Adsorption Isotherm and Kinetics of Tannic Acid on to Carbonized Chrome Tanned Leather Solid Waste

by

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Abstract

The disposal of chrome tanned leather shavings (CTLS) waste is a serious concern for the environment due to the presence of chromium. In this study, an attempt has been made to prepare adsorbent from CTLS through carbonization process. Carbonization of CTLS at temperature 600°C had provided surface area of 620 m^2 g^{-1} and total pore volume of 0.49 cm^3 g^{-1}. The adsorption study is conducted by employing adsorbent prepared from CTLS on adsorbate tannic acid. The effects of various experimental parameters have been investigated using a batch adsorption technique to obtain information on treating wastewater containing tannic acid. The extent of tannic acid removal was studied by varying parameters such as pH, contact time, initial concentration of the tannic acid and amount of adsorbent. The removal efficiency of tannic acid in aqueous solution is found to be about 95%. The experimental equilibrium data for this system has been analyzed using the linearized forms of Langmuir and Freundlich isotherms. The Langmuir isotherm was found to provide the best theoretical correlation of the experimental data for the adsorption of tannic acid. The adsorption of tannic acid on adsorbent increased from 57 to 63 mg g^{-1}, when the temperature was increased from 30 to 60°C. The adsorption was found to follow pseudo-second order kinetics. In short, this study provides a greener solution for CTLS and tannin containing wastewater.

Introduction

The leather industry generates chromium based waste such as chromium sludge, chrome tanned leather shavings (CTLS), chrome leather trimmings etc. Thus, only 20% of the raw material weight is converted to leather.[1] Worldwide chromium based tanning process is predominantly followed[2] due to versatility of chromium. These wastes are unavoidable and possess serious threat to the environment. Nearly, 0.8 million ton of CTLS could be generated per year globally.[3] Large quantities of CTLS are disposed by landfill in many parts of the world.[4] Land filling scenario faces the highest cost, which is explained by the combination of the overall high pollution emissions and low energy recovery. The CTLS has the potential to be used as a low cost adsorbent for the removal of surfactants, dyes and heavy metals (As (V) and Cr (VI)) from wastewater.[5-7] The removal of vegetable tannins from mixed effluents using CTLS has been attempted.[8] Use of CTLS for the removal of dyes from wastewater has been studied and the dye-adsorbed solid wastes were used for the preparation of pigments.[9] Adsorption is the most versatile and widely used technology, and activated carbon, the most commonly used sorbent for all kinds of wastewater treatment. However, the use of activated carbon is expensive, so there has been increased interest in the past years in the use of low cost adsorbent materials. CTLS used as raw material for activated carbon production by physical and chemical activation methods.[10] Chrome containing activated carbon prepared from CTLS was studied for removal of organic dyes in wastewater.[11-12] Activated carbon produced from CTLS had high specific surface area and high capacity for removal organic substance in aqueous medium.[13] The potential application of these activated carbons obtained from CTLS as adsorbent for removal of water pollutants have been studied for phenol, methylene blue, and Cr (VI).[7, 14]

Tannic acid is a commercial polyphenolic tannin and widely used in various industries. It is an organic pollutant of relatively high molecular weight contributes to chemical oxygen demand in wastewater. It is known as poor biodegradable substance. Tannins are a basic ingredient in the chemical staining of wood. Tannic acid is a commonly used in mordanting of cellulose fibers such as cotton and leather tanning. Tannic acid is also used to improve wash fastness properties of acid dyed polyamide. It is highly found in industrial wastewater discharged from coir and cork process, plant medicine, paper, and leather industries. In addition, as a water soluble polyphenolic compound, tannic

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acid has toxicity for aquatic organisms such as algae, phytoplankton, fish and invertebrates. Therefore, it is of great importance to remove tannic acid from water and wastewater in terms of protecting human health and environment. Wang *et al*., have studied adsorptive behavior tannic acid onto polyaniline and amino-functionalized magnetic nano adsorbents.[15-17]

In this study, an attempt has been made to carbonize chrome shaving (CTLS) into adsorbent after removing leachable chromium from carbonized matter through acid wash followed by chrome recovery treatment to avoid chromium contamination in to the environment. Carbonization of chrome shaving (CTLS) was carried out at different temperatures. Scanning electron microscopy analysis and Energy Dispersive X-ray Analysis (EDAX) were done to characterize the carbonized CTLS. Carbonized material was used as adsorbent for the removal of tannic acid in wastewater. Adsorption isotherms and kinetics of sorption was studied to describe the adsorption process.

Experimental

Materials

Leather waste - chrome shaving was collected from Tata International, Dewas, MP, India, for this study. Tannic acid was sourced from SD Fine chemicals, India. All chemicals used for analysis were of reagent grade.

Preparation of Carbonized CTLS

CTLS was washed with deionized water and dried in oven at 105°C±2°C for 3 h 100 g of dried CTLS was carbonized in a closed furnace at two different temperatures such as 300°C±5°C and 600°C±5°C at heating rate 5°C/min and hold for 4 h after achieving desired temperature. All carbonized material obtained from various temperature was washed with 50 ml 1N sulphuric acid in a bottle shaker for 1 h to remove soluble minerals. After acid wash carbonized matter was washed twice with 50 ml deionized water in a bottle shaker for 30 min to remove free acid and dried at 105°C for 3 h. The spent water obtained from washings were analyzed for Cr (VI) and treated with 0.5g sodium metabisulphite for reducing Cr (VI) to Cr (III) followed by 1g MgO for precipitation of Cr (III) as chromium hydroxide. Dried carbonized material was ground into small particles of about 0.005-0.01 mm sizes and used as adsorbent. Adsorbent surface and chemical composition were analyzed using scanning electron microscopy and energy dispersive X-ray. Dried CTLS and Carbonized CTLS were analyzed for moisture content, total ash, chromium (III) and (VI) according to APHA standard methods.[18] The elemental analysis such as carbon, nitrogen and hydrogen has been performed using CHNS 1108 model Carlo Erba Analyzer (CE Elantech, USA). Surface area has been determined using standard nitrogen adsorption porosimetric technique employing the BET method in a Quantachrome NOVA automated gas sorption system. Total pore volume has been calculated as per BJH theory.[19]

Preparation of Aqueous Solution of Tannic Acid as Adsorbent

The simulated solution containing tannic acid was prepared by dissolving 2500 mg of tannic acid in 1000 ml of deionized water. Working concentrations were generated by suitable dilutions. Determination of tannic acid content was performed using Folin Ciocalteu reagent.[20]

Adsorption Studies

Batch mode adsorption studies were carried out in water bath using carbonized material obtained from 600°C with predetermined quantities (2.5–10 g L^{-1} on dry weight basis) and simulated tannic acid solution (100 ml) of varying concentrations in 150 ml stopper glass bottles. At the end of a predetermined time interval a small aliquot was taken, the contents were centrifuged, and the supernatant analyzed for tannic acid content as per standard procedure.[20] The amount of tannic acid adsorbed was calculated from the difference in the tannic acid remaining in solution and the initial concentration. Studies on the effect of initial tannic acid concentration (50–200 mg L^{-1}) and duration of the treatment (0–210 min) on adsorption were also carried out. Adsorption studies were carried out triplicate and average values are reported.

Isotherm Studies

Isotherm studies were conducted by treating a fixed mass of carbonized material (0.25g) obtained from 600°C in contact with 100 ml of tannic acid solution in a 150 ml stoppered bottle. The desired concentration of tannic acid solution (25 - 250 mg L^{-1}) was achieved by dilution of the stock solution with the acetate buffer solution of pH 4.0. The bottles were sealed and agitated in a water bath shaking apparatus at different temperatures (30, 40, 50 and 60°C) until the equilibrium was reached. At time t=0 and equilibrium, the concentration of tannic acid left in the solution was measured. The tannic acid concentration at equilibrium, q_e, was calculated from:

$$q_e = ((C_o - C_e) \times V)/W_s \quad (1)$$

where, q_e (mg g^{-1}) is tannic acid concentration in sorbent (CTLS) at equilibrium; C_o (mg L^{-1}) is initial tannic acid concentration in liquid phase; C_e (mg L^{-1}) is liquid–phase tannic concentration at equilibrium; V (L) is the total volume of tannic acid solution used; and W_s (g) is the mass of the carbonized waste used.

The maximum adsorption capacity Q^o (mg g^{-1}) and the energy of adsorption b (L g^{-1}) can be calculated from the Langmuir isotherm, which is simplified and represented as:

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \quad (2)$$

The C_e and q_e are the equilibrium sorbate concentration in the aqueous (mg L^{-1}) and solid phases (mg g^{-1}), respectively. When tannic acid adsorption follows a Freundlich isotherm, it satisfies equation of the type:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

Where, K_F and 1/n are the Freundlich constants related to the adsorption capacity and intensity of adsorption. Isotherm studies were carried out triplicate and average values are reported.

Adsorption Kinetics

The procedures for the adsorption kinetics studies were similar to those for adsorption isotherms, but the concentration of tannic acid during adsorption process was analyzed at a regular time interval. Adsorption kinetics were carried out triplicate and average values are reported.

Results and Discussion

Characteristics of Adsorbent

It is possible to observe macropore region of carbonized material through SEM micrographs. SEM images of carbonized material produced by carbonization of CTLS at 300°C and 600°C, are given in Figure 1a and 1b, respectively. There are white particles aggregated and dispersed on the carbon surfaces in all micrographs. In Figure 2a and 2b, EDAX analysis of the carbonized material produced from 300°C and 600°C are presented. The inorganic constituents (white particles) on carbonized material containing considerable amount of chromium is clearly visible. Carbonization temperature plays a vital role on formation of micro pores on carbonized materials. Higher magnified SEM images of CTLS carbonized at 600°C shows (Figure 1d) clear and visible pores hence it will have better adsorption compare to CTLS carbonized at 300°C (Figure 1c). Hence, further studies have been carried employing carbonized CTLS obtained from temperature 600°C.

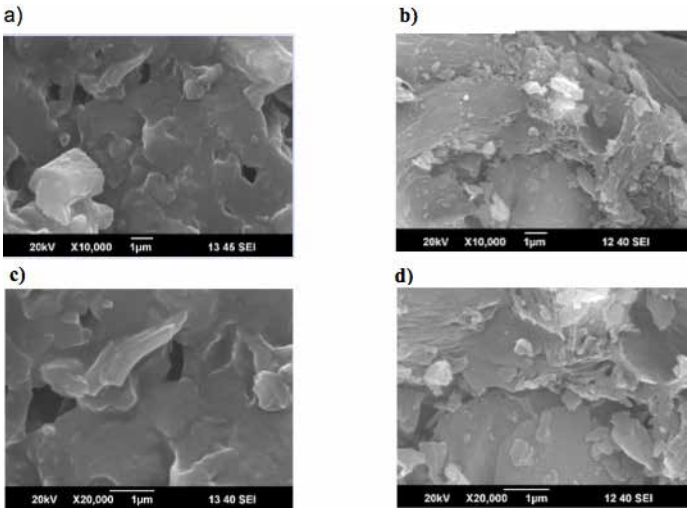

Figure 1. Scanning Electron Micrographs of Carbonized CLTS obtained from different temperatures and magnifications a) 300°C (x10000); b) 600°C (x10000); c) 300°C (x20000) and d) 600°C (x20000).

Table I

Physio-chemical characteristics of CTLS and Carbonized CTLS at 300 and 600°C.

Parameters	CTLS	CTLS Carbonized at 300°C	CTLS Carbonized at 600°C
Moisture (%)	9.25 ± 2	5.2 ± 1	4.4 ± 1
Ash (%)	19.5 ± 1	8.1 ± 0.6	4.2 ± 0.3
Cr (III) (%)	3.21 ± 0.4	2.1 ± 0.2	1.2 ± 0.1
Cr (VI)	n.d	n.d	n.d
Carbon (%)	38.21 ± 1	56.1 ± 1	70.6 ± 1
Nitrogen (%)	11.9 ± 0.5	16.5 ± 0.5	18.9 ± 1
Hydrogen (%)	5.2 ± 0.5	7.3 ± 0.5	8.7 ± 0.5
Surface area - BET (m^2 g^{-1})	8.42	380	620
Total pore volume (cm^3 g^{-1})	0.02	0.43	0.49

n.d: not detectable level

Physio-chemical characteristics of CTLS and carbonized CTLS obtained from 300 and 600°C are given in Table I. It is clear seen from Table I that surface area of carbonised CTLS produced from 600°C is more than 300°C. There is no significant difference in total pore volume of CTLS obtained from both 300 and 600°C. It is evident from Table I that there is significant level of physical and chemical nature of CTLS has changed by carbonisation.

Effect of pH, Initial Concentration and Treatment Period on the Removal of Tannic Acid

In order to study the influence of pH on the removal of tannic acid, the pH of the tannic acid solution was varied from 1.5 to 9.5. Tannic acid removal is optimal at pH 4.5 (Figure 3). The removal of tannic acid by adsorbent is related to the concentration of the tannic acid. The percentage removal of tannic acid at various concentrations with respect to time is given in Figure 4. When the concentration of tannic acid was varied from 50 to 200 mg L^{-1}, the percentage uptake of tannic acid varied from 95 to 65% at 120 min of treatment. The initial uptake of tannic acid was predominantly fast, reaching about 76% within 10 min of treatment and reaching an equilibrium value of around 95% (for C_o=50 mg L^{-1}) at 120 min. No observable change in tannic acid removal was noticed after 120 min, in the entire concentration range selected for investigation in this study. As the ratio of sorbent to the sorbate was increased from 2.5 g L^{-1} to 10 g L^{-1}, the percentage removal of tannic acid increased from 65 to 98% with increasing dosage of sorbent (for C_o = 200 mg L^{-1}) as shown in Figure 5. The total surface area increases as the amount of sorbent increases and as a result more tannic acid is adsorbed. This trend was found to hold good at all concentrations of tannic acid investigated in the study.

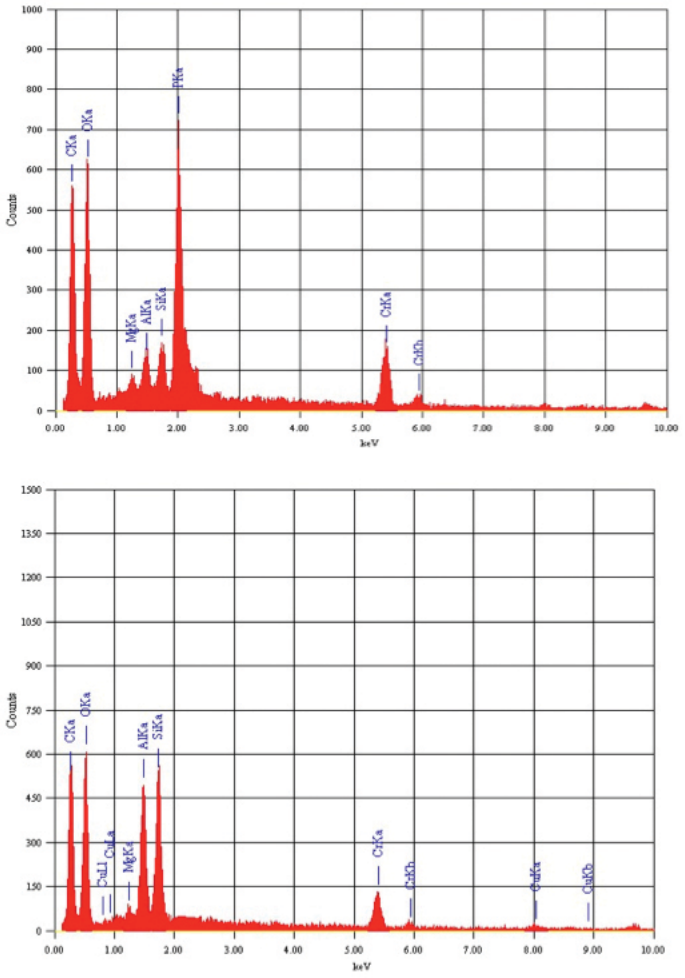

Figure 2. EDAX analysis of Carbonized CTLS obtained from difference temperatures 300°C and b) 600°C.

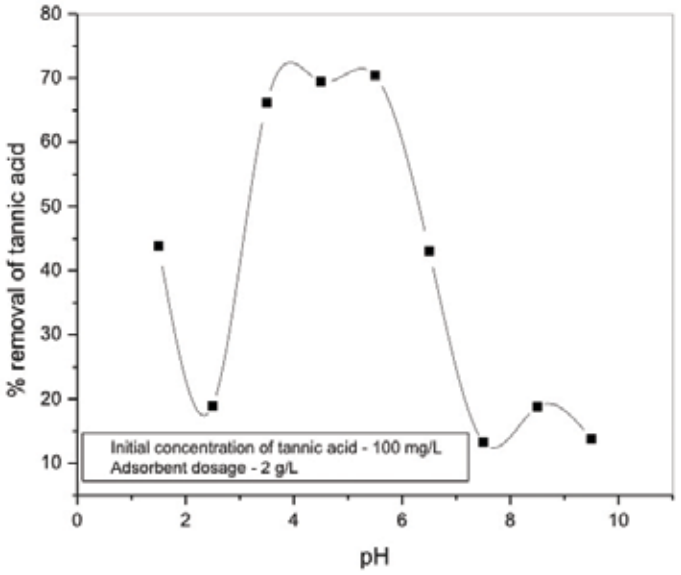

Figure 3. Effect of pH on removal of tannic acid by carbonized CTLS.

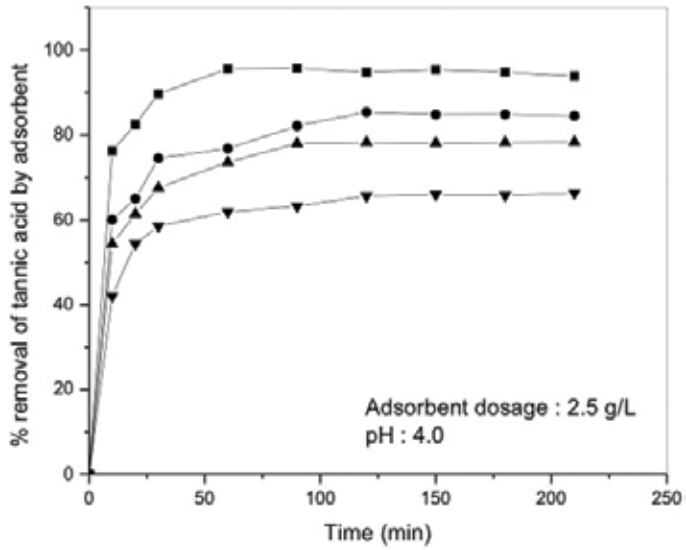

Figure 4. Plot of time versus tannic acid removal for varying concentrations of tannic acid: –■– 50, –•– 100, –▲ – 150 and –▼ – 200 mg L^{-1}.

Adsorption Isotherms

Adsorption isotherms at 30, 40, 50 and 60°C were obtained at pH 4.5 by varying initial tannic acid concentration (25-250 mg L^{-1}). The adsorption isotherm thus obtained is depicted in Figure 6. As seen from the asymptotic nature of the curves, the isotherm can be classified as L-type according to Giles classification system.[21] The adsorption of tannic acid on adsorbent increased from 57 to 63 mg/g, when the temperature was increased from 30 to 60°C indicating that the adsorption process is endothermic in nature. Similar trend of results has been reported by Wang et al. for aqueous phase adsorption of tannic acid onto polyaniline.[16] The increase of adsorption with temperature may be due to the agglomeration of the tannic acid molecules on the sorbent surface. The data were further analyzed by Langmuir and Freundlich isotherm models. Langmuir equation can be used to calculate the maximum adsorption capacity Q^o (mg g^{-1}) and the energy of adsorption b (L g-1), which are given by:

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \quad (2)$$

The C_e and q_e are the equilibrium sorbate concentration in the aqueous (mg L^{-1}) and solid phases (mg g^{-1}), respectively. A plot of $\frac{C_e}{q_e}$ versus C_e was made for the adsorption of tannic acid on adsorbent at different temperatures. The values of Q^o and b are given in Table II. The values of Q^o and b increased from 57.03 mg g^{-1} and 0.130 (L mg^{-1}) at 30°C to 62.99 mg g^{-1} and 0.180 (L mg^{-1}) at 60°C, respectively. A direct comparison of carbonized CTLS with other adsorbent material is difficult, because of the difference in experimental conditions, the values of Q^o and b trends were found to be more or less equal to the values reported for tannic acid onto polyaniline based adsorbent.[16]

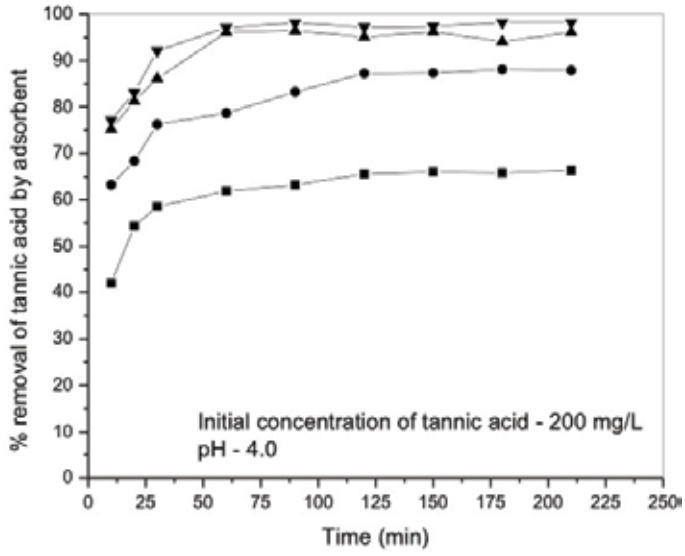

Figure 5. Plot of tannic acid removal versus time for various adsorbent to adsorbate ratios: −■− 2.5, −•− 5, −▲ − 7.5 and −▼ − 10 g L^{-1}.

The equilibrium adsorption data were also fitted to the Freundlich equation as given below.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

Where, K_F and 1/n are the Freundlich constants related to the adsorption capacity and intensity of adsorption. The values of these constant at different temperature are presented in the Table I. K_F increases with increasing temperature, showing that the rate of adsorption also increases with increasing temperature. Values of 0.1<1/n<1.0 show the favourable adsorption of tannic

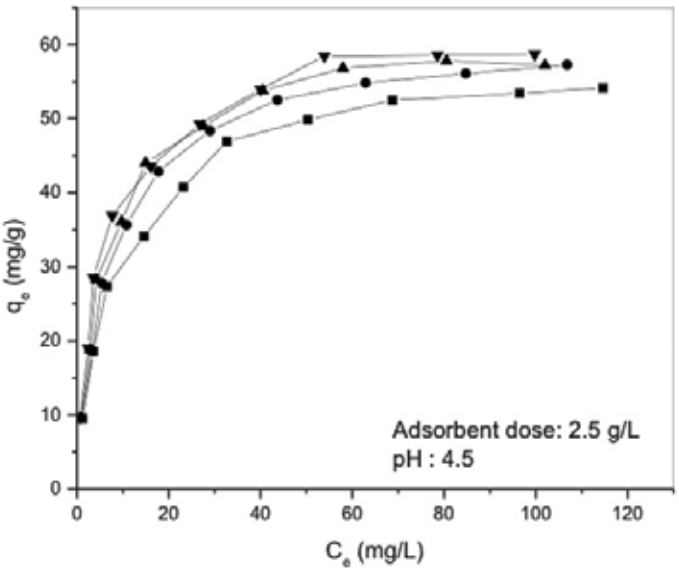

Figure 6. Adsorption isotherms of tannic acid onto Carbonized CTLS at various temperatures: −■− 30, −•− 40, −▲ − 50 and −▼ − 60°C.

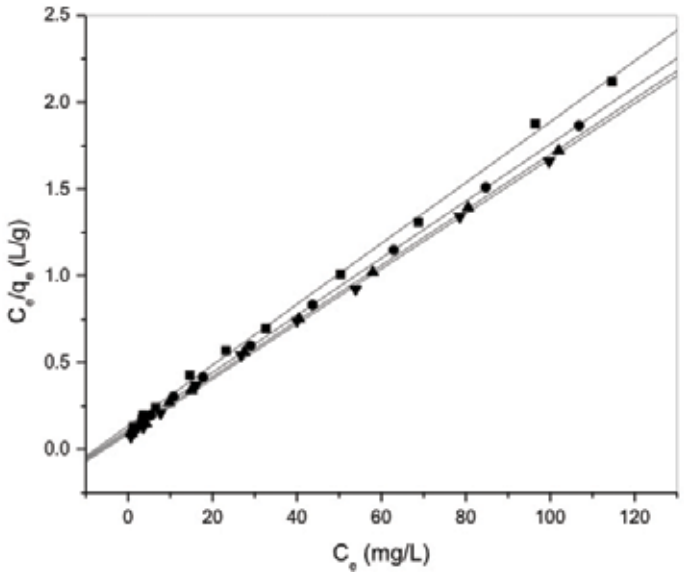

Figure 7. Langmuir isotherm plots for the adsorption of tannic acid onto Carbonized CTLS at different temperatures: −■− 30, −•− 40, −▲ − 50 and −▼ − 60°C.

acid on to adsorbent. For an equilibrium concentration of 1 mg L^{-1}, each gram of adsorbent can hold 11.47 mg of tannic acid at 30°C, which is increased to 14.65 mg at 60°C.

Figure 7 shows the fit obtained when the linearized form of Langmuir isotherm is taken and plotted. Tannic acid adsorption onto carbonised CTLS follows a Langmuir isotherm models and gives good linear fits to the adsorption, based on the correlation co-efficient (r^2) values. The hybrid fractional error function (HYBRID) has further been used to compare the validity of the isotherm models and is calculated using the equation:

$$\frac{100}{n-p}\sum_{i=1}^{n}\left[\frac{\left(q_{e,meas}-q_{e,calc}\right)^2}{q_{e,meas}}\right]_i \quad (4)$$

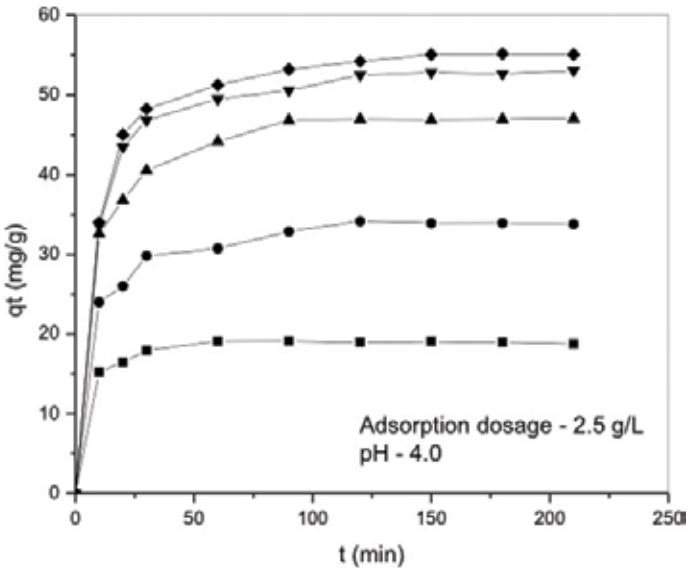

Figure 8. Adsorption kinetics of tannic acid onto Carbonized CTLS at various initial concentrations: : –■– 50, –•– 100, –▲ – 150, –▼ – 200 and –♦– 250 mg L^{-1}.

Where, n and p are the number of data points and parameters, respectively. The values of Langmuir and Freundlich isotherm error values are presented in Table II. Lower hybrid error functions substantiate the Langmuir isotherm as the best-fit model for describing the adsorption of tannic acid on the adsorbents. Generally, Freundlich isotherm is expected for CTLS as it is a heterogeneous material.[8] This heterogeneous CTLS is become homogeneous substrate due to carbonisation hence it follows Langmuir isotherm model. Further, Langmuir isotherm model was reported for adsorption of methylene blue on to activated carbon prepared from leather waste.[14]

Adsorption Kinetics

To investigate, the mechanism of adsorption, the pseudo-first-order, pseudo-second-order and intraparticle diffusion models

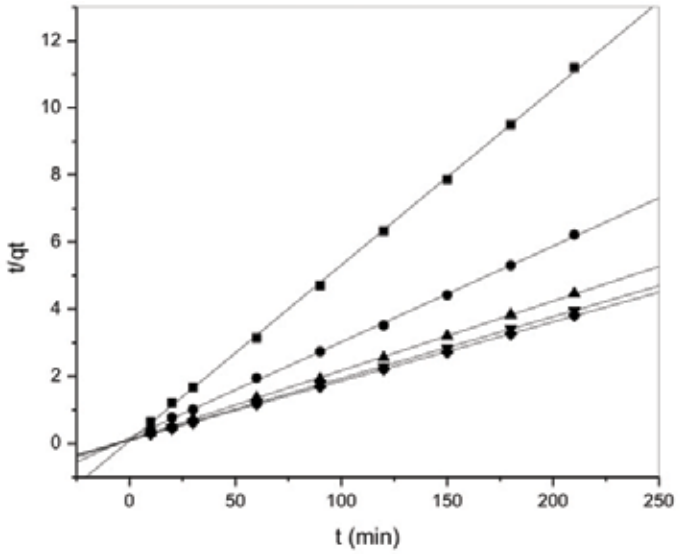

Figure 9. Pseudo-second-order rate kinetic plot for the adsorption of tannic acid onto adsorbent at various initial concentrations: –■– 50, –•– 100, –▲ – 150, –▼ – 200 and –♦– 250 mg L^{-1}.

Table II
Langmuir and Freundlich isotherm constants with correlation co-efficients.

Temp (°C)	Langmuir model				Freundlich model			
	Q^o (mg g^{-1})	b (L mg^{-1})	r^2	hybrid values	K_F (mg g^{-1})	1/n	r^2	hybrid values
30	57.03	0.130	0.998	11.815	11.47	0.364	0.927	73.254
40	60.79	0.144	0.999	10.505	12.51	0.367	0.925	87.060
50	62.50	0.160	0.999	13.443	13.47	0.362	0.916	95.405
60	62.99	0.180	0.990	24.480	14.65	0.347	0.920	87.830

were used to test adsorption kinetic data. The pseudo-first order-rate expression[22] of Lagergen is given as:

$$\log(q_1 - q_t) = \log q_1 - \frac{k_1}{2.303} \quad (5)$$

Where q_1 is the amount of tannic acid sorbed at equilibrium (mg g^{-1}); q_t is the amount of tannic acid sorbed at time t (mg g^{-1}), and k_1 is the equilibrium rate constant of first order sorption (min^{-1}).

The pseudo-second-order rate model[23] is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^{\,2}} + \frac{1}{q_2} t \quad (6)$$

Where q_2 is the amount of tannic acid sorbed at equilibrium (mg g^{-1}) and k_2 is the equilibrium rate constant of pseudo-second order chemical sorption (g mg^{-1} min^{-1}).

The intraparticle diffusion[24] equation can be described as:

$$q_t = k_i t^{0.5} \quad (7)$$

Where, k_i is intra-particle rate constant (mg g^{-1} $(min^{0.5})^{-1}$) which can be determined by the slope of the straight line portion of a plot of q_t versus $t^{0.5}$.

Figure 8 shows the adsorption kinetics of tannic acid on adsorbent. The sorption capacity at equilibrium increases from 18.9 to 54.2 mg g^{-1} where the initial tannic acid concentration increases from 50-250 mg L^{-1}.

Table III lists the results of the rate constants studies for different initial tannic acid concentrations by the pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The value of correlation coefficient r^2 for the pseudo-second-order adsorption model is extremely high (>0.999) and the adsorption capacities calculated by the model are close to those determined by the experiments. However, the values of r^2 for pseudo-first-order and intraparticle diffusion adsorption models are not satisfactory. Therefore, it can be concluded that the pseudo-second-order adsorption model (Figure 9) is more suitable to describe the adsorption kinetics of tannic on adsorbent. Similar phenomena have also been observed in the adsorption of tannic acid on to polyaniline.[16]

Conclusions

The biological treatment of wastewater containing tannins is difficult due to the non-biodegradable nature of tannins. This is a significant problem for tannin based industries to manage the wastewater. The leather industry also generates significant quantities of chrome tanned leather solid waste and therefore needs innovative management methodologies. This study emphasizes preparation of an adsorbent using CTLS through carbonization process and demonstrates the adsorptive removal of tannic acid by this adsorbent. The removal efficiency of tannic acid was found to be about 95%. The two isotherm study reveals that the adsorption process follows the Langmuir model more than the Freundlich. Kinetic study shows that the adsorption process follows the pseudo-second order rate. This work demonstrated the use of one industrial waste to treat another industrial waste toward a more sustainable environment.

Table III

Comparison of first and second order adsorption and intraparticle diffusion rate constants.

Initial concentration (mg L^{-1})	q_e (exp) (mg g^{-1})	Pseudo-first order kinetic model			Pseudo-second order kinetic model			Intraparticle diffusion model	
		k_1 (min^{-1})	q_1 (mg g^{-1})	r^2	k_2 (g mg^{-1} min^{-1})	q_2 (mg g^{-1})	r^2	k_i (mg g^{-1} $(min^{0.5})^{-1}$)	r^2
50	18.95	$1.30x10^{-2}$	2.77	0.887	$3.31x10^{-2}$	19.12	0.999	0.270	0.622
100	34.14	$1.95x10^{-2}$	9.51	0.909	$5.03x10^{-3}$	34.90	0.999	0.848	0.842
150	46.93	$2.46x10^{-2}$	13.11	0.901	$4.12x10^{-3}$	48.40	0.999	1.186	0.810
200	52.49	$2.62x10^{-2}$	16.89	0.907	$3.29x10^{-3}$	54.48	0.999	1.360	0.750
250	54.20	$3.43x10^{-2}$	21.37	0.966	$2.97x10^{-3}$	56.88	0.999	1.488	0.751

Notation

1/n	exponent in the Freundlich isotherm, dimensionless
b	Langmuir constant (L mg^{-1})
C_o	initial tannic acid concentration (mg L^{-1})
C_e	equilibrium solution phase tannic acid concentration (mg L^{-1})
K_F	Freundlich equilibrium constant (mg g^{-1})
k_1	pseudo-first order rate constant (min^{-1})
k_2	pseudo-second order rate constant (g mg^{-1} min^{-1})
k_i	intraparticle diffusion rate parameter (mg g^{-1} $(min)^{0.5}$)
n	number of experimental measures
p	number of parameters
q_e	mass of tannic acid adsorbed onto carbonized CTLS at equilibrium (mg g^{-1})
Q^o	Langmuir monolayer sorption saturation capacity (mg g^{-1})
q_1	equilibrium mass of tannic acid sorbed on carbonized CTLS based on pseudo-first order model prediction (mg g^{-1})
q_2	equilibrium mass of tannic acid sorbed on carbonized CTLS based on pseudo-second order model prediction (mg g^{-1})
q_t	mass of tannic acid sorbed at time t (mg g^{-1})
r^2	statistical correlation co-efficient based on least squares best fit analysis of a straight line correlation
t	contact time (min)
V	solution volume (L)
W_s	mass of sorbent (g)

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