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Removal of Chromium (VI) from Tannery Effluent Using Bio-Char of *Phoenix reclinata* Seeds

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Abstract

The potential of the Senegal date palm (*Phoenix reclinata*) seed bio-char to remove chromium (VI) ions from aqueous solutions by adsorption was investigated. Adsorption experiments were performed on the tannery effluent and standard aqueous solutions of chromium (VI) for varying adsorbent doses, contact times, pH, temperatures, and interfering anionic ions by batch mode. *Phoenix reclinata* seeds (PRS) bio-char was used in the investigation and the residual chromium (VI) was determined using the atomic absorption spectrophotometer (AAS). Results showed that the bio-char removed up to 86% of chromium (VI) ions in the effluent at pH 2. The highest percentage adsorption registered was 97% in an aqueous solution of chromium (VI) at pH 1 and this dropped to less than 10% at pH greater than 2. A general increase in adsorption with the increase in temperature was observed but reduced when the temperature was raised beyond 60°C. The presence of interfering anions caused a reduction in the adsorption of chromium (VI) ions. The adsorption process fitted both Langmuir and Freundlich adsorption models and the maximum adsorption capacity, Q_o, was 0.6593 mg/g. Thus, PRS bio-char can therefore be used by industries and institutions like secondary schools to treat effluents that contain chromium (VI).

Keywords

Phoenix reclinata, Chromium (VI), Tannery Effluent, Adsorption

1. Introduction

Chromium is one of the top sixteen most toxic pollutants and because of its carcinogenic and teratogenic characteristics, it has become a serious health concern

[1]. There are two stable oxidation states of chromium, that is, chromium (III) and chromium (VI). Whereas chromium (III) is essential in human nutrition (especially in glucose metabolism), most of the chromium (VI) compounds are toxic and can cause lung cancer [2]. There are many industries in Uganda that use chromium compounds as raw materials and then release the wastes into the environment. Among such industries include leather tanning, textiles, cement mining, electroplating, photography, paint manufacturing and fertilizer production [3]. There is a swift growth of such industries in Uganda due to the increasing demand for their finished products. Most of the industries do not have adequate treatment facilities for wastes and therefore, channel untreated or partially treated effluents into nearby water bodies [4].

Tannery effluent is of great concern in waste water management since it is laden with heavy metals, mainly chromium in form of chromium (VI) and chromium (III) [5]. The major source of the chromium in tannery effluent is the chromium sulphate (chrome) used as the tanning agent [4]. In Uganda, many if not all, small-scale tanning industries in urban and peri-urban areas cannot afford the expensive conventional methods of waste water treatment such as precipitation and ion exchange [6]. Those that use such methods cannot completely remove the toxic heavy metals from the effluent. Further to note is that most conventional methods used have inadequate efficiencies at low metal concentrations, particularly in the range of 1 - 100 mg/l [7]. The end result is that industries channel untreated or partially treated effluents with chromium and other heavy metals into the neighbouring water bodies or deposit precipitated chromium into landfills from where it leaches into groundwater in rainy seasons. It becomes necessary therefore, to find an environmentally friendly and inexpensive method of removing toxic heavy metals like chromium from tannery effluent before it is released to the environment.

The use of biological materials to adsorb metal ions is at its infancy but it is a good alternative measure since it is inexpensive and can efficiently remove metal ions from solutions with concentrations as low as 1 mg/l [7]. This study, therefore, investigated the potential of *Phoenix reclinata* seeds (PRS) bio-char to remove chromium (VI) from tannery effluent and standard aqueous solutions at different conditions.

2. Materials and Methods

2.1. Collection and Preparation of Materials

The adsorbates were: 1) the tannery effluent obtained from a tannery at Kijjabwemi, Masaka Municipality in Masaka District, Uganda in January 2018, at the point where the waste water enters Namajuzi swamp. The effluent was analysed at the Government Analytical Laboratories at Wandegeya and 2) the standard aqueous solution of chromium (VI), which was prepared by dissolving analytical grade potassium dichromate (0.283 g) in a litre of double distilled water to form a stock solution of 100 mg/l chromium (VI) ions. This stock solution was diluted appro-

priately to provide solutions of different concentrations as used in the study [8].

Ripe fruits of *Phoenix reclinata* were collected by hand picking from the palm trees in Lweera wetland, Kalungu District, Uganda and sealed in a sample bag then transported to the Chemistry laboratory at Mbarara University of Science and Technology at ordinary conditions for further preparations. The seeds were dried under the sun for two weeks, and the fruit coat was removed. The bio-char was obtained by roasting the dry seeds in an oven at 220˚C until they were black and easy to grind. An electric blender (model LBC15) was used to grind the seeds into powder, sieved using a plastic mesh (710 μm) [8], to obtain the particle size of the PRS bio-char for the study.

2.2. Parameters of the Effluent

The pH, biological oxygen demand (BOD), colour and chemical oxygen demand (COD) of the effluent were determined as per American Public Health Association (APHA) [9]. The concentrations of the heavy metals (chromium, lead, nickel, zinc copper and cadmium) in the effluent were determined by first diluting the effluent (10 ml) with double distilled water to a litre. Then three samples of the diluted effluent (5 ml) were used to determine the total concentration of each of the heavy metals by flame atomic absorption spectrophotometer (AAS) (model Agilent 200 series) at their respective wavelengths [10]. The concentration of chromium (VI) in the effluent was determined by the standard calorimetric method using 1,5-diphenycarbazide in an acid medium [9]. The concentration of chloride, sulphate and nitrate ions were determined by Volhard's [11], lead nitrate [12] and ferrous ions [13] titration methods respectively.

2.3. Batch Adsorption

Adsorption studies were conducted in triplicate by using the batch technique on both the tannery effluent and standard aqueous solution of 5.0 g/l potassium dichromate so as to establish the adsorption of chromium (VI) ions onto the PRS bio-char adsorbent [14]. The adsorption factors studied on the tannery effluent were varying; adsorbent dosage, contact time and pH. Other additional factors of varying temperature, chromium (VI) concentration and salinity were also studied when the standard aqueous chromium (VI) solution was used.

2.3.1. Adsorption of Chromium (VI) from the Effluent

To investigate the effect of adsorbent dosage, all other factors were kept constant and the amount of PRS bio-char used was varied. Briefly, 0.5 g PRS bio-char was added to each of the three 250 ml conical flasks containing 100 ml effluent at 25˚C. The flasks were corked and placed on an end-to-end shaker agitated for one hour at 250 rpm. The mixture was then filtered using a Whatmann 42 filter paper. The filtrates obtained were filled into three different sample bottles and the residual chromium in each was determined using AAS. The total chromium remaining in the effluent after adsorption was recorded as the average residual chromium (VI). The difference between the chromium concentration before (C_o) and after treat-

ment with the bio-char (C_e) was determined as the amount of chromium (VI) adsorbed by the bio-char. Percentage adsorption (A_{eq}) and adsorption capacity (Q_e) at equilibrium were determined using Equations (1) and (2) respectively [15].

$$A_{eq} = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

$$Q_e = \frac{V(C_o - C_e)}{W} \tag{2}$$

V is the volume of solution and W is the amount or mass of the adsorbent.

The procedure was repeated using different masses (0.8, 1.0, 1.5, 2.0 and 3.0) g of the bio-char.

The effect of varying contact time (10, 20, 40, 60, 80, 100 and 120) minutes on the adsorption of chromium (VI) from the effluent was investigated at 25°C [2], 2.0 g adsorbent dosage, and 100 ml effluent was used. The difference between the chromium concentration in the effluent before and after treating the mixture with bio-char was determined to give the amount of chromium (VI) adsorbed, the A_{eq} and Q_e [15].

The same experiments above were repeated using another sample of the same effluent but adjusting its pH to 2 with dilute sulphuric acid (0.1 M). In both cases, the adsorption percentage and adsorption capacity were determined [15].

2.3.2. Adsorption of Chromium (VI) from Aqueous Potassium Dichromate Solution

To ascertain the efficiency of PRS bio-char in adsorption of chromium (VI) from a medium, a standard aqueous solution of chromium (VI) of 5.0 mg/l was prepared. The effect of various parameters on the adsorption of chromium (VI) from the standard solution was studied by keeping all other factors constant and varying the studied factor of adsorbent concentration, contact time, temperature, pH, chromium (VI) concentration and salinity. While studying other factors, the pH was fixed at 2 since most studies have showed that it is the optimum pH for the adsorption of chromium (VI) on the binding sites of natural adsorbents at 25°C [2] [8] [16].

The effect of factors on the adsorption of chromium (VI) from 100 ml of the standard aqueous chromium (VI) solution were varied as follows: adsorbent dosage (0.5, 0.8, 1.0, 1.5, 2.0 and 3.0) g, contact time (10, 20, 40, 60, 80, 100 and 120) minutes, chromium (VI) ion concentration (5, 10, 15 and 20) mg/l, temperature (25°C, 30°C, 40°C, 50°C, 60°C, and 70°C), pH (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10), and salinity for nitrate and chloride ions (0, 5.0, 10 and 20) mg/l. Where adsorbent dose was not the factor under study, 2.0 g of PRS bio-char was used. This is because it was the optimum adsorption mass established from this study in one hour contact time. Sulphuric acid (0.1 M) and sodium hydroxide (0.1 M) was used to adjust the pH of the standard aqueous solutions to the required value. In all treatments, the average residual chromium (VI) was calculated; hence A_{eq} and Q_e were determined [2] [8] [15].

3. Results and Discussion

3.1. Parameters of the Effluent

The average values of the parameters determined in the effluent are as shown in Table 1.

The effluent studied did not fully meet the national standards for industrial effluents disposal set by the Uganda National Environment Management Authority (NEMA) [17]. The parameters that did not meet the set standards were pH, Cr, Pb, BOD, and COD, Table 1. The pH of the effluent was found to be 9, indicating that the effluent is slightly alkaline. The effluent had much higher concentrations of both total chromium (12.3 ± 0.006 mg/l) and chromium (VI) (5.17 ± 0.05) mg/l than the recommended discharge limits, 1.0 and 0.05 mg/l, for industrial effluents [17] respectively. This shows that the effluent from the tannery causes accumulation of toxic chromium (VI) in the environment. Thus, the people who obtain water from Nabajjuzi swamp for use are likely to be exposed to chromium poisoning which may cause health hazards like lung cancer and abnormal formation of embryos [1]. The high values of BOD (536 ± 4.5) mg/l and COD (772 ± 5.0) mg/l in the effluent indicated a high demand for oxygen by the microorganisms for the oxidation of chemical substances in the effluent respectively. This leads to depletion of oxygen in the water of Nabajjuzi swamp into which the effluent is discharged and this eventually leads to suffocation of aquatic living organisms [18]. The concentration of lead (0.66 ± 0.01 mg/l) was over six times above the limit Table 1 [17]. The effluent therefore introduces to the environment much lead which is known to be toxic to humans and is a priority pollutant observed in municipalities [19]. The concentration of nitrate (59.7 ± 1.2 mg/l) was higher than the recommended limit of 20 mg/l,

Table 1. Parameters of effluent from Novelty Tannery Factory at Kijjabwemi, Masaka (Units where applicable is (mg/l)).

Parameter	Quantity	Permissible limits [17]
pH	9.0	6 - 8.0
Colour (PtCo units)	492.0 ± 4.5	300.0
BOD	536.0 ± 4.5	50.0
COD	772.0 ± 5.0	100.0
Cl^-	245.0 ± 3.0	500.0
NO_3^-	59.7 ± 1.2	20.0
SO_4^{2-}	101.30 ± 1.4	500.0
Cr (total)	12.3 ± 0.01	1.0
Cr (VI)	5.17 ± 0.05	0.05
Pb	0.66 ± 0.01	0.1
Ni	0.29 ± 0.01	1.0
Zn	0.50 ± 0.01	5.0
Cu	0.17 ± 0.003	1.0
Cd	0.07 ± 0,002	0.10

which could eventually lead to eutrophication that depletes the water of oxygen upon dying and decomposition of organic matter, causing the death of other aerobic organisms [18].

3.2. Effect of Adsorbent Dosage

There was a general increase in adsorption percentage with increase in adsorbent dose for both standard aqueous chromium (VI) solution and the effluent at pH 2, **Figure 1** and **Figure 2** respectively. This was attributed to the increased probability of the chromium (VI) ions getting into contact with the available active sites of the bio-char which increases with increase in the amount of adsorbent [2].

However, the adsorption capacity decreased with increase in adsorbent dose for the standard aqueous chromium (VI) solution as in **Figure 1**. This is because adsorption capacity is inversely proportional to adsorbent dosage level [8]. Increase in the amount of adsorbent, increases the available active sites for the uptake of chromium (VI) ions, but, if the concentration of its ions remains constant, the maximum holding capacity of a given active site may not be reached since many active sites are available to take up the few chromium (VI)
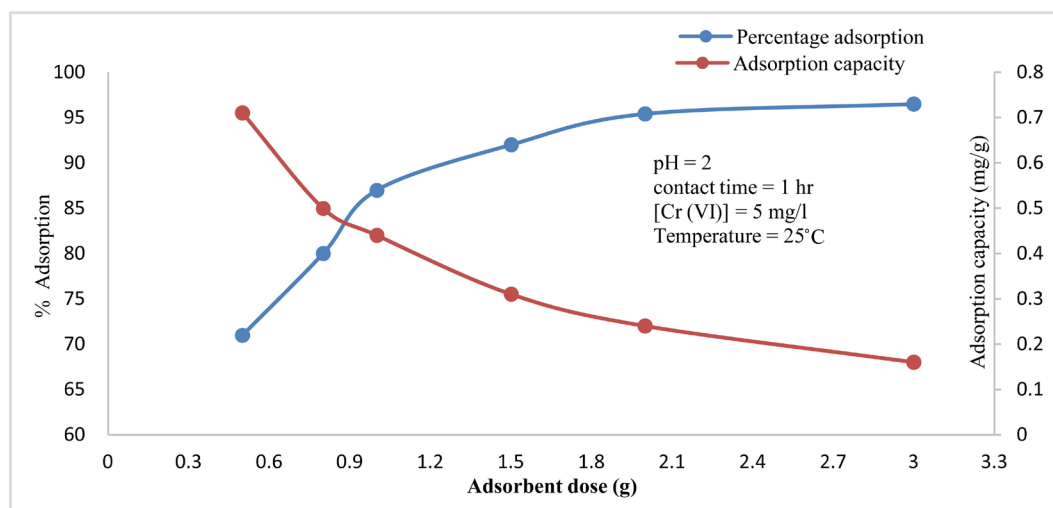

Figure 1. Effect of adsorbent dosage on percentage adsorption and adsorption capacity of chromium (VI) from the standard aqueous chromium (VI) solution.
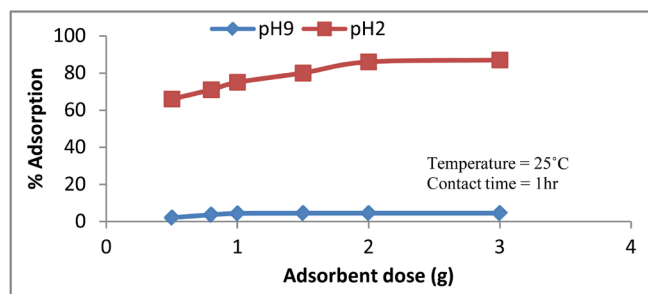

Figure 2. Effect of adsorbent dosage on percentage adsorption of chromium (VI) from the effluent at pH 9 and 2.

ions in that solution,leading to a decrease in the holding capacity (adsorption capacity) as observed.

At pH 9, the highest chromium (VI) adsorption percentage from the tannery effluent was 4.5% and this was attributed to the alkaline nature of the effluent. In alkaline systems the protonation of the active sites decreases, lowering the magnitude of the positive charge on the adsorbent sites [8], thus the attraction of the anionic chromium (VI) ions reduces. When the pH of the effluent was adjusted to 2, adsorption percentage was raised to 87%. The high adsorption percentage at pH 2 agrees with the work of [2] [8], who found out that adsorbents of plant origin have an optimum working pH of 2. This behaviour was attributed to the fact that in strongly acidic solutions, the functional groups on the adsorbent surface become positively charged due to protonation by many hydrogen ions in the acidic solution which enables the high attraction of chromium (VI) ions that exist at pH 2 predominantly as $HCrO_4^-$ [2]. The adsorption percentage from the effluent (87%) was less than that for the standard aqueous chromium (VI) solution (95.7%) under the same conditions. This is because the effluent contained anionic species like Cl^-, NO_3^- and SO_4^{2-} which may have interfered or competed with the chromium (VI) ions for adsorption surfaces onto the same positively charged active sites on the PRS bio-char particles.

3.3. Effect of Contact Time

The trend observed for the adsorption percentage of chromium (VI) from the standard aqueous solution and the effluent at pH 2 and pH 9 is illustrated in **Figure 3**. The adsorption percentage of chromium (VI) generally increased with increase in contact time. At pH 2, the increase in adsorption percentage was slightly more for standard aqueous solution than for the effluent. The highest adsorption percentage was 96.1% for the standard aqueous chromium (VI) solution and the lowest adsorption observed was 4.6% for the effluent. The increase in percentage removal of chromium (VI) at pH 2 was attributed to increased
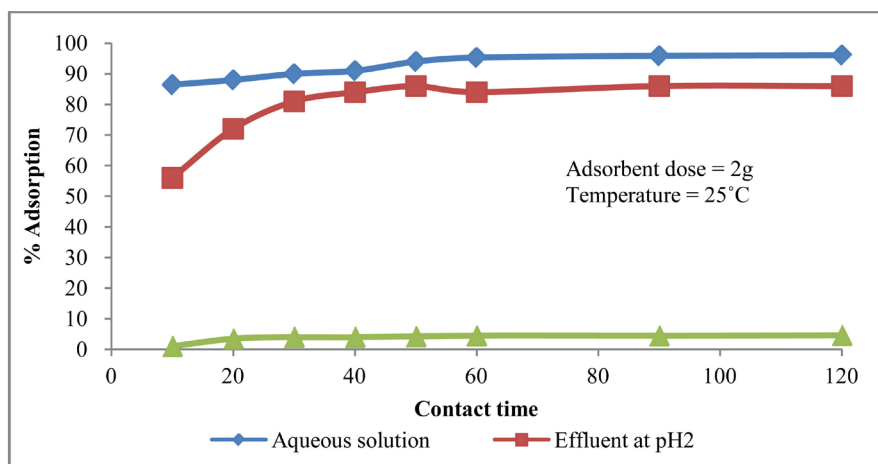

Figure 3. Effect of contact time on percentage adsorption of chromium (VI) from the effluent and standard aqueous chromium (VI) solution by PRS biochar at pH 2 and pH 9.

contact time allowed for the interaction of the chromium (VI) ions with the active sites on the bio-char. The initial rapid increase in adsorption percentage up to 30 minutes was due to the availability of many free active sites on the adsorbent surface. The gradual increase in adsorption after one hour was due to the reduced probability of the incoming $HCrO_4^-$ containing chromium (VI) ions to find free active sites and also due to the electrostatic repulsion between the incoming ions by the already adsorbed ions [8]. The low percentage removal of chromium (VI) from the tannery effluent at pH 9 was due to its alkaline nature which hinders adsorption to occur.

Adsorption capacity of the bio-char for both the standard aqueous chromium (VI) solution and the effluent at pH 2 increased with increase in contact time as in **Figure 4**. This was due to the longer time allowed for the bio-char to interact with the chromium (VI) ions leading to greater amount of ions to be adsorbed per unit mass of the bio-char, hence higher adsorption capacity [8].

3.4. Effect of pH

At low pH values, the adsorption of chromium (VI) by PRS bio-char is extremely higher than that at high pH values as shown in **Figure 5** from aqueous solution.

The highest adsorption percentage (97%) was at pH 1, and an increase in pH beyond 2 resulted into a rapid decrease in both adsorption percentage and adsorption capacity. This may be attributed to the fact that at pH 2 and below, the dominant species in the solution is hydrogen chromate ions ($HCrO_4^-$) and at such low pH, the concentration of protons in the solution is high [2], which causes the active sites of the adsorbent (PRS bio-char) to become positively charged due to protonation of the functional groups which may be amines and carboxyl in nature [8]. This promotes the electrostatic attraction for the $HCrO_4^-$ ions since they are negatively charged. The protonation of the active sites decreases as the pH increases and thus, the attraction of the anionic chromium (VI) ions decreases due to reduction in the magnitude of the positive charge on
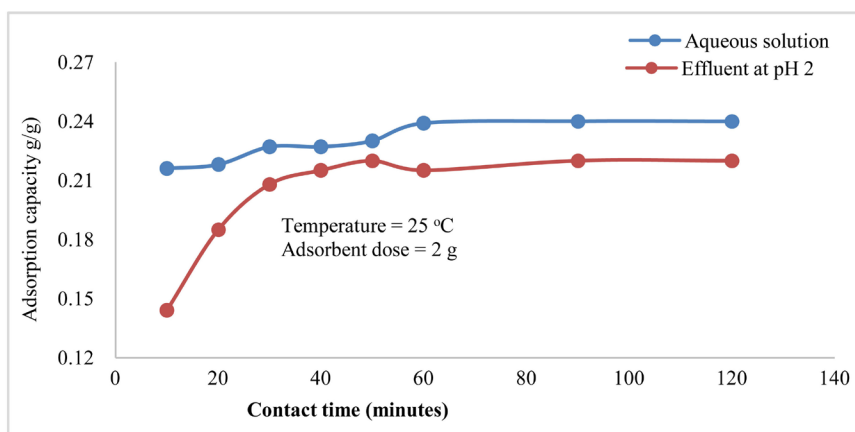

Figure 4. Effect of contact time on chromium (VI) adsorption capacity by PRS bio-char from the effluent at pH 2 and the standard aqueous chromium (VI) solution.

the adsorbent. These findings agree with the results reported in [2] [8] [16], which found out that the suitable pH for the adsorption of chromium (VI) species by plant materials is 2 and below.

3.5. Effect of Temperature

The percentage adsorption and adsorption capacity of chromium (VI) from the standard aqueous solution increased with temperature up to 60°C, beyond which it decreased as in **Figure 6**. This is because increase in temperature provides the necessary energy required for the endothermic adsorption process of the ions during migration onto the active sites of the PRS bio-char [20]. The increase in temperature also increases the diffusion rate of the chromium (VI) ions in the solution. When the temperature exceeded 60°C, the percentage adsorption decreased because increase in thermal energy at temperatures beyond
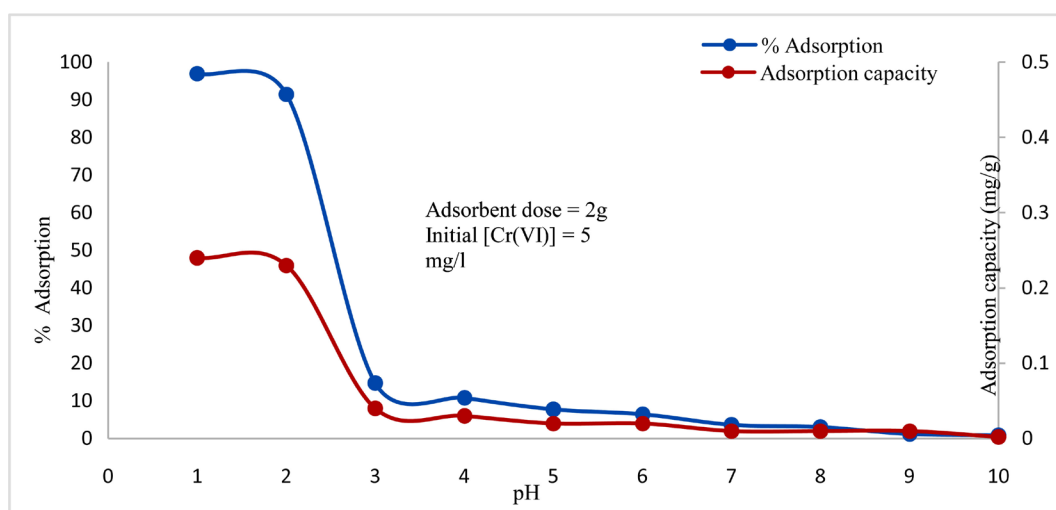

Figure 5. Effect of pH on percentage adsorption and adsorption capacity of chromium (VI) from standard aqueous solution.
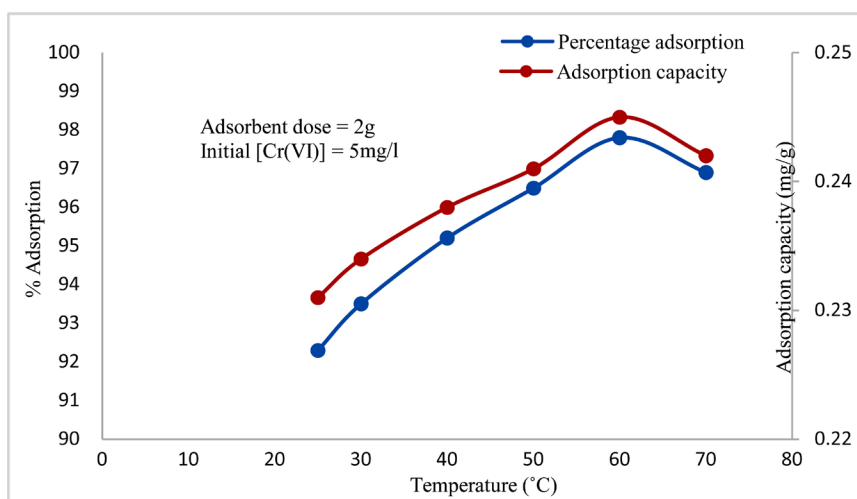

Figure 6. Effect of temperature on percentage adsorption and adsorption capacity of chromium (VI) from the standard aqueous solution.

60˚C increases the mobility of the chromium (VI) ions in the solution to such a level that desorption rate is higher than adsorption rate [20]. The results of this study agree with [8] who reported that beyond 60˚C, the adsorption efficiency of the raw jackfruit seed powder reduced for chromium (VI) in aqueous solutions. From this study, therefore, the adsorption of chromium (VI) ions by PRS bio-char is most efficient at 60˚C, with 97.8% percentage removal from the aqueous solution with corresponding adsorption capacity of 0.245 mg/g.

3.6. Effect of Varying Chromium (VI) Concentration

The adsorption efficiency of PRS bio-char decreased with increase in chromium (VI) concentration as given in **Figure 7**. As the concentration of chromium (VI) ions was increased, their competition for the PRS bio-char active sites increased, and the chance of the ions getting adsorbed decreased which in turn reduces the adsorption percentage [8]. However, increase in the chromium (VI) concentration increased the adsorption capacity (holding capacity of the bio-char) due to the increase in the availability of chromium (VI) ions on the interface which enhanced the degree of holding the chromium (VI) ions by the adsorbent [21].

3.7. Effect of Salinity

Salts that contain anionic species (NO_3^-, Cl^-) were introduced into the standard aqueous chromium (VI) solution at pH 2, to observe their effect on the adsorption efficiency of chromium (VI) ions by the PRS bio-char. From **Figure 8**, it is observed that the introduction of nitrate ions (NO_3^-) in solution decreased the percentage adsorption of chromium (VI) ions by PRS bio-char. Increase in the concentration of the nitrate ions in solution, decreased the adsorption efficiency of chromium (VI) by the bio-char. The same trend was observed with chloride ions (Cl^-). The observed trend is attributed to the fact that NO_3^- and Cl^- anions competed for the same positively charged active sites on the adsorbent with
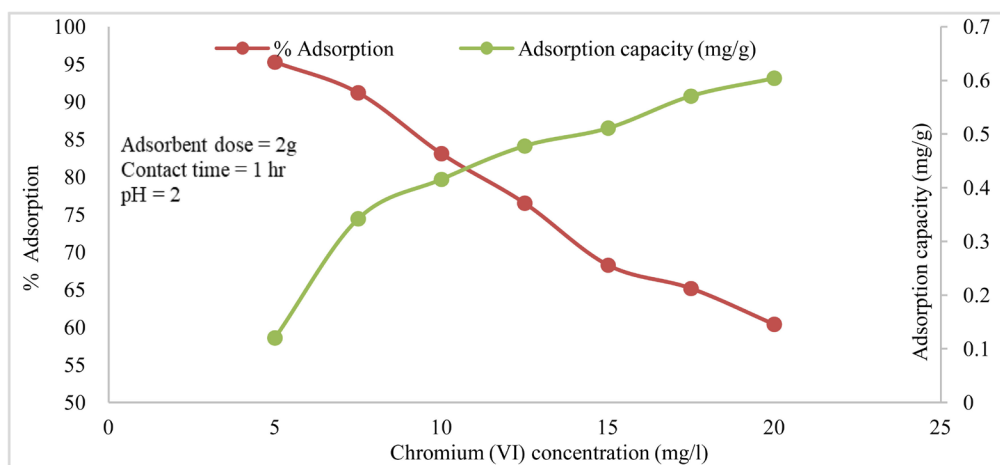

Figure 7. Effect of varying chromium (VI) ion concentration on percentage adsorption and adsorption capacity.
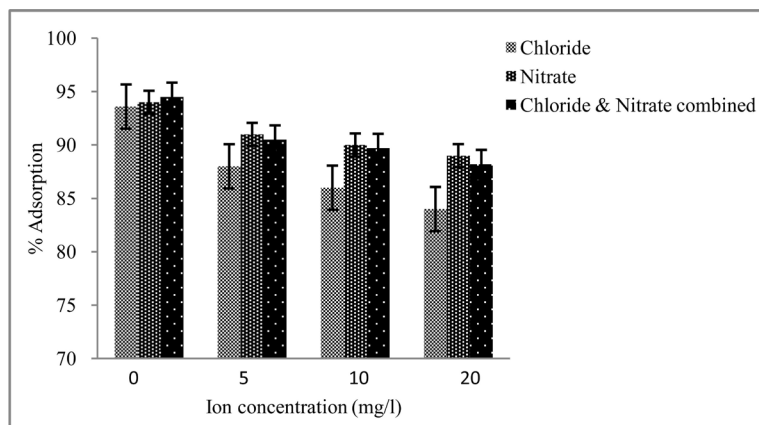
Figure 8. Effect of interfering anions on the adsorption of chromium (VI) from aqueous solution by PRS bio-char.

chromium(VI) ions, which at pH 2 exist mainly as anionic hydrogen chromate ion ($HCrO_4^-$) [8]. Since both NO_3^- and Cl^- ions are lighter than the $HCrO_4^-$ ions, they have a higher mobility in solution, hence get adsorbed onto the active sites much faster, which in turn reduced the percentage of $HCrO_4^-$ that gets adsorbed. The combined effect of chloride and nitrate ions on adsorption showed the same trend at any given concentration as with the individual ions. The decrease in adsorption caused by combining the two ions was less than the individual decrease caused by the chloride ions **Figure 8**. This is explained by the fact that the combined average mass of the chloride and nitrate ions is higher than the mass of the individual chloride ion. Therefore, the average velocity of the two ions combined as they diffuse in solution is slower and hence, their competition with the chromium (VI) ions for adsorption at the active sites on the PRS bio-char surface is less than that caused by the same amount of individual chloride ions. Effect of SO_4^{2-} ions was not studied because sulphuric acid was used to adjust the pH to 2 during the study.

3.8. Adsorption Thermodynamics

The adsorption thermodynamic parameters were determined from the relations as described by [22]. The change in standard Gibbs free energy, ΔG^o and the equilibrium constant, K_c, were calculated from Equations (3) and (4) respectively. The standard enthalpy change, ΔH^o of +27186.78 J/mol and standard entropy change, ΔS^o of +112.355 J/K/mol, were obtained from the slope and intercept of the plot in **Figure 9**, respectively, using the linear Vant Hoff isotherm Equation (5).

$$\Delta G^o = -RT \ln K_c \tag{3}$$

$$K_c = \frac{C_{ad}}{C_{eq}} \tag{4}$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{5}$$
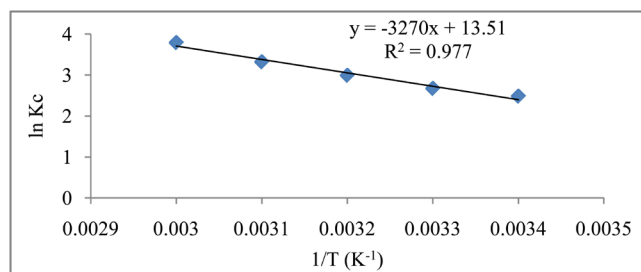
Figure 9. A plot of $\ln K_c$ against $1/T$ for the determination of ΔH^o and ΔS^o.

Table 2. Thermodynamic parameters for adsorption of chromium (VI) ions from aqueous solution by PRS bio-char.

Temp K	$1/T$/K	K_c	$\ln K_c$	ΔG^o (J/mol)	ΔH^o (J/mol)	ΔS^o (J/K/mol)
298	0.0034	11.987	2.48	−6144.379		
303	0.0033	14.385	2.67	−6726.109		
313	0.0032	19.833	2.99	−7780.823	+27,186.78	+112.355
323	0.0031	27.571	3.32	−8915.601		
333	0.0030	44.455	3.79	−10492.850		

where, C_{ad} is concentration of chromium (VI) adsorbed, C_{eq} is equilibrium chromium (VI), R is the universal gas constant and T is the temperature in Kelvin.

The values of ΔG^o obtained were negative as shown in **Table 2** and the magnitude of these values increased within the temperature range investigated in this study. This indicates that the adsorption of chromium (VI) ions by PRS bio-char is feasible and it occurs spontaneously. Also, all the values of ΔG^o are above 41.86 kJ/mol, an indication that the adsorption is a chemical process, and the increasing magnitude of ΔG^o with temperature shows that the adsorption is favoured by increase in temperature [16]. The value of ΔH^o is positive showing that the adsorption process is endothermic [22], a sign that monolayer chemisorption occurred according to [20], which require absorption of some heat energy to overcome the energy barrier. The positive value of ΔS^o showed that the degree of disorder or randomness of the system increased with increase in temperature and it also indicates an increase in the affinity of the bio-char for chromium (VI) ions from the aqueous solution.

3.9. Adsorption Isotherms

The data was fitted to both the common linear Langmuir and Freundlich isotherm models as given in Equations (6) and (7) respectively. The Freundlich isotherm model is an empirical relationship used to describe the adsorption of solutes (chromium (VI) from a liquid to a solid surface (PRS bio-char), and assumes that different sites are available with several adsorption energies and allows for multilayer formation [23]. However, the Langmuir model is restricted to the uniformity of sites and only assumes monolayer capacity [24].

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_o} + \frac{C_e}{Q_o} \tag{6}$$

$$\log Q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e \tag{7}$$

where K_L and Q_o are Langmuir constants related to rate of adsorption and adsorption capacity respectively, K_f and n are Freundlich constants representing adsorption capacity or distribution coefficient and intensity of adsorption. The essential features of the Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant, R_L, which is defined by the relationship in Equation (8).

$$R_L = \frac{1}{1 + K_L C_o} \tag{8}$$

where C_o is initial chromium (VI) concentration.

From the linear Langmuir adsorption isotherm as given by equation (6), a graph of C_e/Q_e against C_e was plotted and a straight line graph obtained as shown in Figure 10 with correlation coefficient of 0.9923 and a slope $1/Q_o$. This linear plot was used to determine Q_o and K_L. The slope obtained was 1.5168 from which Q_o was found to be 0.6593. Using the value of the intercept as 1.4788, and Q_o (0.6593), K_L was obtained as 1.0257 as given in Table 3. The R_L values were also obtained and these values lie between 0 and 1, which shows that the adsorption is favourable and fits the Langmuir isotherm under the conditions of the study.

The linear Freundlich isotherm equation, as given in equation (7), was used to obtain the constants, n (adsorption intensity) and K_f (distribution coefficient). These were obtained by plotting $\log Q_e$ against $\log C_e$ as shown in Figure 11. This gave straight line with slope of 1/n, showing that the adsorption of chromium
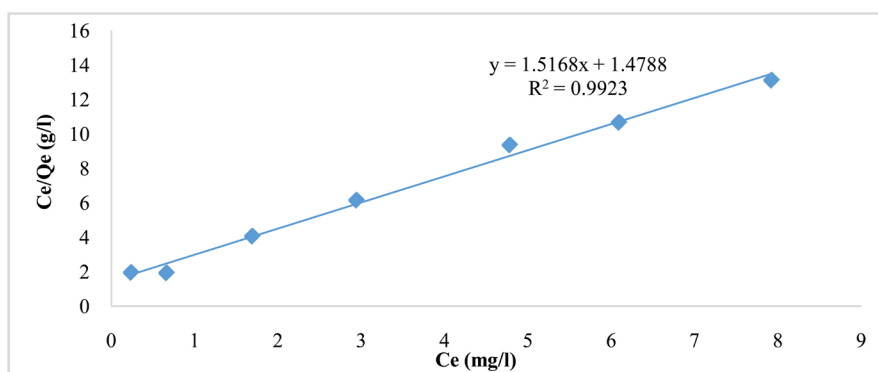

Figure 10. Langmuir isotherm for adsorption of chromium (VI) by PRS bio-char.

Table 3. R_L values for adsorption of chromium (VI) from aqueous solution by PRS bio-char.

C_o = [Cr(VI)] (mg/l)	5.0	7.5	10.0	12.5	15.0	17.5	20
R_L	0.1632	0.1150	0.0888	0.0724	0.0611	0.0528	0.0465

(VI) follows the Freundlich model with correlation coefficient of r^2 = 0.8699. The K_f and n values were calculated to be 0.2909 and 2.4667 respectively as given in Table 4. The slope obtained, ranging between 0 and 1, it is a measure of adsorption intensity or surface heterogeneity, and the surface becomes more heterogeneous as the value of n value gets closer to zero [25]. A comparison was made of PRS biochar against other adsorbents that have been used to remove chromium (VI) from aqueous solution. It can be observed that PRS biochar compare well with the other adsorbents listed in Table 5.

4. Conclusion

PRS bio-char demonstrated the ability to remove chromium (VI) from both the tannery effluent and the standard Cr (VI) aqueous solution, particularly at pH 2
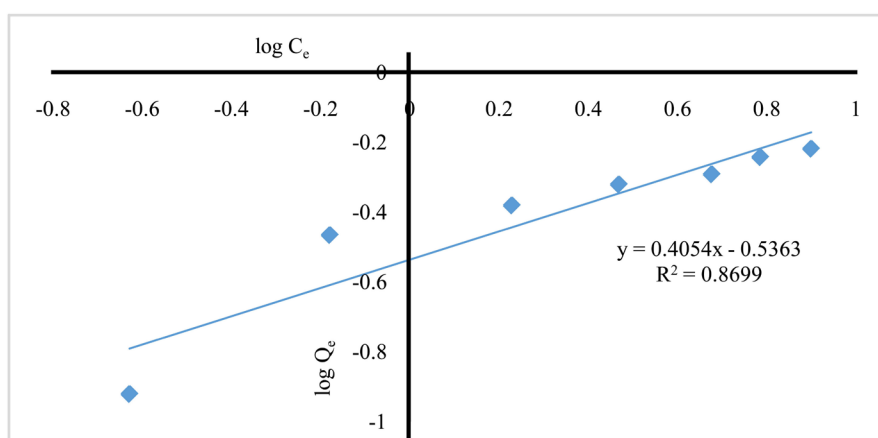

Figure 11. Freundlich isotherm for adsorption of chromium (VI) by PRS bio-char.

Table 4. Estimated isotherm parameters for chromium (VI) adsorption by PRS bio-char.

Isotherm	R^2	Parameters
Freundlich	0.8686	K_f = 0.2909
		n = 2.4667
Langmuir	0.9922	Q_o = 0.6593 mg/g
		K_L = 1.0257 l/mg
		R_L = 0.0465 - 0.1632

Table 5. Comparison of adsorption capacity of PRS bio-char with other adsorbents.

Adsorbent	Q_o (mg/g)	pH	C_o	Reference
Activated rice husk carbon	0.80	2	10	[26]
Activated alumina	1.60	4	5	[26]
Raw rice bran	0.07	2	5	[27]
Wheat bran	0.94	2	5	[2]
Jackfruit seed powder	0.57	2	5	[8]
Phoenix reclinata seed bio-char	0.66	2	5	Present study

and below. For a solution containing 5 mg/l chromium (VI), to bring about effective adsorption, one would need to use 1.5 g of PRS bio-char powder on 100 ml of solution for one hour at 25˚C. The adsorption process of chromium (VI) onto PRS bio-char was spontaneous even at 25˚C as given by the thermodynamic parameters and it was found to be endothermic. The data fitted the Langmuir model better than the Freundlich model with a high regression coefficient and thus can be used to describe and explain the adsorption of chromium (VI) on PRS bio-char. According to the Langmuir model, the maximum adsorption capacity, Q_o, of PRS bio-char powder was found to be 0.6593 mg of chromium (VI) per gram of adsorbent. Therefore, the bio-char of *Phoenix reclinata* seeds can be used, for example, by ternaries and secondary schools to effectively remove chromium (VI) from aqueous systems under ordinary conditions at a low cost.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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