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Removal of chromium from aqueous solution by *borasus flabellifer coir powder* as adsorbent

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ABSTRACT

Chromium has been widely used in various industries like textile, leather, chemical manufacture, metal finishing, paint industry and many other industries. Since hexavalent chromium is a priority toxic, mutagenic and carcinogenic chemical when present in excess, it is very much required to remove chromium from effluents before allowing it to enter any water system or on to land. In the present study, the removal of hexavalent chromium by adsorption on the Borasus flabellifer coir powder as adsorbent has been investigated in the batch experiments. The agitation time, the adsorbent size, adsorbent dosage, initial chromium concentration, temperature and the effect of solution pH are studied. Adsorption mechanism is found to follow Freundlich. The adsorption behavior is described by a second order kinetics. Percentage removal of chromium (VI) is found to be 97.16% at pH=2, w=0.5g, d_p=63µm and temperature=303 K. The results obtained in this study illustrate that Borasus flabellifer coir powder is an effective and economically viable adsorbent for hexavalent chromium removal from industrial waste water.

1. Introduction

Water contamination with heavy metals is a very severe problem all over world [1, 2]. The world production of chromite ore is several millions of tons in a year. Ferrochromite is obtained by direct reduction of the ore while chromium metal is produced either by chemical reduction (the aluminothermic process) or by electrolysis of either CrO_3 or chrome alum solutions. Chromium and its compounds are extensively used in industry with important sources from metal finishing, leather tanning, electroplating, textile industries, and chromate preparation [3]. In aqueous phase chromium mostly exists in two oxidation states, namely, trivalent chromium (Cr^{+3} and $Cr(OH)^{2+}$) and hexavalent chromium ($HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$, etc). Most of the hexavalent compounds are toxic, carcinogenic and mutagenic. For example, it was reported that $Cr_2O_7^{2-}$ can cause lung cancer [4, 5].

Chromium (III) and Chromium (VI) have major environmental significance because of their stability in the natural environment. Cr (VI) is known to have 100 fold more toxicity than Cr (III) because of its high water solubility and mobility as well as easy reduction [6]. International agency for research on cancer has determined that Cr (VI) is carcinogenic to humans. The toxicological effect of Cr (VI) originates due to oxidizing nature as well as the formation of free radicals during the reduction of Cr (VI) to Cr (III) occurring inside the cell [8].Therefore, the World Health Organization (WHO) recommends that the toxic limits of chromium (VI) in waste water at the level of 0.05mg/l, while total Chromium containing Cr (III), Cr (VI) and other species of chromium is regulated to be discharged below 2mg/l [7].

Several methods are used to remove chromium from the industrial wastewater. These include reduction followed by chemical precipitation [9], ion exchange [10], reduction [11], electrochemical precipitation [12], solvent extraction [13], membrane separation [14], evaporation [15] and foam separation [16]. Above cited conventional chromium elimination processes are costly or ineffective at small concentrations. In recent years biosorption research is focused on using readily available biomass that can remove heavy metals. This process involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. This process can be applied as a cost effective way of purifying industrial waste water whereby drinking water quality can be attained. A lot of research was focused on bio-adsorbent materials which can efficiently remove heavy metals from aqueous bodies. These materials are identified as biosorbents and the binding of metals by biomass is referred to as biosorption. Since this noble approach is effective and cheap many researchers exploring appropriate biomaterials that effectively remove Cr (VI) from aqueous solutions [17, 18]. A variety of adsorbents like tamarind seeds [19], rice husk [20], azadirachta indica [21], maize bran [22], red saw dust [23], wall nut hull [24], groundnut hull [25], limonia acidissima coir powder [26] were reported in literature for removal of chromium from aqueous solutions or waste waters in a batch or column reactor system. Table 1 gives the brief findings and chromium (VI) metal uptake by different bisorbents.

In the present investigation, the use of Borasus flabellifer coir powder as an effective and inexpensive material for the removal of Cr (VI) from aqueous solution was described. The paper is organized as follows: Section 2 deals with the material and methods used for the estimation of chromium (VI) and the experimental description of the batch adsorption study. The results of the present study are given section 3 in which adsorption isotherms, kinetics, thermodynamics of the absorption of Cr (VI) on Borasus flabellifer coir powder are discussed and conclusions are given in section 4.

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2. Materials And Methods

2.1 The Diphenyl carbazide Method

A 0.25percentage W/V solution of diphenyl carbozide was prepared in 50percentage acetone. 15 ml each of the sample solutions containing various concentrations of Cr (VI) were pipette out into 25 ml standard flasks. To this 2 ml of 3M H_2SO_4 was added followed by 1 ml of diphenyl carbozide and total volume was made up to 25 ml using deionised, double distilled water. Chromium (VI) concentrations estimated by the intensity of the red brownish color complex formed, was measured using U-V-Visible spectrophotometer at 540nm. The absorbance was measured indicating adherence to the Beer Lambert's law (0 to 30 mg/l).

2.2 Preparation of the adsorbent

The Borasus flabellifer coir was obtained from local market; washed, dried, and crushed in primary crusher and air dried in sun for several days until its weight remains constant. After drying, it is crushed in roll crusher and hammer mills. The material obtained through crushing and grinding is screened through BSS meshes. Finally the products obtained were stored in glass bottles for further use. All the materials were used as such and no pretreatment was given to the materials. The average particle sizes were maintained in the range of 63 to 125 µm.

2.3 Preparation of chromium stock solution

Potassium dichromate ($K_2Cr_2O_7$) is used as the source for chromium stock solution. All the required solutions are prepared with analytical reagents and double-distilled water. 2.835 g of 99% $K_2Cr_2O_7$ is dissolved in distilled water of 1.0 L volumetric flask up to the mark to obtain 1000 ppm (mg/l) of chromium (VI) stock solution. Synthetic samples of different concentrations of chromium (VI) are prepared from this stock solution by appropriate dilutions. 100 mg/l chromium stock solution is prepared by diluting 100 ml of 1000 mg/l chromium stock solution with distilled water in 1000 ml volumetric flask up to the mark. Similarly solutions with different metal concentrations such as (5, 10, 15, 20, 25 and 30 mg/l) are prepared.

$$\text{Cr equivalent to 1 gm} = \frac{\text{Molecular Wt. of } K_2Cr_2O_7 \times 100}{(\text{Atomic Wt of Cr} \times 2) \times \text{purity}}$$

2.4 Batch mode adsorption studies

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration (5-30mg/l), adsorbent dosage (0.1-0.6 gm in 50ml solution), agitation time (0 -120min), pH (1-10), adsorbent size (63µm, 89µm and 125µm) and temperature (303-323 K). The solution containing adsorbate and adsorbent was taken in 250 ml capacity conical flasks and agitated at 180 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-1).

2.5 Metal analysis

Final residual metal concentration after adsorption was measured by UV-Spectrophotometer after sample was complexed with 1-5 Diphenyl carbazide. To estimate the percentage removal of chromium (VI) from aqueous solution, the following equation was used.

$$\text{Percentage removal of Cr (VI)} = \frac{C_{initial} - C_{final}}{C_{initial}} \times 100$$

Where, $C_{initial}$ and C_{final} are the concentrations of chromium (VI) at the beginning and at the end of the adsorption process. The metal uptake (q_e) at equilibrium time was calculated from the following equation

$$q_e = \frac{(C_0 - C_e)v}{1000w}$$

Where q_e (mg/g) is the amount of chromium adsorbed per unit weight of adsorbent, C_0 and C_e are the initial and equilibrium chromium ion concentration (mg/l), v is the volume of aqueous solution (ml), and w is the adsorbent weight (g).

3. Results And Discussions

3.1 Effect of various parameters on the adsorption of Chromium (VI) by Borasus flabellifer coir powder

3.1.1 Effect of agitation time and Initial Cr (VI) concentrations

The equilibrium agitation time is determined by plotting the percentage removal of chromium (VI) against agitation time for different concentrations as shown in Fig 1. The percentage removal of chromium (VI) increases up to 60 min of the agitation time and thereafter no further increase is recorded by Borasus flabellifer coir powder as adsorbent. Adsorption equilibrium time is defined as the time required for heavy metal concentration to reach a constant value. It is observed that percentage removal of chromium decreases with increase in the initial concentration. Evidently such a behavior can be attributed to the maintenance of fixed number of binding sites in the dosage while increasing the concentration.

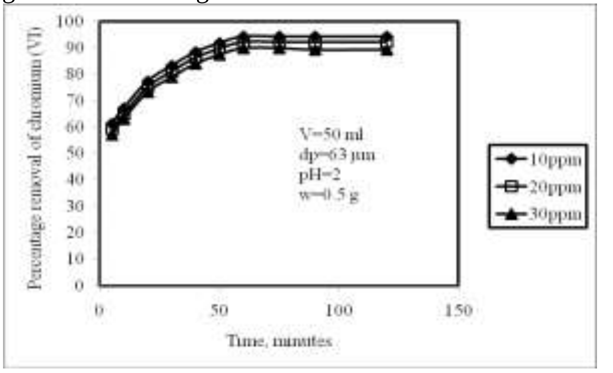

Fig 1. Variation of percentage removal of chromium (VI) with agitation time by Borasus flabellifer coir powder at different initial concentration of Cr (VI) in solution

3.1.3 Effect of adsorbent dosage and size in aqueous solution

The variations in percentage removal of chromium (VI) and also metal uptake in aqueous solution with adsorbent dosage are shown in Fig 2. The percentage removal of chromium (VI) from aqueous solution increases from 61.83% to 93.43% and also metal uptake decreases from 6.183 to 1.5572 mg/g with an increase in the adsorbent dosage from 0.1 g to 0.6 g in 50 ml solution at 303 K for 63 µm size. The percentage removal of chromium (VI) from aqueous solution with adsorbent size is reported in Table 2. The percentage removal of chromium (VI) increases from 80.97 % (1.6194 mg/g) to 92.15 %(1.843 mg/g) for 0.5 g of dosage in 50 ml for the initial chromium (VI) concentration of 20 mg/l at 60 min equilibrium agitation time with decrease in the adsorbent size from 125 to 63 µm. This phenomenon is expected as the decrease in size of adsorbent results in the increase of the surface area of it, thereby the number of active sites are better exposed to the adsorbate.

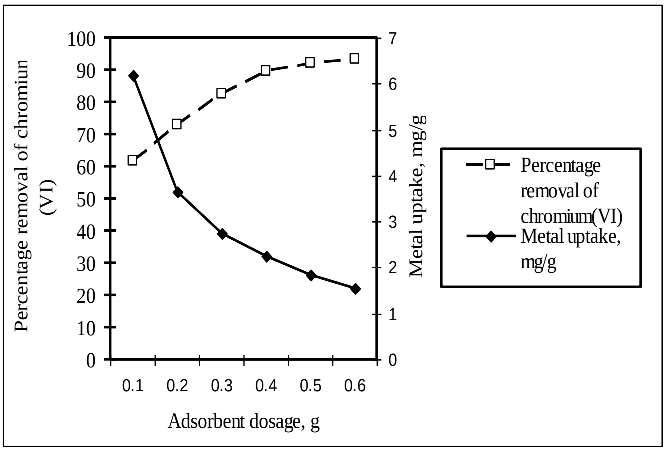

Fig 2. Variation of percentage removal of chromium (VI) and metal uptake with adsorbent dosage by Borassus flabellifer coir powder

Table 2. Effect of adsorbent particle size, C_0=20 mg/l; temp=30^{0}C; v=50ml; t=60 min; pH=2 and w=0.5g.

S.No.	Adsorbent average particle size, µm	Final concentration, mg/l	Percentage adsorption	Metal uptake (mg/g)
1	63	1.570	92.15	1.57
2	89	2.322	88.39	2.322
3	125	3.806	80.97	3.806

3.1.4 Effect of pH of the aqueous solution

pH is an important factor for controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of the adsorbate. The effect of pH on adsorption of chromium (VI) at different initial concentrations is shown in Fig 3. The maximum percentage removal of chromium (VI) for various initial concentrations is reported at pH value of 2. It is confirmed that adsorption of chromium (VI) increases with decrease in pH values. The principal driving force for metal ion adsorption is the electrostatic interaction i.e, attraction between adsorbent and adsorbate. The greater the interaction, the higher will be the adsorption of heavy metal. Negatively charged chromium species ($Cr_2O_7^{2-}$) bind the positively charged functional groups on the surface of biosorbents through electrostatic attraction. At low pH functional groups of the biosorbent become protonated, and easily attract negatively charged chromium, but at high pH deprotonation occurs, functional groups become negatively charged repelling negatively charged chromium.

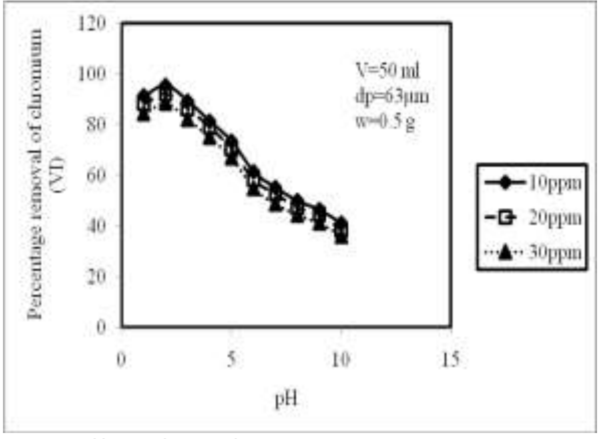

Fig 3. Effect of pH of aqueous solution on percentage removal of chromium (VI) at different initial concentrations by Borassus flabellifer coir powder

3.1.5 Effect of Temperature

The effect of temperature on adsorption of chromium at different initial concentrations is shown in Fig 4. The maximum percentage removal of chromium for various initial concentrations is reported at temperature 323 K. It is confirmed that adsorption of chromium (VI) increases with increase in temperature for all concentrations; it indicates that the present adsorption is endothermic in nature. Further, at a given temperature low initial concentrations of the solution showed improved percentage of adsorption in comparison with higher concentration solutions.. This increase in binding could be due to increase in surface activity and increased kinetic energy of the chromium (VI) metal ions.

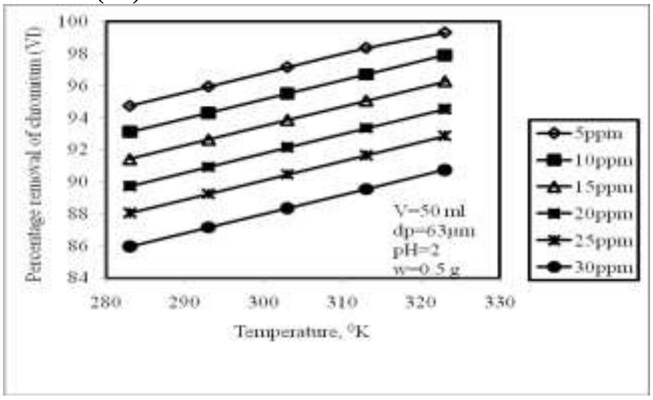

Fig 4. Variation of percentage removal of chromium (VI) with temperature by Borassus flabellifer coir powder

3.2. Adsorption Isotherms

An adsorption isotherm is used to characterize the interaction of the metal ions with the adsorbent. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed to the solid phase when the two phases are at equilibrium.

3.2.1 Langmuir model

The Langmuir isotherm [35] was derived originally from studies on gas adsorption to activated carbon. The Langmuir isotherm model is used to estimate the adsorption of adsorbent used and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir adsorption isotherm is of the form:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad [1]$$

Here q_e is the metal concentration adsorbed in solid (biomass), C_e is the metal residual concentration in the solution. q_{max} is the maximum specific uptake corresponding to sites saturation, and b is the ratio of adsorption/desorption rates. The Langmuir isotherm in Eq (1) can written as

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \quad [2]$$

The adsorption data for adsorption of Cr (VI) on Borasus flabellifer coir powder is plotted in Fig 5 shows good linearity for Langmuir isotherm. The equations with correlation coefficients are shown in Table 3. q_{max} is calculated from the slope and b is calculated from the intercept. It is observed that strong binding of Cr (VI) ions to the surface of Borasus flabellifer coir powder. The separation factor, R_L obtained (from Table 4) between 0.0643-0.2918 for various concentrations shows favorable adsorption ($0<R_L<1$).

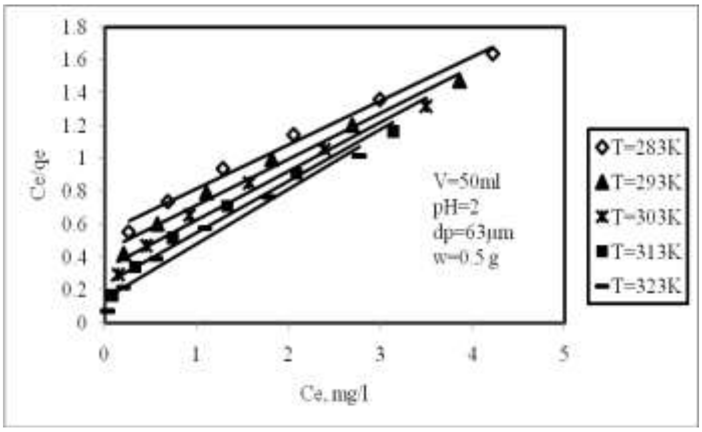

Fig 5. Langmuir isotherm for adsorption of chromium (VI) by Borasus flabellifer coir powder

Table 4. $R_L = \frac{1}{1+bc_i}$ values at pH=2; T=283K

Initial concentration, C_i (mg/l)	**R_L**
5	0.2918
10	0.1708
15	0.1207
20	0.0934
25	0.0761
30	0.0643

3.2.2 Freundlich model

The Freundlich isotherm [36] is based on multilayer adsorption with interaction between adsorbed molecules .The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. This relation can be reasonably applied to the low or intermediate concentration ranges. For adsorption from solution, the Freundlich isotherm is represented by:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad [3]$$

Here K_f is the Freundlich constant and is also known as Freundlich capacity and n stands for adsorption intensity. q_e is the amount of chromium (VI) adsorbed at equilibrium and C_e is the residual concentration of Cr (VI) in solution. The Freundlich equation is expressed linearly as.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad [4]$$

The values of K_f and n can be obtained from intercept and slope of a plot of log q_e versus log C_e.

The adsorption data for the adsorption of Cr (VI) on Borasus flabellifer coir powder was plotted in Fig 6 shows good linearity for Freundlich Isotherm. The equations with correlation coefficients are shown in Table 5. Linearity of the relationship indicates strong binding of Cr (VI) to the adsorbent. The slope of isotherm (n) varies between 1.6367 and 2.5707 fulfilling the condition of n>1 for favorable condition.

3.2.3 Tempkin model

The Tempkin isotherm model [37] contains a factor that takes care of the adsorbent-adsorbate interactions. Tempkin considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms. Tempkin noted experimentally that heats of adsorption would more often decrease than increase with increasing coverage.

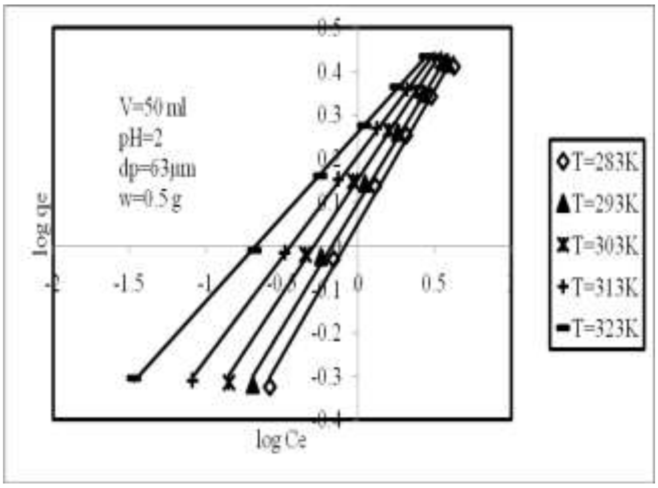

Fig 6. Freundlich isotherm for adsorption of chromium (VI) by Borasus flabellifer coir powder

The nonlinear form of Tempkin equation is given by Eq (5) and the linear form in Eq (6).

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \qquad [5]$$

$$q_e = B_T \ln A_T + B_T \ln C_e \qquad [6]$$

Here B_T= (RT/b_T). T is the absolute temperature and *R* is the universal gas constant. Constant b_T is related to the heat of adsorption. A_T is the equilibrium binding constant corresponding to the maximum binding energy. A plot of q_e versus ln C_e at a fixed temperature will give Tempkin isotherm constants, A_T and b_T.

The adsorption data for adsorption of Cr (VI) on Borasus flabellifer coir powder was plotted in Fig 7 shows good linearity for Tempkin Isotherm. The equations with correlation coefficients are shown in Table 6. Linearity of the relationship indicates strong binding of Cr (VI) to the adsorbent.

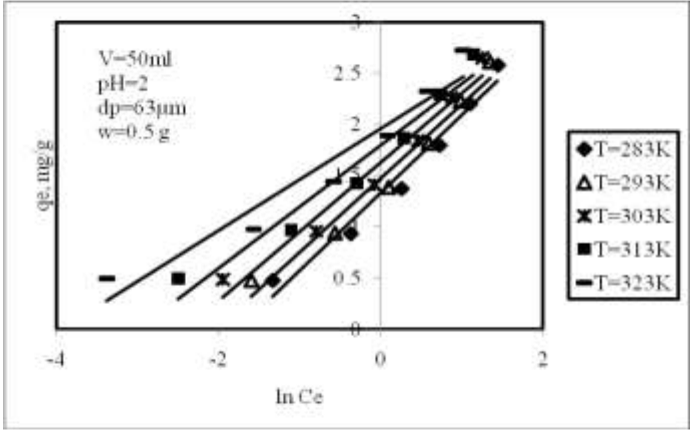

Fig 7. Tempkin isotherm for adsorption of chromium (VI) by Borasus flabellifer coir powder

3.2.4 Dubinin and Radushkevich (D-R) isotherm

Dubinin and Radushkevich equation [38] is represented in a linear form by equation $\ln q_e = \ln Q_0 - K_{DR}\varepsilon^2$ [7]

Where K_{DR} ($mol^2\ KJ^{-2}$) is a constant related to mean adsorption energy and ε is the Polanyi potential which can be calculated from the following equation

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \qquad [8]$$

The slope of plot of ln q_e versus ε^2 gives K_{DR} ($mol^2\ KJ^{-2}$) and the intercept yields the sorption capacity Q_0 (mg/g). T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 $Jmol^{-1}K^{-1}$).

The sorption energy can also be worked out using the following relationship [39]

$$E = \frac{1}{(2 \times K_{DR})^{\frac{1}{2}}} \qquad [9]$$

Where, E is the mean free energy of adsorption. If the value of E is between 1 and 16 KJ/mol, then physical adsorption prevails; and if the is more than 16 KJ/mol, then chemisorption prevails. The adsorption data for adsorption of Cr (VI) on Borasus flabellifer coir powder was plotted in Fig 8 shows non-linearity for D-R isotherm. The equations with correlation coefficients are shown in Table 7. From regression coefficient R^2 value, the present data is not fit for D-R isotherm.

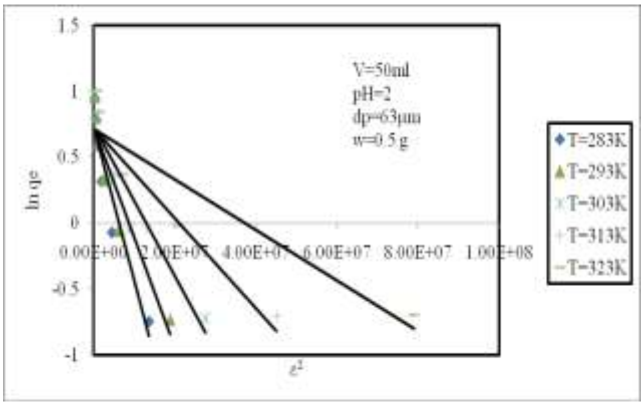

Fig 8. Dubinin and Radushkevich (D-R) isotherm for adsorption of chromium (VI) by Borasus flabellifer coir powder

3.3. Studies on kinetics of adsorption

The study of adsorption dynamics describes the solute uptake rate, and this rate controls the habitation time of adsorbate uptake at the solid –solution interface. Chemical kinetics gives information about reaction pathways and time to reach equilibrium. Sorption kinetics shows a large dependence on the physical and /or chemical characteristics of the sorbent material. Different models have been used to investigate the mechanism of sorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (R^2 value). A relatively high R^2 value (close or equal to one) indicates that the model successfully describes the kinetics of Cr (VI) adsorption.

3.3.1 Pseudo-first order or Lagergen kinetic model

It is the first equation for sorption of liquid/solid system based on solid capacity. The pseudo first order equation is generally expressed as

$$\frac{dq}{dt} = k_1 (q_e - q_t) \qquad [10]$$

Here q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo first order adsorption (min^{-1}). Eq (10) can be arranged to obtain the more useful form

$$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303})t \qquad [11]$$

The plot of $\log(q_e\text{-}q_t)$ vs t is linear from which k_1 can be determined from the slope. First order kinetics for adsorption of chromium (VI) by Borasus flabellifer coir powder is shown in Fig 9. The equations with correlation coefficients are shown in Table 8. From the graph, the q_e is estimated for different process parameters and the estimated value is checked with the experimental value. From Table 8, it can be seen that q_{ecal} and q_{eexp} are not the same. Therefore, first order kinetics may not represent the adsorption kinetics, though the R^2 value is close to 1. The above model is not fit for hexavalent chromium removal on Borasus flabellifer coir powder adsorbent.

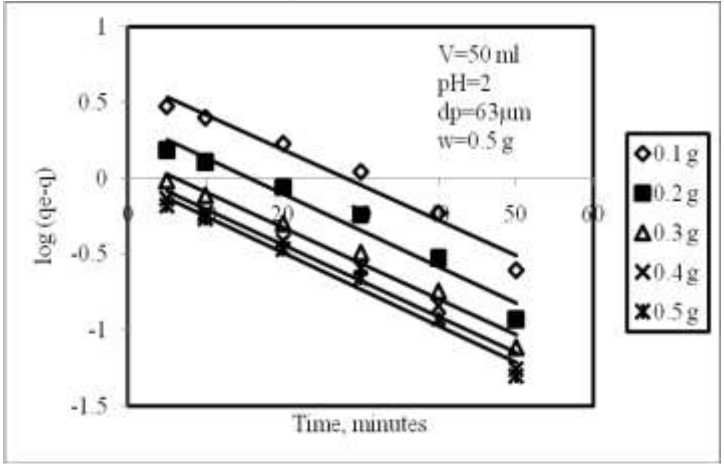

Fig 9. First order kinetics for adsorption of chromium (VI) by Borasus flabellifer coir powder

3.3.2 Pseudo–second order kinetic model

The pseudo-second-order adsorption kinetic rate equation is expressed as

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \qquad [12]$$

Where k_2 is the rate constant of pseudo second order adsorption (g $mg^{-1}min^{-1}$). Eq (12) can be rearranged to obtain more useful form as

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad [13]$$

The linear form is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e} \qquad [14]$$

And k_2 is obtained from the intercept of the plot of t/q_t vs t. The second order kinetics for adsorption of chromium by Borasus flabellifer coir powder is shown in Fig 10. Their equation with correlation coefficients are shown in Table 9, it can be seen that q_{ecal} and q_{eexp} are almost the same. Therefore, the second order kinetic model is fit for hexavalent chromium removal by Borasus flabellifer coir powder adsorbent.

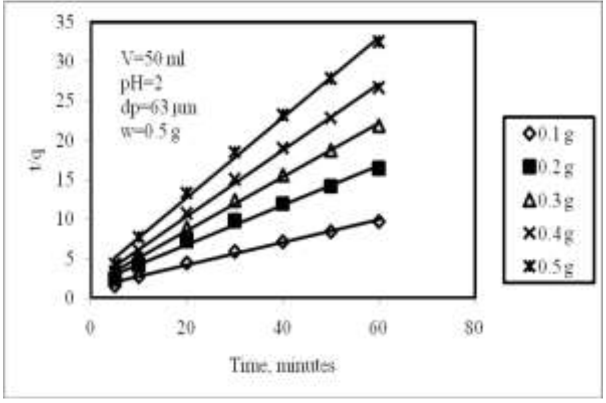

Fig 10. Second order kinetics for adsorption of chromium (VI) by Borasus flabellifer coir powder

Table 1. The brief findings and chromium (VI) metal uptake by various biosorbents

Material	Equilibrium Isotherms it follows	Kinetics it follows	Metal uptake (mg/g)	References
Limonia acidissima hull powder	Langmuir, Freundlich, Tempkin	2nd order	22.414	[26]
Sulfuric acid modified waste activated carbon	Langmuir, Freundlich	----	7.485	[27]
Nitric acid modified waste activated carbon	Langmuir, Freundlich	----	10.929	[27]
Iron (III) hydroxide	Langmuir, Freundlich	-----	0.47	[28]
Blast furnace slag	Langmuir, Freundlich	1st order	7.5	[29]
Activated red mud	Langmuir,Freundlich	----	1.6	[30]
Ground nut hull	Langmuir, Freundlich	2nd order	30.95	[25]
Neem leaf powder	Langmuir, Freundlich	2nd order	7.43	[31]
activated carbon from hazelnut	Langmuir	1st order	170	[32]
Bentonite	Langmuir, Freundlich	----	0.512	[33]
Palygorskite clay	Langmuir, Freundlich	1st order	58.5	[34]
Borasus flabellifer coir powder	Langmuir, Freundlich	2nd order	3.7453	Present work

Table 3. Langmuir isotherms and its coefficients

S.No.	Parameters	Equations	q_m	b	R_L	R^2
1	T=283K	$\frac{C_e}{q_e} = 0.267C_e + 0.550$	3.7453	0.4854	<1	0.987
2	T=293K	$\frac{C_e}{q_e} = 0.280C_e + 0.438$	3.5714	0.6392	<1	0.983
3	T=303K	$\frac{C_e}{q_e} = 0.296C_e + 0.331$	3.3784	0.8943	<1	0.979
4	T=313K	$\frac{C_e}{q_e} = 0.314C_e + 0.232$	3.1847	1.3534	<1	0.973
5	T=323K	$\frac{C_e}{q_e} = 0.333C_e + 0.147$	3.0030	2.2653	<1	0.969

Table 5. Freundlich isotherms and its coefficients

S.No.	Parameters	Equations	K_f	n	R^2
1	T=283K	$\log q_e = 0.611 \log C_e + 0.052$	1.1272	1.6367	0.995
2	T=293K	$\log q_e = 0.577 \log C_e + 0.100$	1.2589	1.7330	0.996
3	T=303K	$\log q_e = 0.531 \log C_e + 0.153$	1.4223	1.8832	0.997
4	T=313K	$\log q_e = 0.469 \log C_e + 0.207$	1.6106	2.1322	0.999
5	T=323K	$\log q_e = 0.389 \log C_e + 0.262$	1.8281	2.5707	0.999

Table 6. Tempkin isotherm and its coefficients

S.No.	Parameters	Equations	b_T	A_T	R^2
1	T=283K	$q_e = 0.758 \ln C_e + 1.331$	3104.04	5.7889	0.97
2	T=293K	$q_e = 0.724 \ln C_e + 1.473$	3364.65	7.6486	0.968
3	T=303K	$q_e = 0.674 \ln C_e + 1.63$	3737.59	11.228	0.964
4	T=313K	$q_e = 0.599 \ln C_e + 1.795$	4344.38	20.018	0.953
5	T=323K	$q_e = 497 \ln C_e + 1.961$	5403.26	51.7112	0.935

Table 7. Dubinin and Radushkevich (D-R) isotherms and its coefficients

S.No.	Parameters	Equations	K_{DR}	E(KJ/mole)	R^2
1	T=283K	$\ln q_e = -1 \times 10^{-07} \varepsilon^2 + 0.715$	1×10^{-7}	2.2361	0.894
2	T=293K	$\ln q_e = -8 \times 10^{-08} \varepsilon^2 + 0.724$	8×10^{-8}	2.5	0.893
3	T=303K	$\ln q_e = -0.6 \times 10^{-07} \varepsilon^2 + 0.729$	0.6×10^{-7}	2.887	0.889
4	T=313K	$\ln q_e = -3 \times 10^{-08} \varepsilon^2 + 0.722$	3×10^{-8}	4.0825	0.875
5	T=323K	$\ln q_e = -2 \times 10^{-08} \varepsilon^2 + 0.711$	2×10^{-8}	5.000	0.858

Table 8. Lagegren pseudo first order coefficients

Kinetics	Parameters pH=2, Temperatue=30^{0}C (adsorbent dosage and initial concentration of Cr(VI))	Model equations	q_{ecal}	q_{eexp}	R^2	Rate constants, K_1, min^{-1}
1st order	0.5g and 10ppm	$\log(q_e - q) = -0.024t - 0.31$	0.4897	0.9433	0.978	0.0553
	0.5g and 20ppm	$\log(q_e - q) = -0.024t + 0 - 0.009$	0.9795	1.8433	0.978	0.0553
	0.5g and 30ppm	$\log(q_e - q) = -0.024t + 0.161$	1.4488	2.692	0.978	0.0553
	0.1g and 20ppm	$\log(q_e - q) = -0.0231t + 0.653$	4.498	6.183	0.97	0.0529
	0.2g and 20ppm	$\log(q_e - q) = -0.023t + 0.37$	2.3442	3.643	0.963	0.0529
	0.3g and 20ppm	$\log(q_e - q) = -0.023t + 0.142$	1.3868	2.746	0.979	0.0529
	0.4g and 20ppm	$\log(q_e - q) = -0.023t + 0.033$	1.0789	2.2435	0.967	0.0529

Table 9. Lagegren pseudo second order coefficients

Kinetics	Parameters pH=2, Temperatue=30^{0}C (adsorbent dosage and initial concentration of Cr (VI))	Model equations	q_{ecal}	q_{eexp}	R^2	Rate constants, K_1, g mg^{-1} min^{-1}
2nd order	0.5g and 10ppm	$\frac{t}{q} = 0.996t + 4.87$	1.004	0.9433	0.997	0.2036
	0.5g and 20ppm	$\frac{t}{q} = 0.508t + 2.575$	1.9685	1.8433	0.997	0.1002
	0.5g and 30ppm	$\frac{t}{q} = 0.347t + 1.795$	2.8818	2.6979	0.997	0.0671
	0.1g and 20ppm	$\frac{t}{q} = 0.144t + 1.272$	6.944	6.183	0.991	0.0163
	0.2g and 20ppm	$\frac{t}{q} = 0.251t + 1.733$	3.9841	3.643	0.993	0.0363
	0.3g and 20ppm	$\frac{t}{q} = 0.342t + 1.66$	2.924	2.746	0.997	0.0705
	0.4g and 20ppm	$\frac{t}{q} = 0..422t + 1.878$	2.3696	2.2435	0.997	0.0948

Table 10. Intra particle diffusion model and constants

S.No.	Dosage, g	Model equations	R^2	K_{diff}	Constant, C
1.	0.1 g and 20ppm	$q_t = 0.562t^{0.5} + 1.938$	0.996	0.562	1.938
2.	0.2 g and 20ppm	$q_t = 0.288t^{0.5} + 1.473$	0.996	0.288	1.473
3.	0.3 g and 20ppm	$q_t = 0.177t^{0.5} + 1.420$	0.992	0.177	1.420
4	0.4 g and 20ppm	$q_t = 0.135t^{0.5} + 1.227$	0.994	0.135	1.227
5	0.5 g and 20ppm	$q_t = 0.123t^{0.5} + 0.924$	0.990	0.123	0.924

Table 11. Thermodynamic parameters

Initial Conc, mg/l	Equation	ΔH, KJ/mole	ΔS, KJ/mole K	ΔG, KJ/mole				
				283	293	303	313	323
5	$\ln K_D = -4624(\frac{1}{T}) + 19.02$ R^2=0.926	38.444	0.158	-6.807	-7.710	-8.899	-10.65	-13.38
10	$\ln K_D = -2769(\frac{1}{T}) + 12.3$ R^2=0.957	23.022	0.1023	-6.129	-6.840	-7.702	-8.789	-10.33
15	$\ln K_D = -1989(\frac{1}{T}) + 9.347$ R^2=0.977	16.537	0.078	-5.567	-6.169	-6.869	-7.695	-8.722
20	$\ln K_D = -1551(\frac{1}{T}) + 7.617$ R^2=0.985	12.895	0.0633	-5.100	-5.616	-6.205	-6.875	-7.658
25	$\ln K_D = -1295(\frac{1}{T}) + 6.55$ R^2=0.988	10.767	0.055	-4.697	-5.153	-5.664	-6.238	-6.893
30	$\ln K_D = -1077(\frac{1}{T}) + 5.598$ R^2=0.990	8.9542	0.047	-4.259	-4.661	-5.102	-5.587	-6.135

3.3.3 Intra-particle diffusion model

The adsorption of hexavalent chromium on a porous adsorbent is the combination of four consecutive steps [40]; diffusion in the bulk solution, then diffusion across the thin film surrounding the adsorbent particles, followed by intra-particle diffusion and adsorption within the particles [40]. According to Weber and Moris [41] if the rate limiting step is the intra-particle diffusion, then amount of adsorbed at any time should be directly proportional to the square root of contact time t and shall pass through the origin which is defined mathematically in Eq (15)

$$q_t = K_{diff} t^{0.5} + C \qquad [15]$$

where q_t is the amount of Cr (VI) adsorbed and t is the contact time. K_{diff} is the intra-particle diffusion coefficient. A plot of q_t against $t^{0.5}$ should give a straight line with a positive intercept for intra particle diffusion controlled adsorption process. The value of K_{diff} can be calculated from slope. The higher values of K_{diff} illustrate an enhancement in the rate of adsorption.

The adsorption data was plotted in Fig 11 shows good linearity for Intra particle diffusion model. The equations with correlation coefficients are shown in Table 10. The R^2 values (refer to Table 12) are close to unity, conforming that the rate-limiting step is actually the intra-particle diffusion process. The values of K_{diff} calculated from slope provide information about thickness of the boundary layer, i.e. the resistance to the external mass transfer. The larger slope indicates higher external resistance.

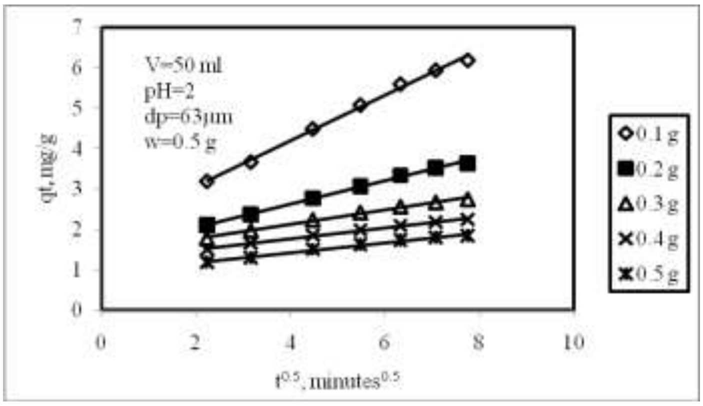

Fig 11. Intra particle diffusion model for adsorption of chromium (VI) by Borasus flabellifer coir powder

3.4 Thermodynamics of adsorption

Adsorption is temperature dependent. In general, the temperature dependence is associated with three thermodynamic parameters namely change in enthalpy of adsorption (ΔH), change in entropy of adsorption (ΔS) and change in Gibb's free energy (ΔG) [42].

The Van't Hoff equation is

$$K_D = \frac{C_{Ae}}{C_e} \qquad [16]$$

$$\Delta G = -RT \ln K_D \qquad [17]$$

Where K_D is the equilibrium constant and C_{Ae} and C_e(both in mg/l) are the equilibrium concentrations for solute on the adsorbent and in the solution, respectively. The K_D values are used in Eq (16) and Eq (17) to determine the ΔG, ΔH and ΔS. Then K_D is expressed in terms of the ΔH (KJ/mol) and ΔS (KJ/mol ^{0}K) as function of temperature.

$$\ln K_D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad [18]$$

The slope and intercept of the plots are determined by plotting ln K_D as a function of (1/T). The values of ΔH and ΔS are calculated for the slope and intercept respectively.

The present data was plotted in Fig 12 shows good linearity for Van't Hoff equation. Their equations with correlation coefficients are shown in Table 11. From positive values of ΔH, the adsorption process is endothermic in nature. If the value of ΔS is less than zero, it indicates that the process is highly reversible. On the other hand, if the value of ΔS is more than or equal to zero, it indicates that the process is irreversible. The negative value for ΔG indicates that the spontaneity of adsorption whereas the positive value indicates the non spontaneity of adsorption. The thermodynamic parameters such as free energy change, enthalpy change and entropy change for the adsorption of chromium (VI) on Borasus flabellifer coir powder is feasible, spontaneous, irreversible and endothermic in nature.

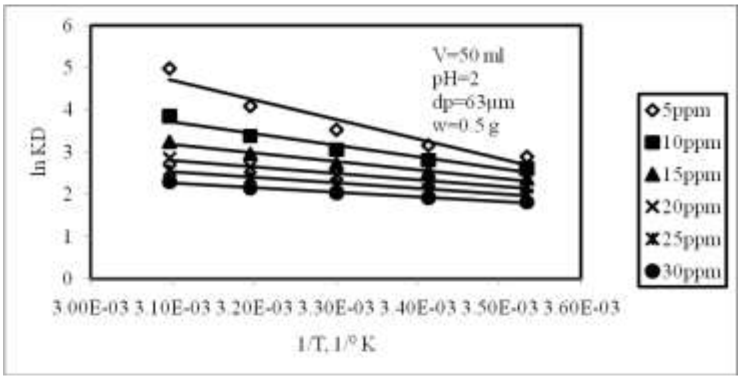

Fig 12. Van't Hoff equation.

4. Conclusions

The Borasus flabellifer coir powder is capable of removing chromium (VI) from aqueous solution, up to 97.16% for an initial concentration of Cr (VI) 5 mg/l , adsorbent dosage of 0.5 g (in 50ml solution), adsorbent size of 63μm, pH=2 and at a temperature of 303 K. The Cr (VI) adsorption performance by Borasus flabellifer coir powder is strongly affected by parameters such as contact time, initial Cr (VI) concentration, pH, adsorbent dosage, adsorbent particle size and temperature.

- The percentage adsorption of Cr (VI) is increased from 61.28% to 94.33% for 10 mg/l with increase in contact time from 5 to 120 minutes. Percentage Adsorption is reached equilibrium stage at 60 minutes of contact time.
- With an increase in pH from 2 to 10, the percentage adsorption of Cr (VI) is decreased from 95.51% to 41.01% for 10 mg/l solution. The optimum pH is taken at pH of 2.
- With an increase in initial concentration of Cr (VI) from 5 to 30 mg/l (for 0.5 g dosage, pH of 2 and a particle size of 63μm), the equilibrium percentage adsorption of Cr (VI) is decreased from 97.16% to 88.34%.
- With the increase in adsorbent dosage from 0.1 to 0.6 g (for 50 ml of solution with initial concentration of 20 mg/l, pH of 2 and particle size of 63μm), the percentage adsorption of Cr (VI) is increased from 61.83 % to 93.43 %.
- The percentage removal of chromium (VI) increases from 80.97 % (1.6194 mg/g) to 92.15% (1.843 mg/g) for 0.5 g of dosage in 50 ml (initial concentration of 20 mg/l, pH of 2) of solution at 60 min equilibrium agitation time with decrease in the adsorbent size from 125 to 63 μm

- The percentage adsorption of Cr (VI) increased with increase in the temperature from 283 to 323 K for all initial concentrations of Cr (VI).
- The Langmuir, Freundlich models for Cr (VI) adsorption onto Borasus flabellifer coir powder is proved to be the best fit followed by Tempkin model for the experimental data. However, the data can not be described by Dubinin-Radushkevich-isotherm, since the correlation coefficient is very low.
- The kinetics of the adsorption of Cr (VI) on Borasus flabellifer coir powder can be better described with pseudo second-order kinetics.
- The thermodynamic parameters such as free energy change, enthalpy change and entropy change show the feasibility, irreversibility, spontaneity, endothermic nature and an increased randomness at the surface of the Borasus flabellifer coir powder for the adsorption of chromium (VI).

The present study is performed in the batch process as this gives a platform for the designing of continuous flow systems with an industrial application at a commercial level also. Further, research is to be carried out to make the process economically viable at industrial scale with focus on Cr (VI) removal and regeneration of Borasus flabellifer coir powder.

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