of 30 ppm concentration for 90 minutes (32). The filtered solutions were given for spectrophotometry analysis and the adsorption percentage was calculated. It was found that as the temperature increases the adsorption percentage also increases but after 37°C temperature it decreases. This is because after a certain temperature, degradation of adsorbent starts. Therefore, it was concluded that among the tested temperature, 37 °C is the optimum temperature for adsorption (Figure 2d). Adsorption study of chromium on MgO, showed a similar observation in the case of temperature. The maximum adsorption occurs at around 30°C for MgO which was given by Mahmood et al., 2010 (31), and the *Pinus palsturis* seeds take 37°C for maximum adsorption. The maximum adsorption of Cr on almond is at 45°C and apricot is 50°C which is given by Khazaei et al., 2011 (27), compared to the *Pinus palsturis* seeds adsorption occurs at higher temperature. This is because the *Pinus palsturis* seeds get decayed at high temperature.

### 3.5 Influence of pH

To optimize the pH the experiment was carried out with the different pH values, i.e. 2, 4, 6, 8 and 10. The pH 2, 4, and 6 are maintained by adding few drops of 0.1N HCl and pH of 8 and 10 are maintained by adding few drops of 1M NaOH. 1.5g of pan size of adsorbent was heated at 37°C in the incubator for 2 hours. The heated adsorbent was kept in 30ml solution of 30ppm concentration for 90 min. The filtered solutions were given for spectrophotometry analysis and adsorption percentage was calculated. It was found that as the pH increases adsorption percentage also increases but after a certain pH it decreases. It was determined from experimental data and it is shown on the graph the influence of pH on adsorption (Figure -2e).

### 3.5 Influence of dosage

The experiment was carried out for different dosage of the pan size adsorbent, i.e. 1.5, 3 and 4.5g. Different weights of the adsorbent were kept in the incubator at 37 °C for 2 hours. The heated adsorbent was kept in 30ml solution of 30ppm concentration with 6.5 pH for 90min. The filtered solution were given for spectrophotometry analysis and the adsorption percentage was calculated. It was found that as the weight increases the adsorption percentage also increases but after a certain dosage it decreases (32). This is because adsorptive force between the adsorbent and chromium gets weak at higher dosage. So it was concluded that 3g of adsorbent is the optimum dosage for adsorption (Figure 2f).

The study of Boehmite nano powder on Chromium uses 2.5g of the powder for maximum adsorption i.e. 60%, given by Sharawy et al., 2013 (33), whereas in this study the *Pinus palsturis* seeds uses 3g and the adsorption percentage is 98.25% in absorbing chromium. The maximum adsorption of chromium on almond and apricot is at 6g, which showed by Khazaei et al.,

2011 (27), compared to the *Pinus palsturis* seeds adsorption occurs at better dosage (Table 1).

### 3.6 Adsorption Isotherms

- **Langmuir isotherm (Model 1) (Figure -3a)**

$$\frac{C_0}{M} = \frac{abC_e}{1 + aC_e}$$

$$\frac{C_0}{M} = \frac{57.4136C_e}{1 - 3.44C_e}$$

$$a = -3.44 \quad b = -16.69$$

- **Freundlich Isotherm (Model 2) (Figure -3b)**

$$\frac{x}{m} = KC^{1/n}$$

$$\frac{x}{m} = 46.5C^{-0.66280}$$

$$K = 46.5$$

$$n = -1.508$$

- **BET Isotherm (Model 3) (Figure -3c)**

$$q_e = \frac{K_B \times C_e \times Q_0}{(C_s - C_e) \{1 + (K_B - 1) \left(\frac{C_e}{C_s}\right)\}}$$

$$q_e = \frac{1.99 \times 10^6 C_e}{(132300 - C_e) \{1 + (3.646 \times 10^{11} - 1) \left(\frac{C_e}{132300}\right)\}}$$

$$C_s = 132300$$

$$K_B = 3.646 \times 10^{11}$$

$$Q_0 = 5.485 \times 10^{-6}$$

- **Temkin Isotherm (Model 4) (Figure -3d)**

$$q_e = \frac{RT}{b_T} \times \ln(K_T C_e)$$

$$q_e = 72.8393 \times \ln(0.4979 C_e)$$

$$B_T = 72.8393$$

$$K_T = 0.4979$$

Table: 1 Adsorption Isotherms with R<sup>2</sup> values

Isotherms	R <sup>2</sup> value
Langmuir Isotherm	0.9857
Freundlich Isotherm	0.9961
BET Isotherm	0.9172
Temkin Isotherm	0.9316

Table 1 shows that the Freundlich isotherm is the most suitable isotherm for the experiment, since the R<sup>2</sup> value of the Freundlich isotherm is 0.9961 which is closer to linearity.

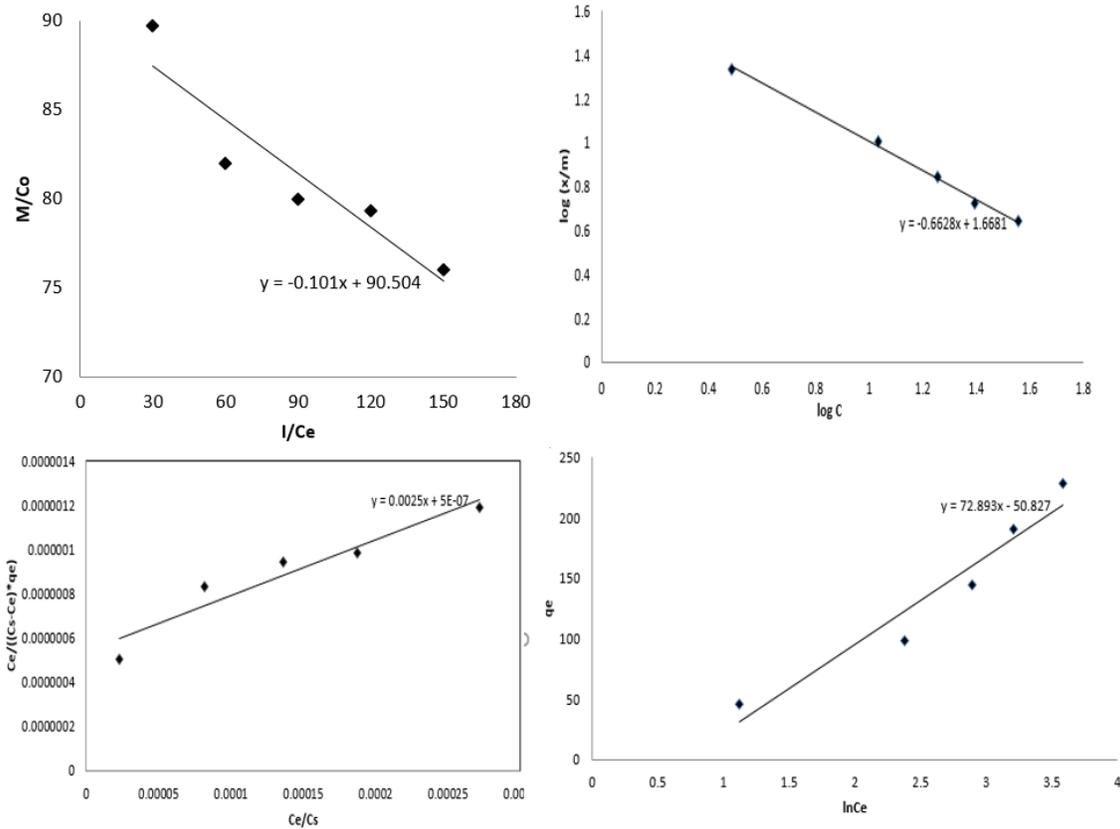


Fig. 3: (a) Langmuir Isotherm; (b) Freundlich Isotherm; (c) BET Isotherm; and (d) Temkin Isotherm

3.7 Adsorption Kinetics

- Pseudo first order kinetics (Figure -4a)

$$\frac{dq_t}{dt} = K_1(q_e - q_t)$$

$$\frac{dq_t}{dt} = 0.0619(118.713 - q_t)$$

$$K_1 = 0.0619 \text{ min}^{-1} \quad q_e = 118.73 \text{ mg/g}$$

- Pseudo second order kinetics (Figure -4b)

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$$

$$\frac{dq_t}{dt} = 0.01915(79.36 - q_t)^2$$

$$K_2 = 0.01915 \text{ g mg}^{-1} \text{ min}^{-1} \quad q_e = 79.36 \text{ mg/g}$$

Table 2 shows that the Pseudo second order is the most suitable kinetics for the experiment, since the R<sup>2</sup> value of the Pseudo second order is 0.9961 which is closer to linearity.

Table 2: Adsorptions Kinetics with R<sup>2</sup> value

Kinetics	R <sup>2</sup>
Pseudo first order	0.8616
Pseudo second order	0.9534

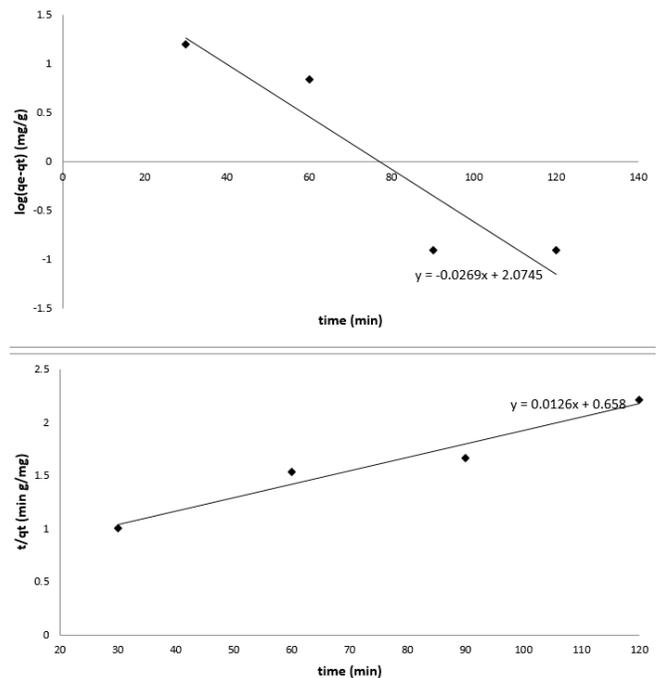


Fig. 4: (a) Pseudo first order and (b) Pseudo second order

The analysis of the adsorbent under the influence of different parameters was concluded as the adsorption isotherms and adsorption kinetics were studied on these parameters. Instrumental analysis was done for the adsorbent to study its characteristics. The studied showed that the adsorption takes place more at lower concentration, so the further studies were done on 30 ppm concentration. Using this concentration value, the size of the adsorbent particle was found. The fine particles have more adsorption, since the surface area increases as the size decreases. So this concluded that pan size is having more adsorption capacity. According to these concentration and size, a study was done on the contact time. It was found that after 90 min there was no adsorption occurring. So this is the optimum time for the adsorption process. By the above characteristics, a study was done based on temperature. The maximum adsorption was determined at 37°C.

A pH of 6.5 was found to be the optimum when a study was conducted on different pH. The adsorbent dosage of 3g per 30ml was found to be the optimum concentration for adsorption. The different isotherms were done, and the regression parameter showed that Freundlich isotherm has the best fit among tested equations used for adsorption models (34, 35). Furthermore, the studies showed that this adsorption follows the pseudo second order kinetics (Fig 3b).

#### 4 Conclusion

The adsorbent was identified as a good candidate for the removal of chromium. Different parameters such as size, temperature, contact time, concentration, pH and dosage were evaluated and the effective adsorption of the compounds. The adsorption was maximum at pan size, 37°C temperature, 30 mins - contact time, 30 ppm - concentration, 6 - pH and 3 g - dosage. The adsorption isotherms showed that the Freundlich Isotherm is a better adsorption model and the characteristic parameters were determined. The results of the kinetic models showed that the pseudo second order kinetics was established to be related with the experimental data. The biosorption process was endothermic and non-spontaneous. Results suggest that *Pinus palustris* seeds is an effective low-cost biosorbent with high biosorption capacity to remove Chromium from aqueous solutions.

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#### Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

#### Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing

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