Removal of Cr (VI) from aqueous solution by adsorption using cooked tea dust

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Abstract: Chromium is considered one of the 14 most noxious heavy metals. In the present investigation, an attempt was made to remove chromium (VI) from aqueous solution using decolorized Cooked Tea Dust (CTD) by adsorption technique. Batch mode adsorptive removal was carried out at varying pH (2 -11), agitation time (5 - 60 min), particle size (125 - 750 μm) and adsorbent dosage (50 - 500 mg/50ml). The optimum pH for Cr (VI) adsorption on CTD was found to be 2.0. Adsorption equilibrium was obtained in 45, 50, 40, 45 and 45 min for the initial Cr (VI) concentrations of 25, 50, 75, 100 and 125 mg/l respectively. Results conformed to both Langmuir and Freundlich adsorption models for adsorption equilibrium of Cr (VI) onto CTD. The adsorption followed the pseudo second-order kinetics. The Langmuir adsorption capacity was found to be 30.39 mg/g while Freundlich constants *Kf* and *n* were 7.524 and 2.673, respectively. Desorption studies indicated 82.28% removal of the hexavalent chromium from the adsorbent.
Key words: Cr (VI) removal, cooked tea dust, adsorption, Langmuir isotherm, Freundlich isotherm.

Introduction

Release of heavy metals into the biosphere by human activity has enormously increased since industrialization there by impacted geochemical cycling and food chain. Anthropogenic sources such as industrial point sources, combustion by-products, automobile emissions, present and former mining activities, foundries and smelters, and diffuse sources such as piping, constituents of products etc, contribute to anomalously high concentrations of metals in the environment relative to the normal background levels (Irwin, 1997; Neytzell-De Wilde, 1991). Concentration of heavy metals namely chromium, lead, nickel, mercury and cadmium in the aquatic environments are known to cause physiological disorders in organisms and phytotoxicity. Among the toxic heavy metals, Chromium, in its hexavalent form is known to cause wide ranging human health effects including mutagenic and carcinogenic risks (Park & Jung, 2001).

Chromium is widely used in electroplating, leather tanning, metal finishing and chromate preparation. The untreated effluent from electroplating industry contains approximately 100 mg/l Cr (VI) (De Filippis & Pallaghy, 1994), which is much higher than the permissible limit of 0.05 mg/l (BIS, 1991).Various kinds of physical, chemical and biological processes are being applied for the removal of Cr (VI) from wastewater. The commonly used techniques include chemical precipitation, reverse osmosis, evaporation, ion exchange and adsorption, of which adsorption has proved to be very effective. Several studies are reported using adsorbents such as wool, rice, straw, coconut husks, peat moss (Dakiky *et al*., 2002), walnut skin, coconut fibre (Espinola *et al*., 1999) and cotton seed hulls (Marshall & Champagnee, 1995; Tarley *et al*., 2004). Some studies had also utilized waste products like distillery sludge (Selvaraj *et al*., 2003), sawdust, mustard seed cakes, (Iqbal *et al*., 2002; Saeed *et al*., 2002), and coconut waste (Selvi *et al*., 2001). In spite of these developments quest for more techniques that are cost effective is still wanting.

Cooked Tea Dust, which is discarded as waste from teashops, restaurant and hotels has been investigated in the current study for its property to remove Cr (VI) from aqueous

Table 1. Characteristics of CTD used in the experiments

Parameters	Values
pH	6.35
Bulk density (g/cm^3)	0.29
Moisture content (%)	9.46
Specific gravity	0.37
Water soluble components (%)	5.3
Water holding capacity (%)	11.29

solutions.

Materials and methods

Adsorbent preparation
The cooked tea dust (CTD) was collected from teashops and hotels in and around the Tiruchirappalli city, Tamil Nadu State, India. CTD was decolorized using distilled water, dried at 105 ^{o}C for 24 hrs. The dried material was ground

and sieved to get the particle size range of 125-250µm (21.30%), 250-500µm (62.74%) and 500-750µm (15.96%), which was used for this study. The physical characteristics of the adsorbent are shown in Table 1.

Batch mode adsorption studies

Batch mode adsorption studies were performed with 50 mg of adsorbent and 50 ml Cr(VI) solution of desired concentrations (25-125 mg/l) at an initial pH of 2 in 250 ml conical flasks, and were agitated at 120 rpm for predetermined time intervals at room temperature (30 ± 2°C) in a mechanical shaker. After agitation, the adsorbent and adsorbate were separated by centrifuging at 10000 rpm for 20 minutes. Cr (VI) was estimated spectrophotometrically at 540nm using 1, 5-diphenyl carbazide method (APHA, 1985). Effect of the duration of agitation on removal was studied with Cr (VI) concentrations varying from 25 to 125 mg/l. Effect of adsorbent dosage was explored with the same concentrations of Cr (VI) solution, by varying the CTD dosage from 50 to 500mg. To study the effect of pH on Cr (VI) removal, Cr (IV) solution containing 75 and 100 mg/l was used.

Fourier transformed infrared spectroscopy

The infrared spectra were obtained using Perkin-Elmer Spectrum One FTIR spectrometer. The FTIR spectra before and after adsorption of CTD are shown in Figure 1A and B.

Desorption Studies

After adsorption experiments with 50 ml of Cr (VI) solution and 50 mg of CTD, the metal ion laden CTD was separated out from the aqueous

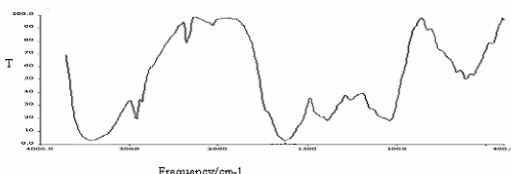*Fig.1. (A) FTIR spectra of CTD before adsorption and (B) FTIR spectra of CTD after adsorption*

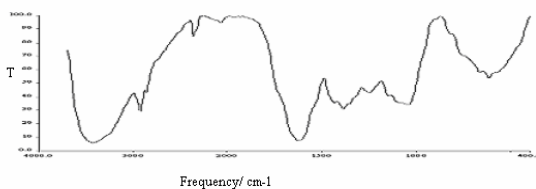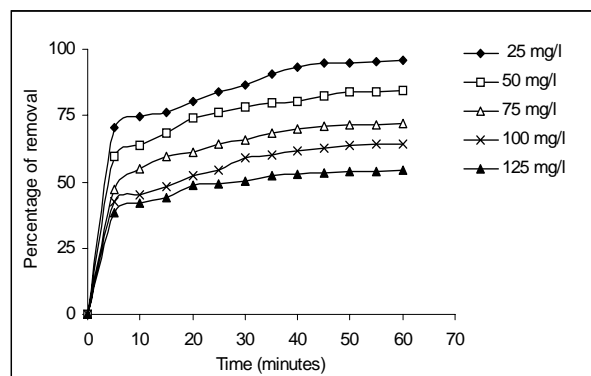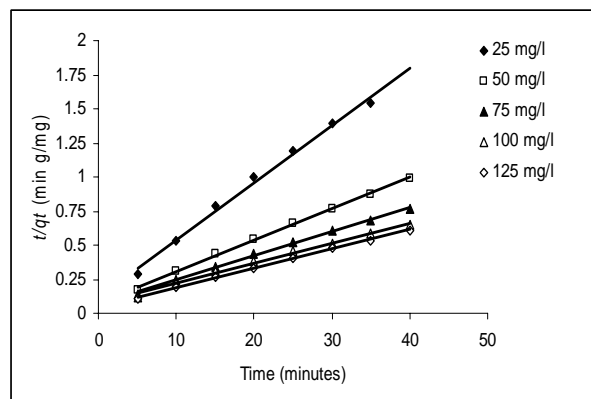Figure (1.B) After Adsorption

Figure (1.A) Before Adsorption

Figure 2. Effect of agitation time on Cr (VI) removal, (Experimental conditions: pH: 2, agitations speed: 120 rpm)

solution. The CTD was given a gentle wash with double distilled water to remove unadsorbed metal ions. Desorption studies were carried out by agitating the metal loaded CTD with 50 ml of NaOH of various strengths (0.001 to 1N). Adsorbent was separated from the aqueous

Figure 3. Second order kinetics, (Experimental conditions pH: 2, adsorbent dose: 50 mg, Cr (VI) concentration: 25-125 mg/l, agitation speed: 120 rpm)

solution by centrifugation and the supernatant was analyzed as mentioned above.

Results

Fourier transformed infrared spectroscopy (FTIR) analysis

The FTIR spectra before and after adsorption of tea factory waste are shown in Figure 1A and B, and the FTIR spectroscopic characteristics are shown in Table 2. As shown in Figure 1A and B, the spectra display a number of absorption peaks, indicating the complex nature of the material examined. The FTIR spectroscopic analysis indicated bands at 3429 cm−1, representing

bonded -OH groups. The bands observed at about 2915-2848 cm−1 could be assigned to the aliphatic C-H group. The peak around 1628 cm^{-1} correspond to the C=O stretch. The peaks observed at 2361 cm^{-1} correspond to the primary amine group. The peaks observed at 1249, 664, 616 cm^{-1} and 1044 cm^{-1} could be assigned to -CN stretching, C-O stretching of ether groups respectively. As seen in Table 2, the spectral analysis before and after metal adsorption indicated that the -CN stretching, aliphatic C-H group, C-O stretching, and bonded -OH groups were especially involved in Cr (VI) adsorption.

Effect of agitation time and initial Cr (VI) concentration on Cr (VI) adsorption

The effect of agitation time on various concentrations of chromium solutions (25 to 125 mg/l) is presented in Figure 2. The removal rate was rapid during first 10 min of agitation. Then the rate slowed down gradually until it attained an equilibrium beyond which there was no significant increase in the rate of removal. Adsorption equilibrium was obtained at 45, 50, 40, 45 and 45 min for the Cr (VI) concentrations of 25, 50, 75, 100 and 125 mg/l respectively. Data indicated that the maximum percentage adsorption was 95.61%, 84.35%, 71.97%, 64.13% and 54.32% respectively, for the initial Cr (VI) concentrations of 25, 50, 75, 100 and 125 mg/l.

Effect of adsorbent dosage

Increasing adsorbent concentration increased the percent removal. For the complete removal of Cr (VI) from 50 ml of 25 mg/l CTD a dosage of 350 mg was required. Availability of more surface functional groups and surface area at increasing dosage is directly proportional to Cr (VI) adsorption (Kadirvelu *et al.*, 2000).

Kinetic study

In order to find out the potential rate-controlling steps involved in the process of adsorption of Cr (VI) onto CTD, both pseudo first-order and pseudo second order kinetic models were used to fit the experimental data at various concentrations.

The pseudo first-order rate expression of Lagergren model is generally expressed as follows Eq. (1)

$$dq/dt = k_{1, ad}(q_{eq} - q) \qquad \mathbf{1}$$

The integrated form of Eq. (2) is

$$Log(q_{eq} - q) = log\, q_{eq} - k_{1, ad}\, t / 2.303 \qquad \mathbf{2}$$

However, to fit Eq. (2) to the experimental data, the value of q_{eq} (equilibrium adsorption density)

must be pre-estimated by extrapolating the experimental data to $t = \infty$. In most cases, the first-order rate equation of Lagergren is usually applicable over the initial 30-50 min of the adsorption process (Aksu, 2001). The rate constants $k_{1, ad}$ and theoretical values of q_{eq} calculated from the slope and intercept of the linear plots are summarized in Table 3, along with the corresponding correlation coefficients.

The pseudo second-order kinetic rate equation is expressed as Eq (3)

$$dq/dt = k_{2, ad}(q_{eq} - q)^2 \qquad \mathbf{3}$$

The integrated form is given as Eq (4)

$$t/q = 1/k_{2, ad}\, q^2_{eq} + t/q_{eq} \qquad \mathbf{4}$$

By plotting t/q against t for the different concentrations, straight lines were obtained as shown in Figure 3. Second order rate constants

Fig. 4. Longmuir isotherms, (Experimental conditions pH: 2, adsorbent dose; 50 mg, Cr (VI) concentration; 25-125 mg/l, agitation speed; 120 rpm)

$y = 28.548x - 1.5246$
$R^2 = 0.94$
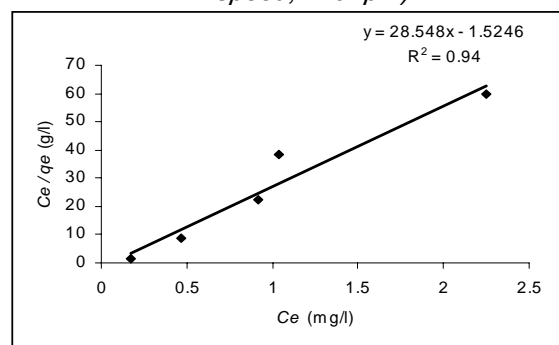
$k_{2, ad}$ and q_{eq} values presented in Table 3 were

Fig. 5. Freundlich isotherms, (experimental condition: pH; 2, adsorbent dose; 50 mg, Cr (VI) concentration; 25-125 mg/l, agitation speed; 120 rpm)

$y = 0.374x + 0.8765$
$R^2 = 0.8973$
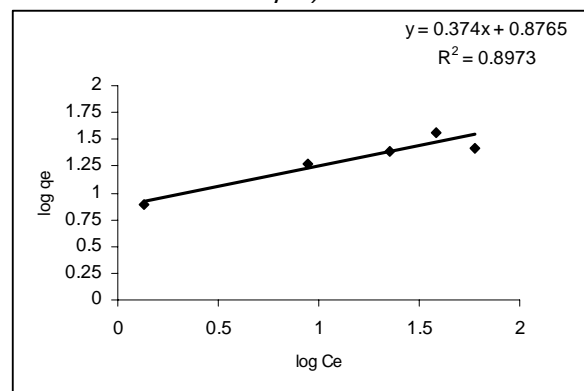
determined from the slopes and intercepts of the plots in Figure 3.

The results of Table 3 shows that the second-order rate constant $k_{2, ad}$ decreased with increasing concentrations. The correlation coefficients for the second-order kinetic model were close to 1.0 for all cases, and the theoretical values of q_{eq} also agreed well with the experimental data. On the other hand, the correlation coefficients for the pseudo first-order kinetics were lower than that from pseudo second-order one. In addition, the theoretical q_{eq} values calculated from the first-order kinetic model did not give reasonable values and it showed obvious deviation from the experimental ones. Furthermore, the values of $k_{1, ad}$ obtained from the former had no obvious trend of rise or fall with increase in concentration. These imply that the adsorption of Cr (VI) on CTD followed

Fig. 6. Effect of Particle size, Experimental Conditions: Cr (VI) Concentrations; 100mg/l, agitation time; 10minutes, agitation speed; 120rpm, pH 2
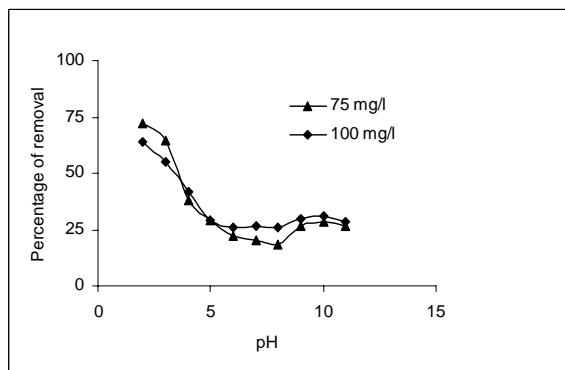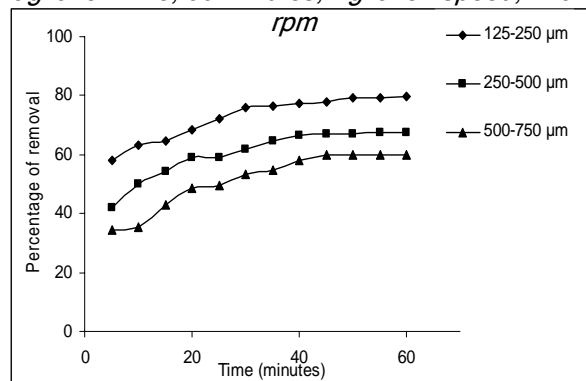

the second-order kinetics.

Adsorption isotherms

    The adsorption of Cr (VI) on the adsorbent particles utilized in this study was analyzed using Langmuir and Freundlich, isotherm models. Isotherm studies were conducted at the effective initial pH 2 and 120

Fig. 7. Effect of pH (Experimental conditions: agitation time; 60 minutes, Agitation speed; 120 rpm

rpm agitation rate. According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at the site. The Langmuir model is given by Eq (5),

$$C_e / q_e = 1 / (Q_0 b) + C_e / Q_0 \qquad \mathbf{5}$$

Where, C_e is the equilibrium concentration mg/l, q_e is the amount of Cr(VI) adsorbed at equilibrium (mg/g) and Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively . The linear plots of C_e/q_e vs. C_e show that the adsorption obeys Langmuir isotherm model Figure 4. Q_0 and b were determined from the slope and intercept of the plot and presented in Table 4.

    The Langmuir parameters can be used to predict the affinity between the adsorbate and adsorbent using the dimensionless separation

Table 2. The FTIR spectral characteristics of CTD before and after adsorption

IR Peak	Before adsorption	After adsorption	Difference	Assignment
	Frequency (cm^{-1})			
1	3429	3430	+1	Bonded -OH group
2	2924	2925	+1	Aliphatic C-H group
3	2855	2856	+1	Aliphatic C-H group
4	2361	2362	+1	Primary amine stretching
5	1628	1626	-2	C=O stretching
6	1385	1389	+4	Aliphatic C-H group
7	1249	1262	+13	-CN stretching
8	1044	1040	-4	C-O stretching of ether group
9	664	666	+2	-CN stretching
10	616	615	-1	-CN stretching

factor, R_L, defined by (Hall *et al.*, 1966) as Eq. (6)

$$R_L = 1/1 + bC_o \qquad \textbf{6}$$

Where C_0 is the initial metal concentration (mg/l) and b is the Langmuir constant (1/mg). R_L values obtained using for Cr(VI) adsorption are greater than zero and less than unity showing favorable adsorption of Cr(VI) onto CTD Table 5.

Freundlich isotherm model was also used to explain the observed phenomenon (Freundlich, 1906). The Freundlich isotherm is represented by Eq. (7) (Slejko, 1985),

$$\log q_e = \log Kf + (1/n) \log C_e \qquad \textbf{7}$$

Where, C_e is the equilibrium concentration (mg/l), Kf and n are constant incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. Linear plots of log q_e vs log C_e shows that the adsorption follows Freundlich isotherm model as well Figure 5. Kf and n calculated from the intercept and slope of the plots were found to be 7.5248 and 2.6737 respectively. According to Treyball (1980) the values of n between 1 and 10 is considered as good adsorbent. Therefore CTD which has an n value of 2.6737 implies effective adsorption.

Effect of Particle Size on Cr (VI) removal

availability of more surface area for adsorption (Shanmugavalli *et al.*, 2007).

Effect of pH

Cr (VI) adsorption increased on to CTD with decreasing pH values with maximum of 71.97% and 64.13% for two different chromium solutions of 75 and 100 mg/l respectively at pH 2 (Fig. 7). At acidic pH, the predominant species of Cr (VI) are $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-}. Under acidic conditions, the surface of the adsorbent becomes protonated and attracts anionic species of Cr (VI).

Desorption studies

Desorption studies attempted to recover Cr (IV) from metal ion loaded adsorbent with various concentrations of sodium hydroxide. The results showed that a maximum desorption of 82.28% Cr (VI) was achieved using 1N NaOH. At higher pH, hydroxyl ions may release chromium ions from the adsorbent following an ion exchange mechanism (Selvaraj *et al.*, 2003).

Conclusions

Cooked Tea Dust, which is discarded as waste material from teashops and hotels, are effective as an adsorbent for the removal of Cr (VI) from aqueous solution. From FTIR study, -CN stretch, C-O stretching of ether groups, aliphatic C-H group and primary amine groups

Table 3. First-order and second-order adsorption rate constants of Chromium (VI) at different concentrations.

Concentration (mg/l)	First-order constants			Second-order constants			Measured $q_{eq, exp}$ (mg/g)
	$K_{1, ad}$ (min^{-1})	$q_{eq,cal}$ (mg/g)	R^2	$K_{2, ad}$ (g/(mg min)	$q_{eq,cal}$ (mg/g)	R^2	
25	0.04675	7.72	0.972	0.01489	23.75	0.994	23.35
50	0.07392	18.84	0.992	0.00709	43.29	0.998	41.23
75	0.06517	24.66	0.978	0.00474	56.17	0.997	53.26
100	0.07185	36.96	0.929	0.00295	68.02	0.991	62.7
125	0.07047	26.49	0.967	0.00042	70.92	0.997	66.11

The percent removal of Cr (VI) decreased with increase in particle size of the adsorbent. The metal removal with particle size of adsorbents 125-250 μm, 250-500 μm & 500-750 μm ranges from 79.49, 67.67 & 59.98 percent respectively Figure 6. The equilibrium time attained was 50, 45 & 45 min for the particle size of 125-250 μm, 250-500 μm and 500-750 μm respectively at 100 mg/l concentration of Cr (VI). Higher percent removal with lower particle size is due to

are the main functional groups of CTD in metal

Table 4. The values of R_L for adsorption of Cr (VI) on CTD

Q_o (mg/g)	b (1/mg)	Initial Cr(VI) concentration C_0 (mg/l)	R_L
30.3951	0.3037	25	0.1163
		50	0.0617
		75	0.0420
		100	0.0318
		125	0.0256

binding. The adsorption depends on solution pH, Cr (IV) concentration, adsorbent dose and particle size of adsorbent. The adsorption followed both Langmuir & Freundlich isotherm models. Desorption study shows that the recycling of adsorbent and adsorbate may be possible.

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Table 5. Characteristics of adsorption - Longmuir isotherms

Separation factor, R_L	Characteristics of adsorption Longmuir isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible