CHAPTER-3

Biosorption of Cr (VI) onto powdered wood apple shell

3.1 Introduction

The use of heavy metals over the past few decades has been tremendously increased due to rapid industrialization in both developed and developing nations, resulting in increased flux of metallic substances in an aquatic environment. The heavy metal enters in tissues through the food chain and accumulates in the body of all living organisms. If the heavy metals are ingested over the permitted concentration, they can cause severe health disorders. Therefore, it is necessary to remove heavy metals from contaminated wastewater before discharge in to the aquatic environment. Normally water treatment is not practiced by the industries and as a consequence, many times heavy metals are found in aquatic environment well above the permissible limit [1]. Hexavalent Chromium Cr (VI) is one of the major pollutant and most dangerous heavy metal in industrial effluent water, because it is a strong oxidizing agent which irritates animal and plant tissues. Cr (VI) is teratogenic, carcinogenic and mutagenic for mammals [2-4]. Cr (VI) is commonly used in the preparation of a large variety of industrial products, such as pigment for the manufacture of paints, inks, rubber, leather, ceramics, fungicides, electroplating, cement, photographic industries producing large quantities of effluents containing toxic metals [5, 6]. Chromium is also found naturally in rocks, soil, plants, animals and volcanic dust [7]. The recommended limit of Cr (VI) in potable water is only 0.05 mg L$^{-1}$ [8]. But the industrial effluents contain much higher concentrations before discharging into the environment [9, 10].

To remove heavy metals from industrial wastewater various conventional methods are available which includes ion exchange, chemical oxidation-reduction, precipitation, reverse osmosis, solvent extraction, electro-dialysis, ultra-filtration, etc. [11]. However, some disadvantages of these methods, such as higher costs, sensitive operating conditions and production of secondary sludge [11], have reduced their popularization in industries.

The adsorption of heavy metals by activated charcoal is another powerful technology, but the high cost of activated charcoal has prevented its application in developing countries. Consequently, instead of activated charcoal, the low cost biomass, such as coconut shell, cotton seed hull, bagasse pitch, hazelnut shell, rice husk, wheat shell, walnut shell, etc are
being used recently for bioremediation of wastewater [11, 12, 13]. Biosorption provides alternative path to the traditional physico-chemical methods to remove heavy metals utilizing low cost biomass [14]. Biomass seems to be a useable option to remove heavy metals due to its natural chemical composition, high abundance, and economical, high efficiency of heavy metals removal from diluted solutions, regeneration of biosorbent and greater possibility of metal recovery [15].

In the present research work, the hexavalent chromium adsorption capacity of wood apple shell (*Limonia acidissima* L.) was studied. Wood apple is native and common fruit cultivated in Bangladesh, India, Pakistan, Sri Lanka, and Southeast Asia East to Java. The fruit pulp of wood apple is used in several culinary preparations and has great medicinal values. Wood apple shell carries the polar functional groups such as alcoholic, carboxylic and ether group which show that it is a lignocellulosic material [16].

The well-known adsorption kinetic, thermodynamic parameters and adsorption isotherm studies have been reported to interpret the adsorption behaviors at different temperature. In addition to the effect of temperature, effects of pH and metal concentration on percentage of biosorption have also been investigated.

### 3.2 Experimental

#### 3.2.1 Preparation and characterization of biosorbent

The wood apple fruits were collected from agricultural land of Pune district area and hard rind or shell was removed manually from fruit pulp and broken into small pieces. To remove dirt the shell was thoroughly washed with distilled water, dried in an oven at 333 K for 24 h, crushed and finally sieved through 80 to 100 mesh sizes. The average particle size of powdered wood apple shell (PWAS) was measured by sieving method. Porosity and bulk density were measured by NaCl tracer and gravimetric studies [17]. The point of zero charge (pH\(_{\text{pzc}}\)) is the pH at which electric charge on sorbent surface is zero, which was determined by batch equilibrium technique [18a]. Initial pH values (pH\(_i\)) of 25 mL of KNO\(_3\) solutions (0.1 M) were adjusted in the pH range of 2 to 8 using 0.01 M HCl or 0.01 M NaOH. Then to each sample 0.1 g of PWAS was added. Equilibrium was carried out by shaking sample flasks for greater than equilibrium contact time (4 hours) at 299 K. After equilibrium, the dispersions were filtered and the final pH of the solutions (pH\(_f\)) was determined. The point of zero charge was found from a plot of pH\(_f\) versus pH\(_i\) [18b]. The surface area of PWAS was measured by
methylene blue adsorption method as this material is known to be adsorbed as a monolayer on solid sorbents [19]. The PWAS was also characterized by SEM analysis. The Surface morphology of PWAS was examined by Scanning Electron Microscope (SEM; Jeol JST-6360A). Samples were dispersed onto carbon tabs (double-adhesive carbon coated tape) adhered to aluminum stubs. These sample stubs were coated with a thin layer (30 Å) of gold by employing Jeol JFC-1600 auto fine coater. Samples were subsequently examined by SEM and photographed under various magnifications with direct data capture of the images onto a computer. Fourier transform infrared spectra of PWAS and Cr (VI) adsorbed wood apple shell were obtained after drying the biosorbent mass at 343 K for 24 h. the spectra were recorded using a Fourier transform infrared spectroscope (SHIMADZU 8400S) by mixing finely powdered sample with potassium bromide (1:10).

The biosorbent characterization results are summarized in Table 3.1

Table 3.1 Physico-chemical characterization of the PWAS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (mm)</td>
<td>0.167</td>
</tr>
<tr>
<td>Bulk density (g L(^{-1}))</td>
<td>0.582</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>56.45</td>
</tr>
<tr>
<td>pHpzc</td>
<td>4.3</td>
</tr>
<tr>
<td>Surface area (m(^2) g(^{-1}))</td>
<td>13.34</td>
</tr>
</tbody>
</table>

3.2.2 Preparation of solutions

Stock solution of Cr (VI) was prepared (1000 mg L\(^{-1}\)) by dissolving the appropriate quantity of K\(_2\)Cr\(_2\)O\(_7\) (A. R. Grade) in distilled water. The experimental solutions were prepared by diluting the stock solution to the desired Cr (VI) concentrations. The chelating agent 1-5, diphenyl carbazide (CDH, New Delhi, India) were prepared by dissolving 250 mg in 50 ml A. R. Grade acetone.

3.2.3 Adsorption experiments

In pH studies 0.3 g of PWAS and 50 mL Cr (VI) solutions (10 mg L\(^{-1}\)) with a range of pH values from 1.0 to 8.0 were transferred into conical flask and shaken on a temperature controlled orbital shaker at 60 rpm for 120 min. The pH of solution was adjusted with 0.01 M
HCl or 0.01M NaOH solution using pH-meter. The chromium removal efficiency was determined as:

\[
\% \text{ Cr(VI) removal} = \left(\frac{C_o - C_f}{C_o}\right) \times 100
\]  

(3.1)

Where, \(C_o\) (mg L\(^{-1}\)) and \(C_f\) (mg L\(^{-1}\)) are initial and final concentrations of Cr (VI) in the liquid-phase respectively.

In the determination of adsorption isotherm at equilibrium, 0.3 g of PWAS and 50 ml of different concentrations (25 – 200 mg L\(^{-1}\)) of Cr (VI) solutions were shaken up to equilibrium time at the initial pH 1.8 and different temperatures (299–319 K). In the adsorption kinetic experiments, batch adsorption were carried out by shaking 0.3 g PWAS with 50 ml different concentrations (25 – 100 mg L\(^{-1}\)) of Cr (VI) solution at initial pH 1.8 and at the temperature 293 K for different contact times (20–160 min). The amount of Cr (VI) adsorbed at equilibrium, \(q_e\) (mg L\(^{-1}\)) and at time t (min), \(q_t\) (mg L\(^{-1}\)), was calculated by general equation:

\[
q = \frac{C_o - C_f}{M} \times V
\]  

(3.2)

Where \(V\) (L) is the volume of Cr (VI) solution, \(M\) (g) is the mass of dry powdered wood apple shell. All the mixtures after adsorption were filtered through Whatman 41 filter paper and the un-adsorbed Cr (VI) concentrations in the filtrate was estimated by diphenyl carbazide method [20] at 540 nm on UV–Visible spectrophotometer (systronic). All the batch experiments were carried out in triplicate and the mean values of three data sets are presented, to ensure accuracy, reproducibility and reliability. The equilibrium data were fitted to the isotherms models and were solved by using the linear regressions. The linear regressions were employed to obtain the optimum adsorption isotherms, kinetic and thermodynamic parameters by using Microsoft Excel applications.

3.3 Result and discussion
3.3.1 SEM analysis

Scanning electron microscopy is a direct appliance for characterization of the fundamental physical properties and the surface morphology of adsorbent. SEM of PWAS is shown in Fig. 3.1. It is clear that, SEM image of PWAS surface exhibited a rough structure
with an irregular and slightly porous surface which is probably a good platform for the adsorption of Cr (VI) ions.

**Fig. 3.1** SEM image of PWAS

**3.3.2 FTIR studies**

The functional groups on PWAS before and after adsorptions of Cr (VI) were determined by FTIR spectrometer. The spectra were measured within the range of 4000–500 cm\(^{-1}\) and shown in Figure 3.2. The Infrared peak positions of PWAS before and after adsorptions of Cr (VI) showed several intense bands (Table 3.2). The adsorption capacity of Cr (VI) is strongly influenced by type and number of functional groups on the surface of biosorbent (21). The absorption peaks in the region of 750 - 900 cm\(^{-1}\) can be assigned to aromatic –C-H stretching vibrations [21, 22]. The –C-O, -C-C, and –C-OH stretching vibrations can be attributed to absorption peaks in the region of the 1300 – 1000 cm\(^{-1}\) [21,22].

The absorption peaks in the region 1730-1390 cm\(^{-1}\) can be assigned to –C=O stretching vibrations of aldehydes, carboxylates and ketones [21]. The absorption peaks at 2939.61 and 2897.18 cm\(^{-1}\) confirms the presence of –C-H stretching vibrations [21, 23]. The peak at 3340.62 cm\(^{-1}\) can be assigned to the –OH and –NH functional groups [21, 24]. When PWAS was loaded with Cr (VI) ions, the shift in the characteristic peaks is observed (Table 3.2). So, –OH, –NH, and –C=O seems to participate in the Cr (VI) binding. These shifts in the IR frequencies support that –COOH, –NH and –OH is responsible for the biosorption of Cr (VI)
onto PWAS. The similar results were observed by other researchers as biosorption of Cu (II) onto chestnut shell [25] and biosorption of Cr (VI) from aqueous solution by the husk of Bengal gram [26].

![FTIR spectrum of powdered wood apple shell (a) before adsorption and (b) after adsorption](image)

**Fig. 3.2** FTIR spectrum of powdered wood apple shell (a) before adsorption and (b) after adsorption

**Table 3.2** IR frequencies before and after Cr (VI) adsorption onto PWAS

<table>
<thead>
<tr>
<th>IR Frequencies (cm⁻¹)</th>
<th>Before adsorption</th>
<th>After adsorption</th>
<th>IR Frequencies (cm⁻¹)</th>
<th>Before adsorption</th>
<th>After adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Before adsorption</strong></td>
<td></td>
<td></td>
<td><strong>After adsorption</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3340.62</td>
<td><strong>3319.60</strong></td>
<td>1371.43</td>
<td>1371.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2939.61</td>
<td><strong>2941.54</strong></td>
<td>1323.21</td>
<td>1323.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2897.18</td>
<td><strong>2889.46</strong></td>
<td>1246.06</td>
<td>1246.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2050.40</td>
<td>2050.40</td>
<td>1161.19</td>
<td>1161.19</td>
<td><strong>1165.04</strong></td>
<td></td>
</tr>
<tr>
<td>1734.06</td>
<td>1734.06</td>
<td>1116.82</td>
<td>1116.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1641.48</td>
<td><strong>1599.04</strong></td>
<td>1053.17</td>
<td></td>
<td><strong>1055.10</strong></td>
<td></td>
</tr>
<tr>
<td>1506.46</td>
<td>1506.46</td>
<td>898.86</td>
<td>898.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1462.09</td>
<td>1462.09</td>
<td>829.42</td>
<td>829.42</td>
<td><strong>831.35</strong></td>
<td></td>
</tr>
<tr>
<td>1427.37</td>
<td>1427.37</td>
<td>669.32</td>
<td>669.32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3. 3 Effect of pH

The pH of aqueous solution affects the adsorption of both cations and anions at the liquid-solid interface. The anion exchange capacity is strongly governed by the surface chemistry of the solid biosorbent and the pH of the solution. From the pH effect on adsorption of Cr (VI) onto the wood apple shell it is seen that the adsorption capacity is increased from 33.2 % to greater than 90 % with decrease in pH from neutral to more acidic (7 to 2) as shown in figure 3.3. The result shows that the biosorption of Cr (VI) is strongly pH dependent. It is totally dependent upon the surface properties of the PWAS and chromium specification in solution [27]. In aqueous solution Cr (VI) species are represented in various forms, such as H$_2$CrO$_4$, HCrO$_4^-$, CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ as a function of pH. The following equilibrium represents the effect of pH on Cr (VI) speciation [28].

$$\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^-\text{, }pK_a = 2.2$$

(3.3)

$$\text{H}_2\text{CrO}_4 \rightleftharpoons \text{HCrO}_4^- + \text{H}^+,\text{ }pK_a = 4.1$$

(3.4)

$$\text{HCrO}_4^- \rightleftharpoons \text{CrO}_4^{2-} + \text{H}^+,\text{ }pK_a = 5.9$$

(3.5)

Fig.3.3 Effect of pH on the biosorption of Cr (VI) ions (10 mg L$^{-1}$) onto PWAS
3.3.4 pH at zero point charge

pH at the point of zero charge \( (\text{pH}_{\text{pzc}}) \) on surface of PWAS was found to be 4.3 (Figure 3.4). This means that the net electric charge on sorbent surface was positive below the pH\(_{\text{pzc}}\) and negative above the pH\(_{\text{pzc}}\) [29]. This indicates that at pH less than point of zero charge, pH\(_{\text{pzc}}\) (4.3) the PWAS surface was positively charged and chromium is mainly present as HCrO\(_4^-\) at pH 1.8 and maximum removal of Cr (VI) was observed at equilibrium condition. Similar observation was reported for adsorption of Cr (VI) onto fly ashes and Puresorbe [30, 31]. Similar observations for the removal of chromium (VI) at optimum pH 2 have been reported for \textit{Rhizopus nigricans} [32], \textit{Bacillus} sp. [33] and \textit{Dunaliella} sp. [34]. The high sorption of Cr (VI) below the pH at zero point charge can be explained by species of chromium and the PWAS biosorbent surface. There is strong electrostatic attraction between HCrO\(_4^-\) species with protonated active site \([\text{Ar-OH}_2]^+\) of biosorbent surface in acidic condition as:

\[
[\text{Ar-OH}_2]^+ + \text{HCrO}_4^- \rightarrow \text{ArHCrO}_4 + \text{H}_2\text{O}, \text{pH} < 4.3
\]  \hspace{1cm} (3.6)

Where \([\text{Ar-OH}_2]^+\) is one of representative protonated active functional group on biosorbent surface. As the pH is increased above the zero point charge, there is reduction in electrostatic attraction between Cr (VI) species and biosorbent surface.

![Fig.3.4 Determination of pH at zero point charge of biosorbent PWAS](image)

74
3.3.5 Effect of contact time

The effect of contact time on sorption of Cr (VI) with PWAS was studied at 50 mg/L concentration at initial pH 1.8 and at 299 K. As the adsorption process proceeds, the adsorbate Cr (VI) reaches the saturation state and then it tends to desorbs back into the solution. Eventually, when the system reaches sorption equilibrium, no further net adsorption occurs and the rates of adsorption and desorption will be equal. The time at which adsorption equilibrium occurs was determined from the plot of removal efficiency (%) versus contact time (min). From the experimental data represented in Fig. 3.5, the process of sorption reaches the equilibrium state after approximately 160 min of contact. The reaction rate is rather fast at first and 80% of total sorption of Cr (VI) occurs in the first 30 min and thereafter it proceeds at a lower rate and finally no further significant adsorption is noted beyond 160 min. In industry, this time is very important for process optimization. Similar results have been reported [30-32].

![Fig. 3.5](image)

**Fig. 3.5** Effect of contact time at 50 mg/L Cr (VI) concentration, pH =1.8 and at 299 K onto PWAS

3.3.6 Effect of initial concentration of Cr (VI)

The sorption capacity of PWAS as a function of the initial concentrations of Cr (VI) have been studied at four different concentrations of 25, 50, 75 and 100 mg/L in batch experiments at previously optimized pH and contact time. Figure 3.5 shows that Cr (VI) adsorption reached equilibrium within 160 min for 50 mg/L initial Cr (VI) concentrations.
The equilibrium time observed is consistent with the fact that metal sorption is relatively fast and can reach equilibrium within 160 min. In addition, increase in initial Cr (VI) concentration from 25 to 100 mg/L increased Cr (VI) uptake from 4.05 to 15.0 mg/g. If the amount PWAS in the suspension is equal to 6 g L$^{-1}$, 80% of the initial Cr (VI) with a concentration of 10 mg/L is removed. Whereas, if the initial concentration is about 60 mg/L, the amount of Cr(VI) removed drops down to 46.66% (Fig. 3.6). Similar results have been reported by researcher [35].

**Fig. 3.6** Effect of initial concentration of Cr (VI) on % removal at pH=1.8, 6 g/L adsorbent dose

### 3.3. 7 Adsorption isotherms

The equilibrium adsorption isotherm shows that how the adsorbate molecule or ions are distributed between the solid phase and the liquid phase. To find out the suitable isotherm model, analysis of isotherm data by adapting to different isotherm models is an important step that can be used for design purpose. In the present research, the sorption equilibrium data of Cr (VI) on wood apple shell were analyzed in terms of Langmuir, Freundlich and Temkin isotherm model. Figure 3.7 shows the typical equilibrium adsorption of Cr (VI) on powdered wood apple shell at 299 K, 309 K and 319 K, the adsorption isotherm curves rises steeply at low concentrations and gradually approach to a plateau at higher concentrations. The pH of Cr (VI) solution before and after adsorption was maintained 1.8 and estimated using digital pH-meter. The pH value remained constant during the adsorption process.
The constants $q_m$ and $K_L$ at different temperature, were determined by plotting the $C_e/q_e$ versus $C_e$ as shown in Table 3.2. The monolayer adsorption capacity ($q_m$) (28.81 to 31.45 mg g$^{-1}$) increases with increase in temperature from 299 to 319 K, indicating that sorption is more favored at higher temperature. Further, increase in Langmuir constant $K_L$ with temperature confirms sorption process was endothermic in nature. The calculated $R_L$ values at different initial concentrations of Cr (VI) and temperatures are in the range 0.04 to 0.20 in all experimental systems shown in Figure 3.8, which confirms the favorable uptake process of chromium adsorption. Lower $R_L$ values at higher initial concentration of Cr (VI) and at higher temperature showed that the sorption was more favorable at higher temperature and at higher concentration of adsorbate. Table 3.3 summarizes the comparison of Cr (VI) monolayer adsorption capacities ($q_m$) by various agricultural biomasses. The PWAS presents higher adsorption capacity than 6 out of 13 different biosorbents, reflecting that utilization of PWAS in Cr (VI) removal from aqueous solutions shows promising future. The adsorption isotherms based on parameters values are compared with experimental data at 299, 309 and 319 K. Relatively higher $R^2$ values (>0.97) compared to the other models indicates that the sorption of Cr (VI) onto PWAS follows the Langmuir isotherm model.
Table 3.3 A comparison of sorption of Cr (VI) ions with other biosorbent

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>q_m (mg g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Husk of Bengal gram</td>
<td>91.64</td>
<td>[26]</td>
</tr>
<tr>
<td>Iron(III) Coordinated Amino-Functionalized Poly (glycidyl-methacrylate)-Grafted Cellulose</td>
<td>72.05</td>
<td>[36]</td>
</tr>
<tr>
<td>Cellulose Modified with D-Glucose</td>
<td>54.59</td>
<td>[37]</td>
</tr>
<tr>
<td>Wool</td>
<td>41.15</td>
<td>[38]</td>
</tr>
<tr>
<td>Olive cake</td>
<td>33.44</td>
<td>[38]</td>
</tr>
<tr>
<td>Pine needles</td>
<td>21.50</td>
<td>[38]</td>
</tr>
<tr>
<td>Saw dust</td>
<td>20.02</td>
<td>[39]</td>
</tr>
<tr>
<td>Beech saw dust</td>
<td>16.10</td>
<td>[40]</td>
</tr>
<tr>
<td>Palm pressed fibers</td>
<td>14.00</td>
<td>[41]</td>
</tr>
<tr>
<td>Wood apple shell</td>
<td>13.74</td>
<td>[42]</td>
</tr>
<tr>
<td>Almond shell</td>
<td>10.65</td>
<td>[38]</td>
</tr>
<tr>
<td>Sunflower stem</td>
<td>4.90</td>
<td>[27]</td>
</tr>
<tr>
<td>Powdered wood apple shell (PWAS)</td>
<td>28.81</td>
<td>Present study</td>
</tr>
</tbody>
</table>

The plot of log q_e versus log C_e enables the determination of isotherm constants K_F and 1/n. The experimental isotherms parameters along with regression coefficient are listed in Table 3.4. The 1/n values reported in Table 3.4 for PWAS were observed in the range of 0.207 to 0.298; indicating only one mechanism has taken place and the surface of adsorbent becoming more heterogeneous as its value gets closer to zero. Increase in Freundlich constant K_F with temperature shows the biosorption of Cr (VI) onto PWAS is more favored at higher temperature [7].
The plot of $q_e$ versus $\ln C_e$ allows the determination of Temkin isotherm constants $B$ (J mol$^{-1}$) and $A$ (L mg$^{-1}$) where $B$ represent the heat of adsorption, $T$ is the absolute temperature (K), $R$ is the universal gas constant (J K$^{-1}$ mol$^{-1}$), $1/K_T$ indicates the adsorption potential of the adsorbent and $A$ (L mg$^{-1}$) is the equilibrium binding constant corresponding to the maximum binding energy. Temkin isotherm constants at different temperatures from Table 3.4 show that there is a linear decrease in the standard enthalpy of adsorption with temperature. The Temkin isotherm represents the poorest fit of experimental data than the other two isotherms ($R^2<0.945$).

**Table 3.4** Isotherm parameters for Cr (VI) adsorption at different temperatures  

($R^2$ is the regression coefficient)

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg g$^{-1}$)</td>
<td>$K_L$ (L mg$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>-----------</td>
<td>----------</td>
<td>------------</td>
<td>--------</td>
</tr>
<tr>
<td>299</td>
<td>28.81</td>
<td>0.086</td>
<td>0.976</td>
</tr>
<tr>
<td>309</td>
<td>29.58</td>
<td>0.215</td>
<td>0.970</td>
</tr>
<tr>
<td>319</td>
<td>31.45</td>
<td>0.400</td>
<td>0.979</td>
</tr>
</tbody>
</table>
3.3.8 Adsorption kinetics

Kinetic investigation was conducted further to reveal the adsorption mechanism of Cr (VI) onto PWAS. The pseudo-first order, pseudo-second order kinetic models and intra-particle diffusion model have been tested for experimental data at different contact time. The effects of contact time on the uptake of Cr (VI) onto PWAS are shown in figure 3.9. The figure shows that the adsorption process can be divided into two steps, the rapid 80 % uptake of Cr (VI) was observed within first 30 minutes, and slow uptake of Cr (VI) observed until equilibrium was reached.

The constants of Pseudo-first order model at 25, 50, 75 and 100 mg/L of Cr (VI) concentrations were determined experimentally by plotting the log (qe - qt) versus t (Fig. 3.9a and 3.9b) and listed in Table 3.5. The calculated values (qe, cal) differ from experimental (qe, exp) indicating that the adsorption process does not follow the pseudo-first order kinetic.

The constants qe, k2 and ho at 25, 50, 75 and 100 mg/L of Cr (VI) were also evaluated by plotting t/qt versus t (Fig. 3.9c) from the Pseudo-second order model. The values of qe, k2, ho and R² are listed in Table 3.5. The plot of t/qt versus t gives an excellent straight line for all the experimental concentrations of Cr (VI) and the values of R² are very close to 1 (Table
3.4), confirming the applicability of pseudo-second order model. In addition, there is only little difference between the experimental equilibrium uptake, $q_e$, exp and calculated equilibrium uptake, $q_e$, cal (Table 3.5), reinforcing the applicability of pseudo-second order kinetic. It can also be seen from Table 3.5 that with increase in initial Cr (VI) concentration, the initial sorption rate ($h_0$) also increases, while the rate constant ($k_2$) of sorption is fairly constant confirms pseudo-second order chemisorptions. Similar results for sorption kinetics have also been reported elsewhere [29, 36, 43].

**Fig. 3.9a** Adsorption kinetics (Pseudo-first order model) at 293 K for Cr (VI) ion concentrations 25 and 75 mg/L

**Fig. 3.9b** Adsorption kinetics: Pseudo-first order model at 293 K for Cr (VI) ion concentrations 50 and 100 mg/L

**Fig. 3.9c** Adsorption kinetics: Pseudo-second order model at 293 K for different Cr (VI) ion concentrations
Table 3.5 Kinetic parameters for Cr (VI) adsorption onto PWAS at different concentrations
(R² is the regression coefficient)

<table>
<thead>
<tr>
<th>Initial Con. C₀ (mg L⁻¹)</th>
<th>qₑ,exp (mg g⁻¹)</th>
<th>Pseudo-first order</th>
<th></th>
<th>Pseudo-second order</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>qₑ,cal (mg g⁻¹)</td>
<td>k₁ (min⁻¹)</td>
<td>R²</td>
<td>k₂ (g mg⁻¹ min⁻¹)</td>
</tr>
<tr>
<td>25</td>
<td>4.05</td>
<td>2.505</td>
<td>0.0257</td>
<td>0.976</td>
<td>4.47</td>
</tr>
<tr>
<td>50</td>
<td>8.26</td>
<td>7.518</td>
<td>0.0331</td>
<td>0.877</td>
<td>8.992</td>
</tr>
<tr>
<td>75</td>
<td>9.90</td>
<td>2.755</td>
<td>0.0101</td>
<td>0.993</td>
<td>10.23</td>
</tr>
<tr>
<td>100</td>
<td>14.80</td>
<td>7.560</td>
<td>0.0230</td>
<td>0.911</td>
<td>15.15</td>
</tr>
</tbody>
</table>

The constant values of K_d and I, at 25, 50, 75 and 100 mg/L of Cr (VI) were also evaluated from the plot of q_t versus t¹/² and are listed in Table 3.6. According to well known intra-particle diffusion model, if the plot of q_t versus t¹/² gives a straight line, then the adsorption process is controlled by intra-particle diffusion, while, if the data exhibits multi-linear plots, then two or more steps influence the adsorption process [44]. In the present study, the plots presents linearity not passing through origin (Fig. 3.10), indicating biosorption was totally controlled by intra-particle diffusion. The values of intra-particle diffusion rate constant, K_d and intercept, I linearly increases with increase in concentration of Cr (VI), indicating that with increase in concentration, increases the diffusion rate and thickness of solid-liquid interface. This indicates that intra-particle diffusion mechanism was involved in the sorption of Cr (VI) onto PWAS and the deviation of straight lines from the origin indicates that the intra-particle diffusion is not the sole rate-controlling mechanism [45].
3.3.9 Adsorption thermodynamics

The values of equilibrium constant, K were determined by the equation as:

\[ K = \frac{C_s}{C_e} \]

C_s and C_e are equilibrium concentrations of adsorbate onto adsorbent surface and in aqueous solution, respectively. The values of \( \Delta G^\circ \) for the sorption of Cr (VI) onto PWAS were estimated from the van’t Hoff’s equation at different studied temperatures and the values of \( \Delta H^\circ \) and \( \Delta S^\circ \) were estimated from slope and intercept of the plot \( \Delta G^\circ \) versus T shown in Figure 3.11. The calculated thermodynamic parameters for the sorption of Cr (VI) onto

---

**Fig. 3.10** Adsorption mechanism: intra-particle diffusion model at 293 K

**Table 3.6** Intra-particle diffusion parameters for Cr (VI) adsorption onto PWAS at different concentrations at 293 K (R^2 is the regression coefficient)

<table>
<thead>
<tr>
<th>Initial Con., ( C_o ) (mg L(^-1))</th>
<th>( k_d ) (mg g(^{-1}) min(^{-1/2}))</th>
<th>I (mg g(^{-1}))</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.1901</td>
<td>1.85</td>
<td>0.975</td>
</tr>
<tr>
<td>50</td>
<td>0.3040</td>
<td>4.62</td>
<td>0.975</td>
</tr>
<tr>
<td>75</td>
<td>0.2577</td>
<td>6.42</td>
<td>0.973</td>
</tr>
<tr>
<td>100</td>
<td>0.5231</td>
<td>8.61</td>
<td>0.983</td>
</tr>
</tbody>
</table>
PWAS are listed in Table 3.7. The negative values of $\Delta G^\circ$ (-3.12, -4.13, and -5.58 kJ mol$^{-1}$) increased with temperature at 299, 309, and 313 K, respectively, indicating the feasibility and spontaneity of the adsorption process. The higher negative value of standard free energy change was found for the sorption system with higher temperature, indicating a Cr (VI) sorption was more energetically favorable at higher temperature. The values of the standard enthalpy and the entropy changes were determined and found to be 33.79 kJ mol$^{-1}$ and 123.20 J mol$^{-1}$ K$^{-1}$ ($R^2$=0.989), respectively. The positive value of $\Delta H^\circ$ further confirms the endothermic nature of the adsorption process while the positive $\Delta S^\circ$ value suggest the increase in concentration of Cr (VI) at solid–liquid interface, indicating thereby the increase in the adsorption of Cr (VI) onto the PWAS. It also confirms the increase in randomness during sorption at the solid–liquid interface [29].

![Figure 3.11 Adsorption thermodynamic of Cr (VI) onto PWAS](image)
Table 3.7 Thermodynamic parameters for the adsorption of Cr (VI) onto PWAS at different temperatures ($R^2$ is the regression coefficient)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>K (kJ mol$^{-1}$)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (J mol$^{-1}$K$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>299</td>
<td>3.504</td>
<td>-3.12</td>
<td>33.79</td>
<td>123.20</td>
<td>0.989</td>
</tr>
<tr>
<td>309</td>
<td>4.747</td>
<td>-4.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>319</td>
<td>7.695</td>
<td>-5.58</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3.12 Determination of standard equilibrium temperature ($T^\circ$) for biosorption of Cr (VI) onto PWAS

The zero standard free energy temperature ($T^\circ$) is the temperature at which standard free energy is zero ($\Delta G^\circ = 0$) [46]. Value of $T^\circ$ for the present sorption system is accurately and precisely obtained from plot of absolute temperature, T versus $\Delta G^\circ$ as shown in Figure 3.12. The intercept on y-axis gives the value of zero standard free energy temperature ($T^\circ$) equals to 274.6 K. This indicates the sorption of Cr (VI) onto PWAS at standard conditions
was spontaneous, feasible at temperatures greater than 274.6 K and non-feasible at temperatures less than 274.6 K up to absolute zero temperature [46].

3.4 Conclusions

1. This study investigated the removal of hexavalent chromium by PWAS from aqueous solution.
2. The removal efficiency of Cr (VI) is seen to increase with decrease in pH and increases with increase in temperature.
3. The pH at point of zero charge on surface of PWAS was found to be 4.3.
4. The sorption process followed the Langmuir isotherm model slightly better than the Freundlich and Temkin isotherm.
5. The Langmuir monolayer adsorption capacities of Cr (VI) on PWAS were 28.81, 29.58 and 31.45 mg g$^{-1}$ at 299, 309 and 319 K, respectively.
6. The adsorption dynamics analysis indicates that the pseudo-second order equation fitted very well to the sorption of Cr (VI) on PWAS ($R^2 > 0.99$).
7. Kinetic study reveals that intra-particle diffusion mechanism was involved in the sorption of Cr (VI) onto PWAS and the deviation of straight lines from the origin indicates that the intra-particle diffusion is not the sole rate-controlling mechanism.
8. Thermodynamic analysis reveals that the removal of Cr (VI) from aqueous solution by PWAS was spontaneous, feasible and endothermic process at all temperatures greater than standard equilibrium temperature ($T^0 = 274.6$ K).
9. The investigations indicate that PWAS is a promising adsorbent for the removal of Cr (VI) from aqueous solutions.
References:

24. V.J.P. Vilar, C.M.S. Botelho, J.P.S. Pinheiro, R.F. Domingos, R.A.R. Boaventura, *J.