REMOVAL OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTION USING ACTIVATED CARBON DERIVED FROM PALMYRA PALM FRUIT SEED

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ABSTRACT. In this study, removal of chromium(VI) from aqueous solutions by Palmyra palm fruit seed carbon (PPFSC) and commercial activated carbon (CAC) was investigated. The metal adsorption capacity has been studied as a function of contact time, pH and carbon dosage. The adsorption yields increased with the increasing of adsorbent dosage and contact time, and subsequently reached the equilibrium. The suitability of the Freundlich and Langmuir models were also investigated for each chromium sorbent system. In order to understand the reaction mechanism, kinetic data has been studied using pseudo first order rate equation. The Lagergren's constants were calculated for different initial concentrations of metal ions. The chromium(VI) ions could be rapidly removed from the sorbents by treatment with HCl acid and at the same time the regenerated sorbent could be used again to adsorb heavy metal ions. The suitability of this material for treatment of tannery wastewater was also examined.

KEY WORDS: Adsorption; Chromium(VI) removal; Palmyra palm fruit seed carbon; Regeneration; Langmuir and Freundlich isotherm; Pseudo first order kinetics

INTRODUCTION

Heavy metals are major pollutants in marine; ground and industrials, and even in treated waste water. The presence of these metals in the environment has been a great concern because of their toxic nature and other adverse effects on receiving waters. Among these heavy metals are chromium, copper and zinc, and ingestion beyond the permissible quantities can cause various chronic disorders in human beings. It is well known that heavy metals can damage nerves, liver and bones, and they also block functional groups of essential enzymes [1]. Also, acute systemic poisoning can result from high exposure to hexavalent chromium [2]. Most of the chromium ions in wastewater especially hexavalent chromium originates from industries such as electroplating, metal finishing and magnetic tape manufacturing. For these industrial groups, chromium is a problematic one. Tanning is one of the oldest and fastest growing industries in India. Chromium, which is on the top priority list of toxic pollutants defined by the US Environmental Protection Agency (EPA) exists in nature mainly in two oxidation states +3 and +6. It is a bio element in the +3 state but mutagenic in the +6 state. Therefore, the speciation of chromium in contaminated environment becomes critical for understanding its fate and exposure. The hydrolysis behavior of Cr(III) is complicated and it produces mononuclear species $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_4^-$ and $Cr(OH)_3^0$, the polynuclear species $Cr_2(OH)_2$ and neutral species $Cr_3(OH)_4^0$. The hydrolysis of Cr^{6+} produces only neutral and anionic species. At pH greater then 6.5, Cr(VI) exists in the form of CrO_4^{2-}. Chromium(VI) compounds are found to be more toxic than Cr(III) compounds because of their high solubility in water and consequently high mobility. The drinking water guideline recommended by the US EPA is 100 µg/L Cr(VI).

Several metal ion removal techniques have been targeted as possible solutions. Ion exchange [3], reduction [4], chemical precipitation [5], polymer based membrane separation [6, 7], adsorption [8], electrochemical precipitation [9], solvent extraction [10], cementation [11] and electro kinetic remediation [12] are among the available methods to accomplish the reduction of metal concentration. Nevertheless many of these approaches are marginally cost effective or

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difficult to implement in developing countries. Therefore, the need arises for a treatment strategy that is simple and robust, and also addresses local resources and constraints. Adsorption is an effective and that versatile method for removing chromium particularly when combined with appropriate regeneration steps. This solves the problems of sludge disposal and renders the system more economically viable especially if low cost adsorbents are used. A variety of activated carbons are commercially available but very few of them are selective for heavy metals and most of them are very costly [13]. Despite the prolific use of activated carbon [14], in wastewater treatment the price of this material is quite expensive and there is a definite need for substitute materials to suit these demanding applications. The solid materials should be able to be regenerated with simultaneous quantitative recovery. For the past few years there has been a developing interest in the preparation of low cost adsorbents as alternatives to activated carbon in water and wastewater treatment processes. In several previous reports, many investigators have studied the feasibility of less expensive materials such as alginate beads [15], wheat straw [16], carbon develop from waste material [17], biosorbents [18], activated sludge [19], fly ash [20], and agricultural waste [21], for the removal of chromium from waste water. However the problems associated with these adsorbents are the regeneration and recovery processes, which made them unattractive for wider commercial applications. This calls for a research effort to develop an industrially viable, cost effective and environmentally compatible technology for the removal of chromium from wastewater. In this study, we have derived a low cost activated carbon from agricultural waste, namely Palmyra palm fruit seed for the removal of hexavalent chromium from synthetic waste water. The same set of experiments was also conducted with a commercial activated carbon for comparison purpose. Palmyra palm tree (Borassus Flabellifer – Arecaceae) is a largely populated tree in south India.

EXPERIMENTAL

Preparation of PPFSC

Palmyra palm fruit seed was cut into small pieces and air-dried. Then it was treated with concentrated sulfuric acid in a ratio of 2:1 (PPFS: H_2SO_4) and the resulting product was kept in oven at 200 ºC for 10 h. The carbonised material was washed with distilled water to remove the free acid and then dried at 105 ºC. The carbon obtained from Palmyra palm seed as well as commercial activated carbon (SD fine chemicals), were sieved to an average diameter of about 0.01125 mm for adsorption experiments. The characterization of carbon [22] was done by ISI procedure. The characteristics of PPFSC and CAC are summarized in Table 1.

Table 1. Characteristics of Palmyra palm fruit seed carbon (PPFSC) and commercial activated carbon (CAC).

S. No.	Control test	PPFSC	CAC
1.	Bulk density (g/L)	0.67	0.56
2.	Moisture %	0.47	0.27
3.	Ash %	3.25	1.20
4.	Solubility in water %	1.40	3.599
5.	Solubility in 0.25 M (HCl) %	2.97	5.41
6.	pH	2.26	9.50
7.	Decolorizing power (mg/g)	15.00	2.25
8.	Phenol number	76.00	88.00
9.	Ion exchange capacity (m. Equiv/g)	0.19	Nil
10.	Surface area (m^2/g)	184.60	421.00
11.	Porosity %	12.16	2.40

Instrument

The chromium(VI) concentration measurements were carried out using Perkin-Elmer 3100 atomic absorption spectrometer. The solution pH was measured with Hanna pH meter using a combined glass electrode. The shaking was carried out in orbital electronic shaker and centrifugation was performed in Hittich EBA20 centrifuge.

Adsorption studies

Stock solution of Cr(VI) was prepared by dissolving appropriate amount of $K_2Cr_2O_7$ in distilled water. This solution was diluted to obtain standard solution containing 3-20 mg/L. Known amounts of PPFSC or CAC were added and solution pH was adjusted using dilute hydrochloric acid or sodium hydroxide. The solution was agitated at 750 rpm in orbital shaker at 30 ºC. The solutions were centrifuged and the amount of Cr(VI) in the supernatant was measured by using atomic absorption spectrometer. Adsorption isotherms were carried out with different initial concentrations of Cr(VI), while the carbon dosage was fixed for the effect of pH. Control experiments were also carried out without adsorbents. The percentage of Cr(VI) adsorption from aqueous solution was computed by the following equation:

$$\text{Adsorption (\%)} = \frac{C_I - C_F}{C_I} \times 100$$

where C_I and C_F are the initial and final chromium(VI) concentrations.

In this study, the contact time was varied between 180 to 300 min, the solution pH of 1.0 to 8.0 and the initial chromium(VI) concentration varying from 3 to 20 mg/100 mL.

RESULTS AND DISCUSSION

Analysis of PPFSC and CAC by SEM and FTIR

The morphological analysis of PPFSC and CAC was performed by scanning electron microscopy. Figures 1 and 2 show the structure of PPFSC and CAC. The irregular surface, bigger holes and cave type of openings are seen on the surface of PPFSC. The pH of PPFSC was found to be 2.26 while CAC found to be 9.84, pH value of PPFSC suggested that the carbon is acidic in nature where as CAC is basic in nature. CAC showed higher surface area of 421 m^2/g than PPFSC, which showed the value of 184.60 m^2/g. The high surface area CAC was mainly due to high temperature carbonisation adopted for CAC in preparation than PPFSC. Commercial carbons have a typical surface area range of about 400 to 1600 m^2/g [23], ion exchange sites compensate lower surface area of PPFSC, by which more removal of metal ion like chromium(VI) may be achieved. Moreover, the high moisture content of PPFSC suggests that the acid treatment has made. The carbon shows more porous, which was shown by porosity value of 12.16 %. This is lower than 2.40 of CAC. The fixed carbon content of a given dry activated carbon is normally obtained by subtracting the ash content from 100, which represents the inorganic portion of the carbon. The ash content indicates that PPFSC has more carbon content. The commercial variety has the least value of ash content indicating that it might have been derived from higher grades of coal such as sub bituminous or semi anthracite. From this it can be concluded that PPFSC is more promising when compared to CAC.
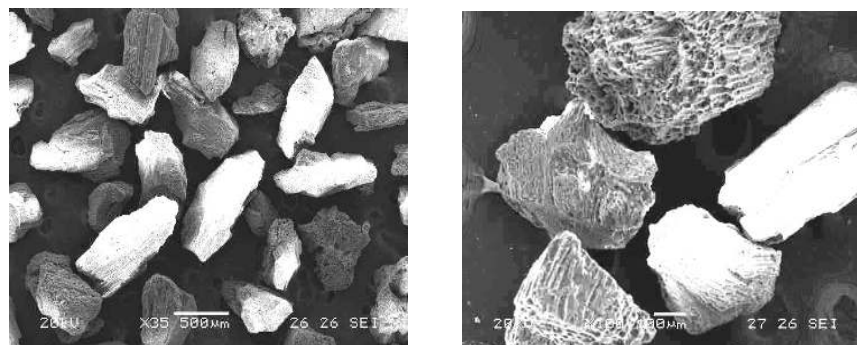
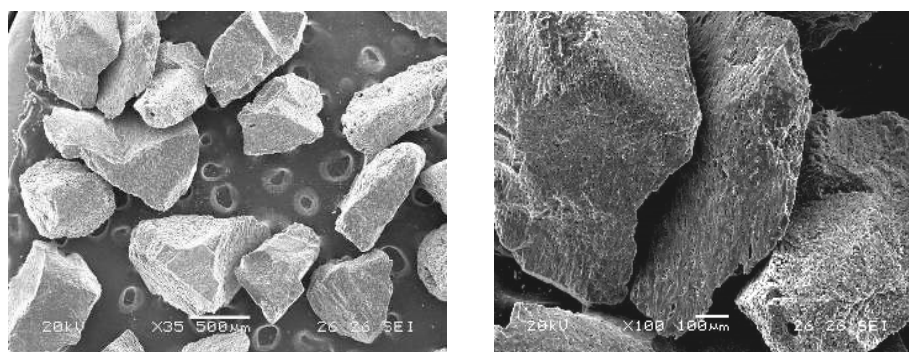Figure 1. SEM-structure of PPFSC (1 x 35) and (1 x 100).

Figure 2. SEM-structure of CAC (1 x 35) and (1 x 100).

The FTIR spectra of PPFSC and CAC are presented in Figure 3 (a) PPFSC and (b) CAC. The FTIR spectra of PPFSC show the absorption band at 3736 cm^{-1} and 3368 cm^{-1} corresponding to the stretching vibration of O-H and N-H, respectively. Strong peaks at 2921 cm^{-1} and 2852 cm^{-1} indicate the presence of C-H, peaks at 2360 cm^{-1} and 2343 cm^{-1} indicate the presence of C≡C. It was reported that the absorption band of both carboxylic and carboxylate groups was about 1716 cm^{-1}, 1706 cm^{-1} and 1669 cm^{-1}, respectively [24] and these major functional groups are responsible for metal ion sorption. The strong peak at 1595 cm^{-1} is due to C=C stretching vibration. The strong peaks at 1201 cm^{-1} and 1167 cm^{-1} are due to the presence of polymeric –SO$_3$H group indicates the favorable for ion exchange mechanism. The presence of sulfonic acid group is confirmed by peaks at 831 cm^{-1} and 786 cm^{-1} due to the stretching vibration of S=O.

The FTIR spectra of CAC show weak absorption bands at 3803 cm^{-1} and 3690 cm^{-1} due to the stretching vibrations of O-H group. Peaks at 2920 cm^{-1} and 2849 cm^{-1} indicate the presence of C-H, while peaks at 2362 cm^{-1} and 2342 cm^{-1} are due to C≡C stretching vibration. The peak at 1561 cm^{-1} is due to aromatic C=C stretching vibration while the weak absorption bands at 1160 cm^{-1} and 1118 cm^{-1} are due to the presence of –SO$_3$H group, indicates the favorable for ion exchange mechanism. The weak absorption bands at 1051 cm^{-1} and 1020 cm^{-1} are the C=O stretching vibration.
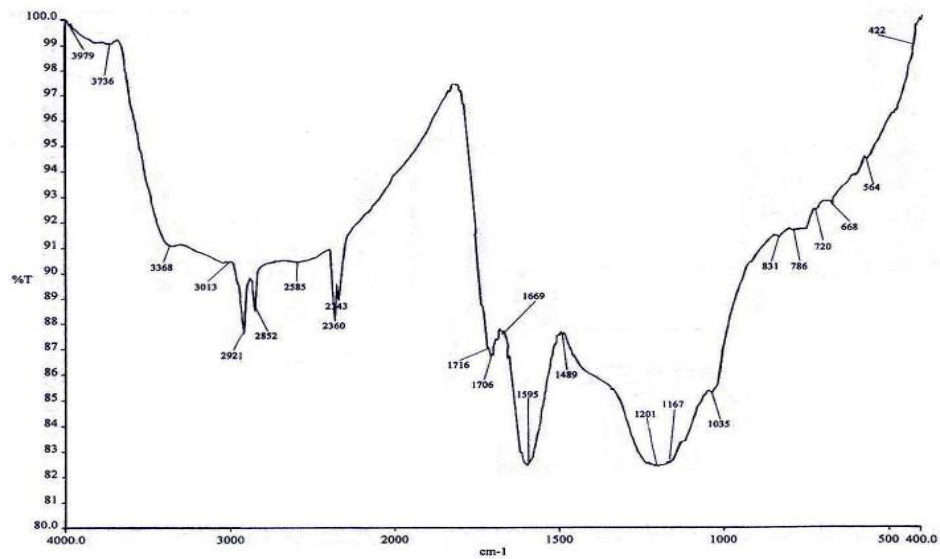
(a) FTIR plot of PPFSC
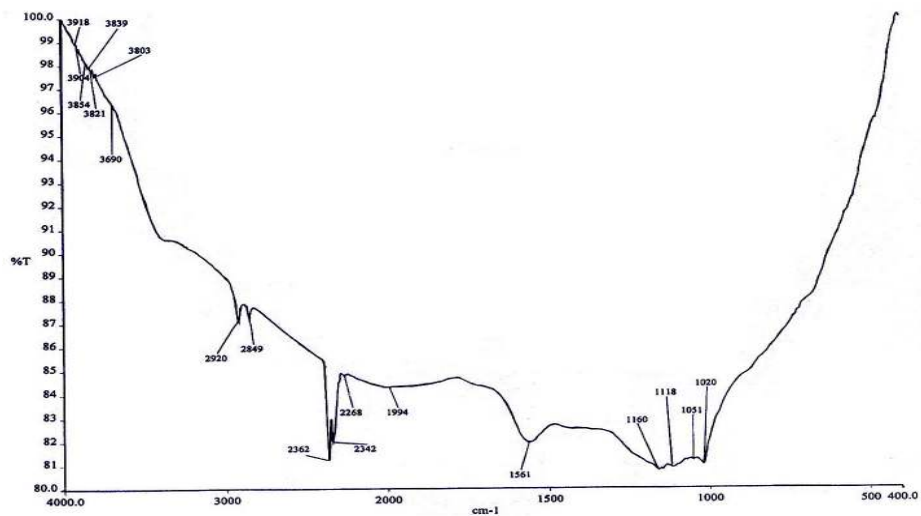
(b) FTIR plot of CAC

Figure 3. FTIR plots of (a) PPFSC and (b) CAC.

Summary of carbon characteristics in Table 1 shows that PPFSC has higher bulk density and ion exchange capacity than CAC. The moisture content in PPFSC suggests that the acid treatment has made the carbon porous. Even though PPFSC shows lower surface area when compared with CAC, it shows considerable ion exchange capacity through which the Cr(VI) removal may be taking place.

Effect of contact time

The effect of contact time on the removal of Cr(VI) was studied in the pH range 1.0 to 2.0 for PPFSC and pH 2.0 for CAC. The amount of adsorbent was fixed 500 mg/100 mL for both carbons and the solutions were equilibrated. An aliquot of the solution was periodically with drawn at an interval of one hour and analyzed using atomic absorption spectrometer to establish the Cr(VI) removal. The results are shown in Figure 4. The percent of removal increases with time and attains equilibrium at 3 h for PPFSC and 5 h for CAC. This indicates that the optimum time required for maximum Cr(VI) removal by PPFSC would be 1.6 times less than that required by CAC.
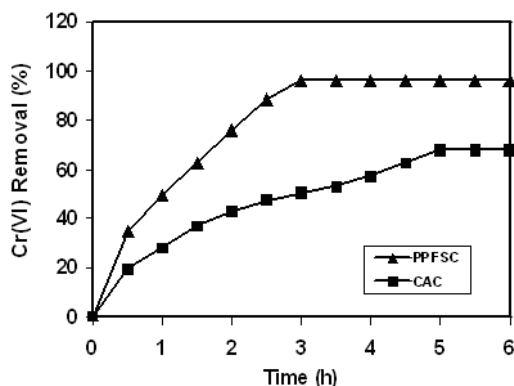

Figure 4. Effect of contact time for the removal of chromium(VI) by PPFSC and CAC.

Effect of pH

pH is one of the most important parameter controlling the metal ion adsorption process. The effect pH on the adsorption of Cr(VI) is attributed to interaction between ions in solution and complex formed at the adsorbent surface. The fact that Cr(VI) in aqueous solution can form different species in the solution at various pH ranges.

This study was carried out at initial Cr(VI) concentration of 20 mg/L. The adsorption of Cr(VI) on the prepared adsorbents decreased with increasing pH. Figure 5 shows that PPFSC and CAC are active in acidic range especially at low pH range. The maximum adsorption of Cr(VI) species on the two different adsorbents was found to be optimum pH 2.0 and negligible at pH over 8.0. Cr(VI) can exist in several stable forms such as CrO_4^{2-}, $HCrO_4^{2-}$, $Cr_2O_7^{2-}$ and $HCr_2O_7^-$, and the relative abundance of a particular complex depends on the concentration of chromium ion and pH of the solution. At low pH, the sorbent is positively charged because of the protonation where as the sorbate like dichromate ions exists mostly as an anion, leading to an electrostatic attraction between the sorbent and the sorbate. This results in increased adsorption at low pH. As the pH of the solution increases, the sorbent undergoes deprotonation, and the adsorption capacity decreases. Therefore all subsequent studies were carried out at pH 2.0. The high removal of Cr(VI) at low pH was reported earlier using different adsorbents [17, 20].
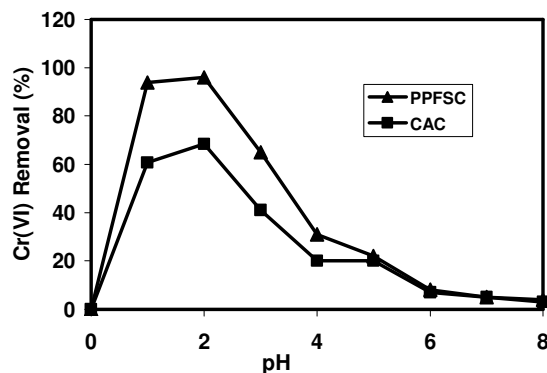
Figure 5. Effect of pH on the removal of chromium(VI) by PPFSC and CAC.

Effect of carbon dosage

The experiments were conducted to find out the minimum amount of carbons required for the removal of Cr(VI). It is evident that for the quantitative removal of 20 mg/L of Cr(VI) in 100 mL reference solution a minimum dosage of 300 mg is required for 94.6 % removal in the case of PPFSC whereas 500 mg is removed only 68 % by CAC as shown in Figure 6. This clearly shows that PPFSC is more effective than CAC.
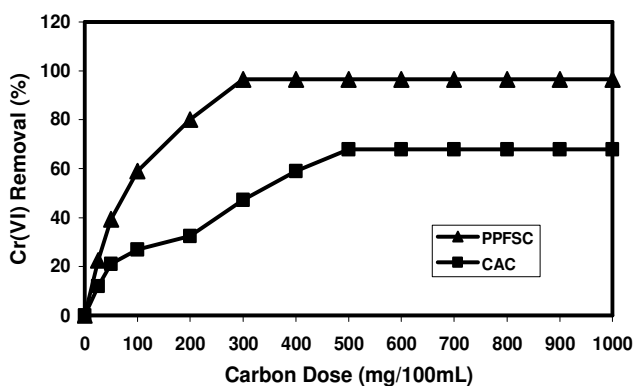

Figure 6. Effect of carbon dosage on the removal of Cr(VI) by PPFSC and CAC, equilibration time 3 h for PPFSC and 5 h for CAC with 20 mg/L of Cr(VI).

Desorption studies

Palmyra palm fruit seed carbon (PPFSC) and commercial activated carbon (CAC) which adsorbed at maximum concentration of Cr(VI) was used for desorption studies. Desorption of Cr(VI) was achieved by using HCl acid strength varying from 0.02-0.2 M. The PPFSC carrying 32.14 mg Cr(VI)/g and CAC carrying 8.23 mg Cr(VI)/g were placed in the desorption medium and stirred at 750 rpm at 30 °C. The final Cr(VI) ion concentration in the aqueous phase was determined by using atomic absorption spectrometer and desorption ratio was calculated from the amount of metal ion adsorbed on the carbons and the final metal ion concentration in the desorption medium using the following equation. The results are shown in Figure 7. It is seen

that 0.2 M HCl from PPFSC and CAC could desorbs maximum of 86.6 % and 55.5 %, respectively. It could be seen that more amount of chromium(VI) could be recovered from PPFSC than CAC.

$$\text{Desorption ratio (\%)} = \frac{Amount\ of\ metal\ ions\ desorbed}{Amount\ of\ metal\ ions\ adsorbed} \times 100$$
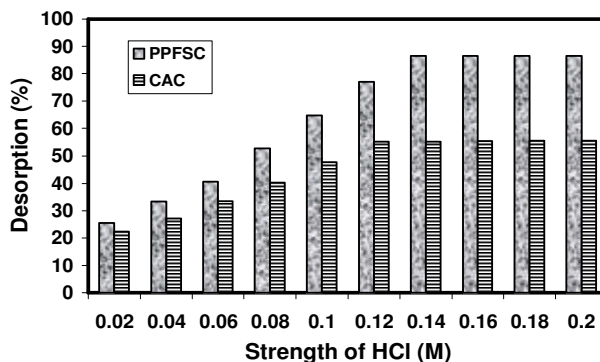

Figure 7. Desorption studies using various strength of HCl by PPFSC and CAC.

Adsorption isotherms

Freundlich adsorption isotherm. The Freundlich equation was applied to describe the analytical results on the adsorption. Its empirical result agrees quit well with Langmuir equation and experimental data over a moderate range of adsorbate concentration. It is represented by the equation [25]

$\log x/m = \log K + 1/n \log C_{eq}$

where C_{eq} is the equilibrium concentration (mg/L), x/m is the amount adsorbed per unit mass of PPFSC or CAC (mg/g), n is the indication of favorability and K is the capacity of the adsorbent. Plotting $\log x/m$ vs. $\log C_{eq}$ gives a straight line with a slope of $1/n$ and $\log K$ is the intercept, and r^2 values of PPFSC 0.9920 and CAC 0.9434 shows the linearity. The plots are represented in the Figure 8. The calculated K values were 1.1885 for PPFSC and 1.3646 for CAC while the values of n were calculated to be 5.1795 and 2.1543 for PPFSC and CAC, respectively. The values of $1 < n < 10$ shows favorable adsorption of Cr(VI) on both PPFSC and CAC [26].

Langmuir adsorption isotherm. Langmuir equation was also applied for adsorption equilibrium for both carbons. The Langmuir model is based on the assumption that maximum adsorption corresponds to monolayer of adsorbate molecules on the adsorbent surface, the constant energy of adsorption given by Langmuir isotherm and there is no transmigration of adsorbate in the plane of the surface.

$C_e/q_e = 1/Q_0 b + C_e/Q_0$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), Q_0 is the monolayer adsorption capacity (mg/g) and b is a constant related to the free energy of adsorption.

The linear plots of C_e/q_e vs. C_e in Figure 9 show that the adsorption obeys Langmuir adsorption model for PPFSC, CAC and r^2 values of PPFSC 0.9751 and CAC 0.8232 shows the linearity. Q_0 and b were determined from the plots and found to be 32.14 mg/g and 1.00 mg/L

for PPFSC and 8.23 mg/g and 2.05 mg/L for CAC, respectively. The ratio of Q_0 between PPFSC and CAC works out to be 3.9052. The essential characteristics of Langmuir isotherm are expressed in terms of a dimensionless constant separation factor or equilibrium parameter RL, which is defined by

RL = 1 / (1 + bC_o)

where b is the Langmuir constant and C_o is the initial concentration of Cr(VI). The parameter indicates the isotherm shapes as shown in Table 2. The observed values of RL between 0 and 1 indicate favorable adsorption of Cr(VI) on both PPFSC and CAC at the concentration studied at 30 ˚C. RL values for both PPFSC and CAC are 0.0476 and 0.2500, respectively.
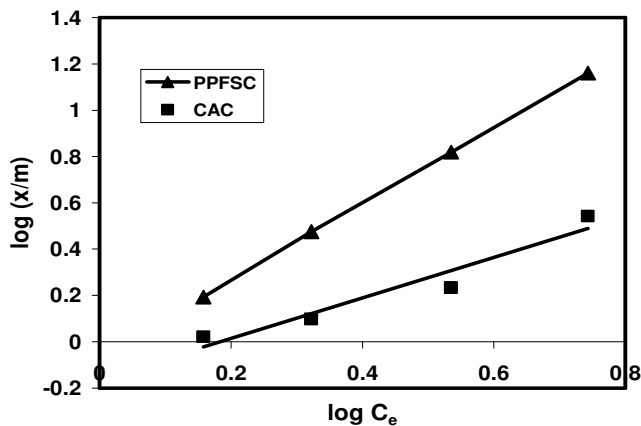

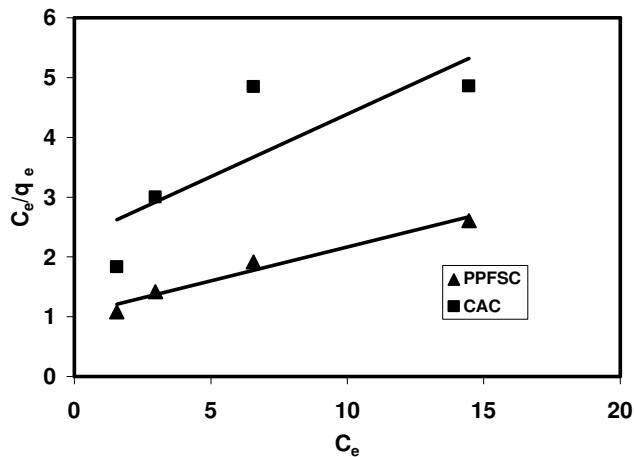Figure 8. Freundlich adsorption isotherm for chromium(VI) with PPFSC and CAC.

Figure 9. Langmuir adsorption isotherm for chromium(VI) with PPFSC and CAC.

Table 2. Characteristics of langmuir adsorption isotherms.

S. No.	Separation factor R_L	Types of Isotherm
1	$R_L > 1$	Unfavorable
2	$R_L = 1$	Linear
3	$0 < R_L < 1$	Favorable
4	$R_L > 0$	Irreversible

Kinetic studies

The kinetics of Cr(VI) adsorption on both PPFSC and CAC were evaluated by the first order rate expression [27].

$$\ln (1-U_t) = -K_t$$

where $U_t = (C_0-C_t) / (C_0-C_e)$. C_0, C_t and C_e are concentration in mg/L of Cr(VI) at initially, time t and equilibrium, respectively. A straight-line plot of $\ln (1-U_t)$ vs. time Figures 10 and 11 indicate that the adsorption process follows the first order kinetics. The straight-line portions of the curves were used for calculating the slope which gives the overall rate constant, K of the process.

The forward (k_1) and backward (k_2) rate constants were calculated using the following equation

$$K = k_1 + k_2$$

$$k_2 = (k_1/K_c)$$

$$K = k_1 (1 + (1/K_c))$$

$$K_c = k_1/k_2$$

where K_c is the equilibrium constant. The kinetic data are given in Table 3. It is evident that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is clearly dominant for both carbon. In order to assess the nature of diffusion process reasonable for the adsorption of Cr(VI) on PPFSC and CAC, attempts were made to calculate the pore and film diffusion coefficients for various concentration of Cr(VI) using the following equation [28].

$$D_p = 0.03 \; r_o^2 / t_{1/2}$$

$$D_f = 0.23 \; r_o \; \partial \; C^*/C \; t_{1/2}$$

where D_p and D_f are the pore and film diffusion coefficients, respectively, both expressed in cm^2/s, r_o is the radius of the sorbent expressed in cm, and $t_{1/2}$ is the half-life period in sec. ∂ is the film thickness expressed in cm and C^*/C is equilibrium loading of the sorbent. According to the adsorption of heavy metals on carbon surface, for film diffusion to be the rate determining process, the value of film diffusion co-efficient should be between 10^{-6}-10^{-8} cm^2/s [29]. If pore diffusion were to be the rate-limiting factor, the pore diffusion co-efficient must be closer to the range of 10^{-11}-10^{-13} cm^2/s. It is evident that the removal of Cr(VI) follows film diffusion process, since the coefficient values are close to the range of 10^{-6}-10^{-8} cm^2/s and these values are shown in Table 4.
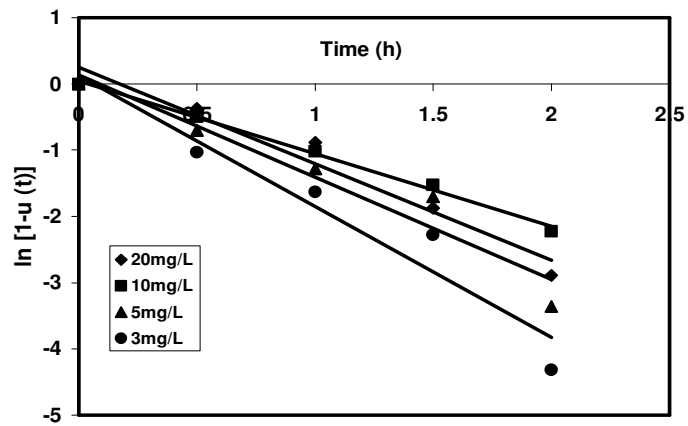
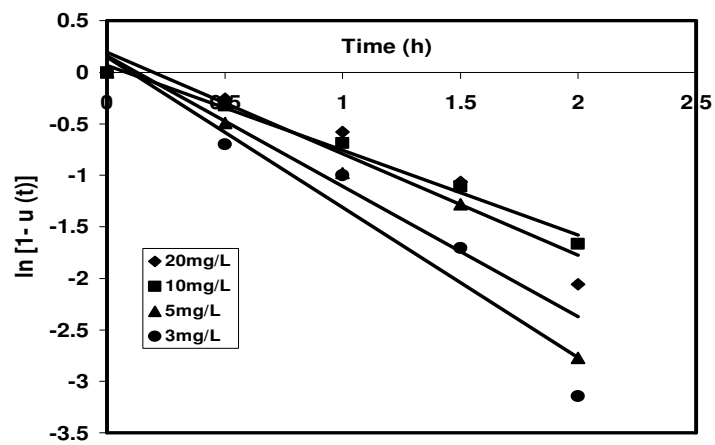Figure 10. Lagergren plots for the removal of Cr(VI) by PPFSC.

Figure 11. Lagergren plots for the removal of Cr(VI) By CAC.

Table 3. Rate constants for the removal of chromium(VI) by PPFSC and CAC.

Carbon	Initial concentration of Cr(VI) ions(mg/L)	Overall rate constant $K\ h^{-1}\ (k_1 + k_2)$	Forward rate constant $k_1\ h^{-1}$	Backward rate constant $k_2\ h^{-1}$
PPFSC	20	0.5600	0.4077	0.1523
	10	0.6000	0.3942	0.2058
	5	0.6000	0.3576	0.2869
	3	0.7000	0.4131	0.2869
CAC	20	0.5833	0.4818	0.1015
	10	0.5833	0.4836	0.0997
	5	0.6333	0.4750	0.1583
	3	0.7000	0.4550	0.2450

Table 4. Diffusion coefficient of the sorbents for the removal of chromium(VI) by PPFSC and CAC.

Sorbent	Initial concentration of Cr(VI) ions (mg/L)	Film diffusion (D_f) (cm^2/s)	Pore diffusion (D_p) (cm^2/s)
PPFSC	20	2.0996×10^{-9}	2.1307×10^{-10}
	10	2.2829×10^{-9}	2.0442×10^{-10}
	5	2.2829×10^{-9}	1.8544×10^{-10}
	3	2.6634×10^{-9}	1.8876×10^{-10}
CAC	20	2.2193×10^{-9}	2.4985×10^{-10}
	10	2.2193×10^{-9}	2.5076×10^{-10}
	5	2.4095×10^{-9}	2.4630×10^{-10}
	3	2.6634×10^{-9}	2.3595×10^{-10}

Experiments with tannery industrial wastewater

The suitability of the carbon derived from Palmyra palm fruit seed carbon (PPFSC) and commercial activated carbon (CAC) was also evaluated for the removal of chromium(VI) in tannery industrial wastewater. Experiments were conducted with chromium(VI) effluent from tannery industry around Vellore district, Tamil Nadu, India. The characteristic of the wastewater is shown in Table 5. The wastewater was taken and diluted 20 times because of its high Cr(VI) concentration. The experiments were conducted at optimum pH with 100 mL of 167 mg/L of Cr(VI) solution with different carbons doses of PPFSC and CAC. Then the solutions were equilibrated for 5 h. The percent of Cr(VI) removal in each instance was established by usual procedure. Figure 12 shows that maximum Cr(VI) removal was 89 % using 3.5 g of PPFSC and only 63 % achieved with 5.75 g of CAC. This indicates that PPFSC is more effective for treatment of tannery wastewater when compared to CAC.

Table 5. The characteristics of tannery industrial wastewater.

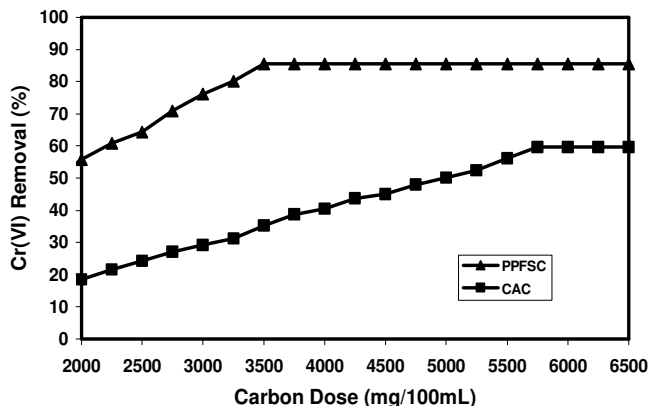| Parameters	Concentration (mg/L)
pH	8.5
Total solids	8540
Chromium(VI)	4520
Potassium	87.0
Magnesium	138.3
Sodium	748.5
Chloride	679.0
Sulfate	520.0

Figure 12. Application to tannery wastewater using various amounts of carbon on the removal of
       Cr(VI) by PPFSC and CAC.

CONCLUSIONS

This study shows that Palmyra palm fruit seed carbon was an effective adsorbent for the removal
and recovery of Cr(VI) from aqueous solution. Adsorption of Cr(VI) was highly pH dependent
and the results showed that the optimum pH for the removal was found to be in the range of 1.0
to 2.0, at which Cr(VI) exists as the most easily adsorbed form. These two carbons confirm to
Freundlich and Langmuir equations based on the assumption of monolayer adsorption. Q_0 values
show that 3.9 times as higher as commercial activated carbon shows the higher adsorption
capacity of PPFSC. The adsorption capacity of PPFSC is found to be higher than CAC based
upon its carboxylic and carboxylate as major functional groups that responsible for Cr(VI)
sorption. It is also abundantly available as a waste material, which can be processed as an
alternative to replace of CAC. The adsorption of Cr(VI) on both carbons has been well fitted for
the reversible first order kinetics with film diffusion being the essential rate-controlling step.
The kinetic data would be useful for fabrication and designing the wastewater treatment plants.
It is concluded that in addition to the above advantages, activated carbon prepared from Palmyra
palm fruit seed could also be considered for commercial application.

AKNOWLEDGEMENTS

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