Chromium Adsorption on Banana Rachis Adsorbent from Tannery Wastewater: Optimization, Isotherm, Kinetics and Desorption Studies

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ABSTRACT

This study investigates the banana rachis adsorbent for adsorption characterization, removal, and recovery of the chromium ion from the chrome tanning wastewater. The batch analysis was conducted to find out an adsorbent dose, contact time, relative pH of the aqueous solution, and initial and final chromium value in the filtrate. The equipped adsorbent was studied by the Fourier transform infrared spectroscopy (FT-IR) analysis to reveal the associated functional groups during adsorption. Batch adsorption examination reveals the optimum conditions of 3 g adsorbent input for 75 mL wastewater at 15 min contact time. The adsorption mechanism showed chromium removal 99.64% with the obtained reduction of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and chloride (Cl⁻) 96.65%, 93.18%, and 59.62%, respectively. The adopted method followed the pseudo-second-order kinetics and Freundlich isotherm for physical adsorption. Primary desorption studies exhibit a scope for the reuse of chromium from the adsorbed adsorbent. Moreover, in comparison with other studies, the study discloses that banana rachis might be utilized as a feasible adsorbent to be adopted in industrial wastewater treatment, especially chrome tanning wastewater in the tannery.

INTRODUCTION

The non-degradable and persistent nature of heavy metals-polluted waste streams, controversial side effects of industrialization and modernization, causes devastating and permanent contamination of the environment [1]. Most of the common heavy metals found, like chromium (Cr), lead (Pb), arsenic (As), nickel (Ni), cadmium (Cd), and zinc (Zn) are posing great threats to the environment because of their harmful effects. Chromium (Cr) may form in several oxidation states, mainly trivalent and hexavalent forms [2]. Hexavalent chromium, Cr(VI) is 100 times more toxic than trivalent Cr(III), since it is highly soluble in water, mobile, and easily reduced [3]. Trivalent chromium, Cr(III) is essential for human nutrition since it controls sugar level in mammal bloodstream in trace amounts, but noxious to fish at a concentration greater than 5.0 mg/L [4]. The Cr(VI) has been classified as belonging to group 1, which is carcinogenic to humans, whereas metallic chromium and Cr(III) are in group 3 (not classifiable as to their carcinogenicity to humans) [5].

Despite all the concerns, Cr has been widely used in different industries (leather tanning, textile, metal, power plant, etc.) [6]. It is reported that about 15×10^3 tons of chromium salt (basic chromium sulphate) [7] is used globally for the production of 18 billion sq. ft. of tanned leather [8].

It has been assessed that around 22×10^3 m^3 of wastewater, including chromium, is discharged daily into the Buriganga River of Bangladesh without any treatment [9]. Studies found that every day 1.25 tons of chromium is discharged into the river as waste liquor at a peak level of 21,000 m^3 per day [10].

Researchers all over the world have been developing numerous methods and techniques to make diminution in Cr exposure to the environment. Different methods like chemical precipitation [11], ion-exchange resins [12], membrane separation [13], solvent extraction [14], and so on, have been tried for chromium removal from aqueous solutions.

In the chrome tanning process, the wastewater contains not only the chromium ion but also other biological and chemical substances that are separated from the pelt during operation. As a result, the already developed techniques for chromium separation from aqueous solutions might not be as efficient in the case of the tannery wastewater. This urges for the specific operational method developed for the chrome-tanning wastewater.

Some researchers have been trying to develop treatment process particularly for the tannery wastewater, e. g. membrane separation [15] or membrane electroflotation [16]; however, high energy and process cost, disposal of toxic precipitates or other sludge that requires further treatment process restrains its appeal in the application.

These problems force the researchers to move towards the adsorption method which overcomes most of the previously mentioned side effects. Different adsorption studies using Brazilian sawdust [17], biological activated carbon [18] or *Galactomyces geotrichum* fungi [19] have been tried for tannery wastewater treatment, but these are either based on Cr(VI) removal, or do not provide a high removal efficiency. Promising results are reported in removing Cr(III) ions from the tannery effluent by using *Syzygium cumini* bark [20]. However, in terms of abundant sources, the study showed a deficient supply of the adsorbent.

In this contribution, the adsorbent prepared from the waste banana rachis was used to adsorb Cr from the tannery wastewater. According to the FAO [21] report, world's total gross export and import for bananas in 2017 was 18.08×10^6 tons and 17.75×10^6 tons, respectively. The estimated amount of the banana rachis waste in Costa Rica (one of the biggest banana producers in the world) is 797,000 metric tons per year [22]. In Bangladesh, 800,840 metric tons of banana were produced in 2010-2011 on about 130,589 acres of the cultivated area [23]. In Bangladesh, there is no systematic way to use this waste; generally, it is dumped at the roadside without any purposeful use. This satisfies as a potential opportunity to reuse the rachis waste and makes this technique twice as efficient and attractive.

The goal of this investigation was to develop an industrial-friendly adsorbent from the banana rachis waste to adsorb chromium from the tannery wastewater. The mechanism of chromium removal was analyzed through parameters like the adsorbent input, contact time, and a relative pH impact. Moreover, the kinetics and the reaction mechanism were also evaluated, and FTIR spectroscopy was used to find out different functional groups responsible for the adsorption.

MATERIALS AND METHODS

Adsorbent Preparation

Banana rachis waste was collected from a nearby banana market at Khulna, Bangladesh, free of cost, since they are generally dumped at the roadside. The rachis was washed with water, chopped, sun-dried and

then burnt at 640-650°C in a muffle furnace (Thermo Scientific) for 3 (three) hours, cooled, made into a fine powder with a laboratory mortar (Pulverisette), and kept preserved in a double stoppered polyethylene bottle, in a dry and cool state, for further experiment.

Collection of Wastewater

The tannery wastewater containing Cr, referred to as a sample, was collected just after the chrome tanning process from a tannery at Khulna, Bangladesh. The sample was collected in a plastic container that was pre-washed with diluted nitric acid and rinsed with distilled water. Immediately, it was transported to the laboratory for the experiment.

Reagents

Nitric acid (Merck KGaA, Germany), sulphuric acid (Merck KGaA, Germany), perchloric acid (Merck, India), N-phenyl anthranilic acid (Merck, India), ammonium iron(II) sulphate hexahydrate (Merck, India), filter paper (Whatman No. 1) and anti-bumping agent glass beads (Loba Chemie, India) were purchased from a local scientific store, Khulna, Bangladesh.

Analytical Techniques

The physicochemical properties of the wastewater were analyzed in terms of Cr, pH, total dissolved solids (TDS), electrical conductivity (EC), salinity, biochemical oxygen demand for 5 days (BOD_5) and chemical oxygen demand (COD). The pH of the wastewater was measured by using the pH meter (UPH-314, UNILAB, USA) and the electrical conductivity (EC) was measured by using the conductivity meter (CT-676, BOECO, Germany). Total solids (TS), total suspended solids (TSS), and total dissolved solids (TDS) of the spent chrome liquor and the treated liquor were determined by the APHA-2540 D method. The biochemical oxygen demand (BOD), chemical oxygen demand (COD) and the chloride content of the spent chrome liquor and the treated liquor were determined by following the APHA-5210 B, APHA-5220 C and APHA-4500 B method, respectively. The Cr content in the untreated wastewater and the filtrate after the treatment was measured by the titrimetric method, following the official method of analysis of the Society of Leather Technologist and Chemists [24], the SLC 208 (SLT6/4) method.

Batch Adsorption Test

Batch-wise Cr removal from the wastewater using the prepared adsorbent was performed under different parameters, such as adsorbent dose and contact time. Firstly, the physicochemical parameters of the untreated wastewater containing Cr were analyzed and filtered through a 0.45 μm pore size filter. Secondly, 75 mL of the filtrate wastewater was mixed with the prepared adsorbent and then stirred over a fixed period at a speed of 150 rpm using an orbital shaker (GFL- Model No. 3017) and the mixture was then allowed to settle for a fixed time. After settling, the mixture was filtered through a 0.45 μm pore size filter, and the Cr content measurement was performed, following the SLC 208 (SLT6/4) method.

Method and Adsorbent Selection

From an industrial perspective, wastewater treatment is an unprofitable process. Due to the environmental acts and regulations, the wastewater generated in an industry is treated within the standard limit before the discharge. According to ECR 1997 [25], the tanning industry is classified as the "RED" category which is the

highest pollution-generating group. Thus, treatment is obligatory for the tannery wastewater. The proposed method prefers the adsorption process which can economically meet today's higher effluent standards and water reuse requirements [26]. The adsorption process can be adopted in-situ and can consistently produce high levels of treatment and have a high degree of stability and reliability. In 2017, Bangladesh produced 16592.1 kg bananas per hectare [21]. The selected adsorbent, prepared from the banana rachis is a waste generated in large amounts in Bangladesh without any defined treatment process. The proposed method with the recommended adsorbent could utilize the banana rachis waste as well as mitigate the tannery wastewater problem.

Cr Adsorption

The quantity of the chromium uptake by the adsorbent was calculated by following Eq. 1,

$$q_t = \frac{(C_0 - C_t) \times V}{m} \tag{1}$$

where q_t is the amount of chromium adsorbed expressed in mg per g of the adsorbent, C_o and C_t are the initial concentration (mg/L) and concentration at time t (mg/L), respectively. The V indicates the volume of solutions (L) and m is the weight of the adsorbent (g).
The chromium removal percentage was determined by using the following Eq. 2.

$$R\ (\%) = \frac{(C_0 - C_t) \times 100}{C_0} \tag{2}$$

Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectra of the pure adsorbent and after chromium adsorption was acquired by a Fourier transform infrared spectrometer (FT-IR 1600, PerkinElmer). The pure and the chromium-loaded adsorbent was collected from the same batch adsorption studies at optimized conditions after adsorption. The FT-IR spectra were recorded within the wavenumber of 650 and 4000 cm^{-1}.

Adsorption Isotherm Studies

Adsorption equilibrium isotherms were studied using adsorbent the dosages of 1, 2, 3, 4, and 5 g per 75 mL of the tannery wastewater with the initial concentration and the pH of 3373.5 mg/L and 4.5, respectively. Each batch was carried out at optimum conditions: stirred for 15 min at a speed of 150 rpm and then left to settle for 10 min at the room temperature (25±2°C). The filtration of the mixture was completed by using Whatman no. 1 filter paper (pore size 0.45 μm) and the filtrate was used for the isotherm analysis with two popular isotherm models, viz., the Langmuir isotherm and the Freundlich isotherm. The mass of the adsorbent, the adsorbate, the value of the equilibrium constant, and so on, are collected from this section.

Theory of Adsorption Kinetics

In this experiment, the investigation of adsorption kinetics was continued with 30 g of the adsorbent in 750 mL (as per optimum dose 3 g/75 mL of the wastewater) of the spent chrome liquor. At constant stirring, 75 mL of treated liquor was taken carefully as possible after 1, 5, 10, 15, 20, 25, 30, 35, 40, 50 and 60 minutes. Then, the liquor was filtered and the chromium content was measured for further kinetics analysis.

Desorption Study

To investigate the desorption of the used adsorbent to recover chromium from the wastewater, 1 g of the used adsorbent was mixed in distilled water of different pH, i. e. 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0. Each batch was stirred for 5 min and then left to settle for 24 hrs. The appearance of the distinct color of the basic chromium sulphate powder shows the possibility of chromium recovery for further application.

RESULTS AND DISCUSSION

Characterization of Wastewater

The spent chrome liquor of the raw sample was characterized for the physicochemical parameters, like the chromium content, the pH, the BOD, the COD, TDS, the EC, and the chloride content which is shown in Table 1.

Table 1. Tannery wastewater characterization

Parameters	Unit	Methodology/ Device	Result
Cr	mg/L	SLC 208 (SLT6/4)	3373.5
pH	-	UPH-314, UNILAB	4.5
BOD	mg/L	APHA-5210 B	3197
COD	mg/L	APHA-5220 C	4297
TDS	g/L	APHA-2540 D	29.83
EC	mS	CT-676, BOECO	66.9
Chloride	mg/L	APHA-4500 B	17021

Table 1 indicates that the wastewater content was high in Cr, the BOD, the COD, and that it was acidic in nature (pH 4.5). These high pollution loads in the wastewater are a threat to the environment if discharged without treatment. The same parameters for the treated samples show that, after treatment, the pH, the BOD and the COD were within the discharge limit. The chloride (Cl$^-$) reduction was noticeable, but it was still higher than the discharge limit. The soluble minerals, namely potassium (K), silicon (Si), phosphorous (P), calcium (Ca) and magnesium (Mg), found in banana rachis adsorbent [27], might raise TDS of the treated sample. The presence of the hydroxyl (–OH) functional group in the adsorbent found in the FTIR data possibly added to the EC value.

During treatment, the banana rachis charcoal acts as an adsorbent and the inorganic and organic pollutants are adsorbed by the charcoal surface. Thus, after filtration, the pollutants are removed with the adsorbent from the wastewater, which reduces Cr, the BOD, and the COD.

Chemical Composition of Raw Banana Rachis

The chemical composition (% w/w dry weight matter) of the raw banana rachis of the common Asian banana plant from the Cavendish subgroup of the AAA genetic group [27] is included in Table 2. Lignocellulosic fraction refers to the carbohydrate polymers (the cellulose, the hemicellulose) and an aromatic polymer (lignin) of the plant dry matter (the biomass). Here, the cellulose and the hemicellulose cover the maximum percentage.

Table 2. Global chemical composition (%w/w of dry matter) [27]

Non-lignocellulosic fraction		Lignocellulosic fraction		Relative composition (%) of neutral sugars	
Total ash	30.16±0.10	Cellulose	36.28±0.45	Glucose	71.86±0.97
Water extractives	13.01±1.90	Hemicellulose	17.78±2.97	Xylose	15.76±0.63
Ethanol extractives	0.63±0.20	Acid insoluble lignins	6.58±0.03	Arabinose	6.84±0.17
Proteins	4.88±0.05	Acid soluble lignins	2.06±0.01	Galactose	2.52±0.07

In the case of a non-lignocellulosic fraction, the percentage of total ash content is 30.16±0.10%. Different neutral sugars are also present in a natural banana rachis, e.g. glucose, xylose, arabinose, and so on, where glucose is found in abundance compared to the other sugars.

FT-IR Analysis of Banana Rachis Adsorbent

Fig. 1 depicts the FT-IR spectrum of the adsorbent before and after the adsorption of chromium. The figure reveals the changes in peak intensity. In the case of before the chromium load, peak intensity around 3200-3600 cm^{-1} indicates a strong, broad -OH functional group. Moreover, the presence of C=C, N-H, and =C-H functional group is observed around the 1619, 1387, and 988 cm^{-1} regions, respectively. These functional groups are vital sites for ion adsorption [28].
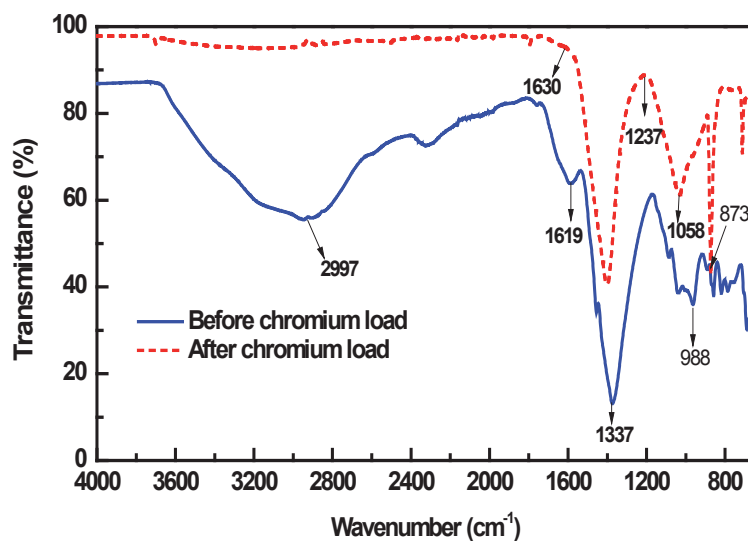

Figure 1. FTIR spectra of banana rachis adsorbent before treatment and after treatment

However, the peak changes for a noticeable portion after the chromium loading. Here, the most considerable functional groups present at the 1630, 1058 and 675-1000 cm^{-1} wavelength are C=C, C-O, and =C-H, respectively. A shift in 1377, 1043 and 965 cm^{-1} wavelengths before the adsorption further indicated that the banana rachis was an important component in the adsorption process of Cr [1]. The absence of the previous functional group after the chromium loading implies that the hydroxyl and other groups of the pure adsorbent were involved in the adsorption process.

Adsorbent Intake Analysis

The effect of the adsorbent dose on chromium removal was investigated through a batch analysis process where 5 samples of 75 mL of wastewater were taken in varying doses - 1, 2, 3, 4, and 5 g, respectively. The solutions were shaken for 10 min with a 10-minute settling time. The corresponding pH of each batch was measured after settling.
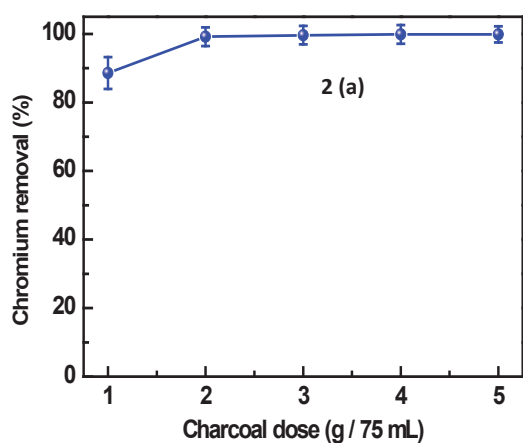

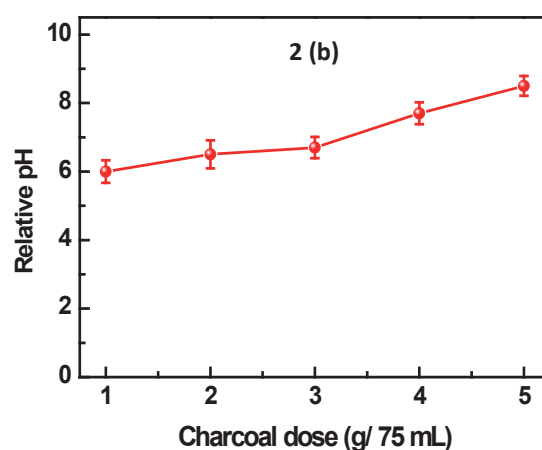Figure 2(a). Chromium removal efficiency on adsorbent doses

Figure 2(b). Chromium removal efficiency on relative pH

Fig. 2 shows the increase in removal efficiency, shown by Fig. 2(a), as well as in the pH, shown by Fig. 2(b), with the increase of the adsorbent dose. The increase of the pH with the adsorbent dose might be elucidated from the data obtained from the FT-IR. It ensures the presence of the -OH group in the adsorbent which could be responsible for the escalation of the pH.

It should also be noted that the increment in the adsorbent dose boosted the removal efficiency. Metal adsorption is well dependent on the pH due to the protonation of metal (chromium) binding sites. At a lower pH (2 to 3) the H^+ ion competes with the Cr^{3+} ion for the metal-binding site, which reduces the adsorption. As the pH rises, the abundance of the H^+ ion lowers, whereas the amount of the OH^- ion increases. This gives the dual effect of weakening the competitiveness of the H^+ against the Cr^{3+} ion, and the adsorption of hydrolysis products and the precipitation of metals as colloidal insoluble hydroxides, $Cr(OH)_3$ [29].

At an adsorbent dose of 3 g per 75 mL of wastewater, the process reaches an equilibrium with a 99.64% removal efficiency. Therefore, it was projected that the maximum chromium removal occurred with 3 g adsorbent dose for every 75 mL of wastewater at pH 6.7.

Contact Time Analysis

Fig. 3 shows that the chromium removal efficiency was increased with the increase of contact time between the chromium ions and the binding sites. For the first two batches, the adsorption rate increases rapidly as more chromium is allowed to adsorb on the binding sites with the increased time. After that, the reaction becomes weaker, because the remaining active sites are less available and the equilibrium phase was reached. The optimized removal efficiency was 99.64% at 15 minutes.
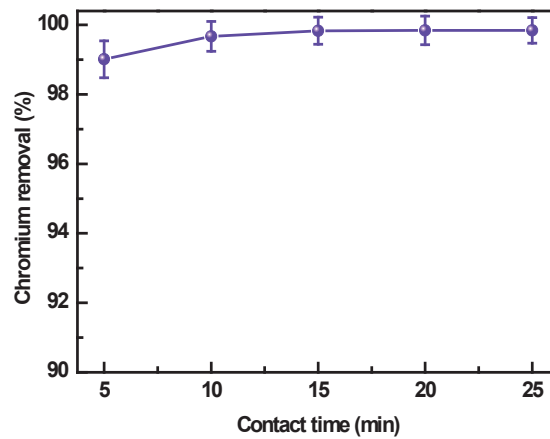
Figure 3. Chromium removal efficiency based on contact time

Adsorption Isotherm Studies

Adsorption isotherms are used to understand the relation between the adsorbate and the adsorbent. The capacity of the adsorbent, the optimization of the adsorbent use, surface characteristics and affinity are evaluated from the equilibrium studies of the adsorption isotherms. In this study, the most common two isotherm models, the Langmuir isotherm and the Freundlich isotherm are investigated [30].
Langmuir Isotherm
According to Langmuir's theory, the adsorption takes place at definite homogeneous sites within the adsorbent [31,32]. The standard model of the Langmuir isotherm [33] is represented below in Eq. 3,

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_a}$$

or

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{C_e} \times \frac{1}{Q_m K_a} \tag{3}$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of ion adsorbed (mg/g); Q_m (mg/g) and K_a (L/mg) are the empirical constants denoting monolayer capacity or limiting adsorption, signifying the solid-phase concentration, and can be charted from the slope and the intercept of the linear plot of $1/Q_e$ versus $1/C_e$ as shown in Fig. 4.
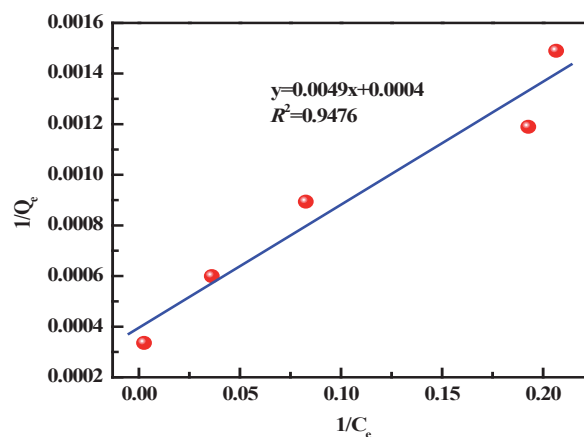

Figure 4. Langmuir isotherm plot for banana rachis adsorbent

The quality of the Langmuir isotherm can be determined by the magnitude of a dimensionless constant R_a known as the separation factor expressed in Eq. 4 [34],

$$R_a = \frac{1}{1+K_aC_o} \tag{4}$$

where C_o is the initial concentration of the Cr ions in mg/L and K_a is the Langmuir constant described earlier. The adsorption process is favorable within the range $0 < R_a < 1$, unfavorable when $R_a > 1$, becomes linear when $R_a = 1$, and the process is irreversible when $R_a = 0$.

Table 3. Adsorption isotherm parameters

Isotherm Models	Parameters	Value
Langmuir model	Q_m	2500
	K_a (L/mg)	0.0816
	R_a	0.004
	R^2	0.9476
Freundlich model	1/n	0.3255
	Kf (mg.g-1)(L.g-1)1/n	476.372
	R^2	0.9985

The data of the adsorption isotherm parameters is presented in Table 3. The correlation coefficient of the Langmuir model is found to be 0.9476, which is close to 1. The maximum monolayer adsorption capacity for banana rachis adsorbent obtained is 2500 mg/g and the value of the separation factor, R_a = 0.004 indicates that the process is favorable. The R_a value of this study is significantly low, suggesting a strong interaction between the Cr molecules and the adsorbents [35].

Freundlich Isotherm

The Freundlich isotherm is derived assuming a non-uniform heterogeneous surface for adsorption. The model used in this study can be represented as below in Eq. 5,

$$lnQ_e = lnK_f + \frac{1}{n}lnC_e \tag{5}$$

where K_f is the Freundlich characteristic constant [$(mg.g^{-1})$ $(L.g^{-1})^{1/n}$] and 1/n is the heterogeneity factor of adsorption, obtained from the intercept and the slope of lnQ_e versus lnC_e as shown in Fig. 5.
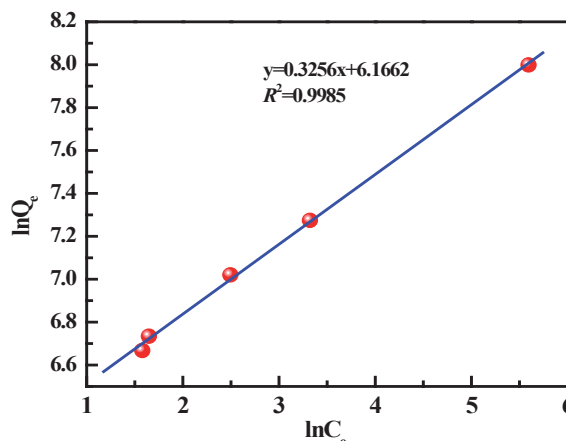

Figure 5. Freundlich isotherm plot for banana rachis adsorbent

The numerical value of 1/n tabulated in Table 3 is less than 1 but positive, indicating an approvable adsorption process [36]. The correlation coefficient obtained for the Freundlich model is 0.9985, which is closer to 1 than it was in the Langmuir model (R^2=0.9476). This implies that adsorption will be a multilayer adsorption on a heterogeneous surface following the Freundlich isotherm.

Theory of Adsorption Kinetics

The adsorption rates as well as suitable rate expressions, characteristic of possible reaction mechanisms of chromium by the banana rachis adsorbent, were estimated by using the kinetic modeling. In this regard, two well-established kinetic models, pseudo-first-order, and pseudo-second-order were studied. The value of the correlation coefficient (R^2) was studied to ensure the effectiveness of the experiment.

The pseudo-first-order model

The Lagergren's model [37] was followed for the pseudo-first-order kinetics analysis.
The pseudo-first-order reaction is expressed by the following Eq. 6,

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

where q_e (mg/g) and q_t (mg/g) denote the adsorption capacity at equilibrium and at time t (min) respectively, and k_1 (L/min) is the constant of the pseudo-first-order adsorption reaction.
Using the integrated linear form by applying boundary conditions, viz. that the initial conditions are q_e - q_t = 0 at t = 0, Eq. 6 can be expressed as follows:

$$\ln(q_e - q_t) = lnq_q - k_1t$$

$$or,$$

$$ln\frac{(q_e - q_t)}{q_e} = -k_1t \tag{7}$$

A plot of ln(q_e –q_t)/q_e versus time, t following Eq. 7 is used to describe the suitability of this kinetic model as done in Fig. 6. The q_e and k_1 are detected from the intercept and slope of the plot, respectively, and tabulated in Table 4.
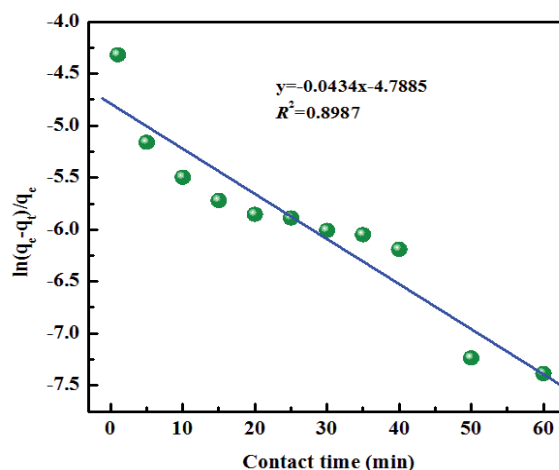

Figure 6. Pseudo-first-order plot for banana rachis adsorbent

The nonlinear form of Eq. 7 can be written as:

$$q_t = q_e(1 - e^{-k_1 t}).$$

The correlation coefficient obtained for pseudo-first-order kinetics is 0.8987 and the values of q_e and k_1 are 0.0355 and 0.0434 respectively.

The pseudo-second-order model

The pseudo-second-order model [38] can be expressed as Eq. 8:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

where k_2 (g/mg.min) is the pseudo-second-order adsorption rate constant, and q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and at time t (min) respectively.

For the boundary conditions t = 0 to t = t and q_t= 0 to q_t = q_t, the integrated form of Eq. 8 becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} - k_2 t$$

This stands for the integrated rate law for a pseudo-second-order reaction. The linear form of this equation [39] is:

$$\frac{1}{q_t} = \frac{1}{q_e} - \left(\frac{1}{k_2 q_e^2}\right)\frac{1}{t} \tag{9}$$

The relevance of this model can be ensured by the correlation coefficient (R^2) gathered from the plot of 1/q_t versus 1/t of Eq. 9 as expressed in Fig. 7.
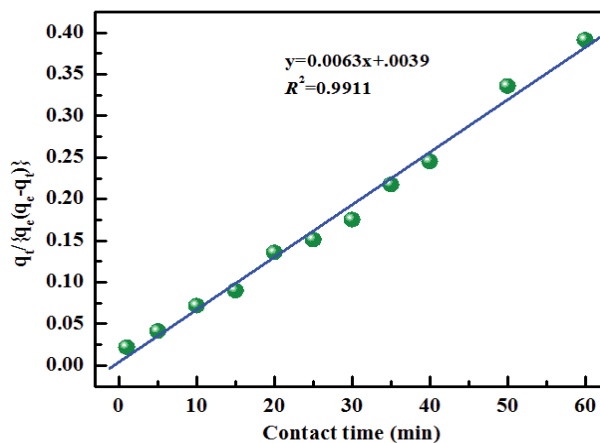

Figure 7. Pseudo-second-order plot for banana rachis adsorbent

The values of q_e and k_2 can be determined from the slope and the intercept of the plot respectively, which is tabulated in Table 4. Fig. 7 shows that the value of the correlation coefficient is 0.9996. The poor linearity of the Lagergren pseudo-first-order plots observed in the present study indicated that the adsorption process did not follow the first-order kinetics, but rather adhered more to the pseudo-second-order kinetics as confirmed by the correlation coefficient. According to the pseudo-second-order model, two reactions

occur, the first one is fast and reaches equilibrium quickly, and the second is slow and can continue for a long time [40].

Table 4. Adsorption kinetics parameters

Kinetics Models	Parameters	Value
	q_e (mg/g)	0.0355
Pseudo-first order	k_1 (min^{-1})	0.0434
	R^2	0.8987
	q_e (mg/g)	2.8827
Pseudo-second order	k_2 (g/mg.min)	0.0077
	R^2	0.9996

Comparison with Previous Studies

The adsorption capacities of some previously used adsorbents are compared with the adsorbent of this study in the case of contact time and chrome removal efficiency and the findings are charted in Table 5.

Table 5. Data comparison of different adsorbents for contact time and chrome removal efficiency

Adsorbents	Initial Cr Conc. (mg/L)	Dose (g/L)	Contact time (min)	Cr removal (%)	Ref.
Activated carbon	48.874	24	15000	46	[18]
Eggshell	3210	20	840	25	[41]
Powdered marble	3210	12	30	40	[41]
Bittern	154.95	5 mL/L	21	32	[42]
Banana rachis	3373.5	40	15	99.64	This study

It is clear that among these adsorbents, the banana rachis adsorbent gives higher removal efficiency without any additional chemicals and with minimum contact time. This result indicates that the banana rachis adsorbent can be used as a better alternative for an adsorbent for tannery wastewater effluent treatment in the case of chromium removal.

The proposed adsorbent follows the Freundlich isotherm and the pseudo-second-order kinetics in chromium removal from the tannery wastewater. Table 6 compiles a data comparison for the Freundlich isotherm and the pseudo-second-order kinetics with some previously tried adsorbents in the tannery wastewater. The value of the Freundlich constant, K_f, represents the adsorption capacity, which is higher for this study compared to the eggshell and the powered marble adsorbent [41]. The higher R^2 value of the experiment ensures the consistency of the experiment. The adsorption capacity at equilibrium, q_e, for the pseudo-second-order kinetics also indicates a higher capacity for the banana rachis. The correlation coefficient, R^2, is also coherent with the found value.

Table 6. Data comparison for Freundlich isotherm and pseudo-second-order kinetics

	Adsorbent / Parameters	K_f $(mg.g^{-1})(L.g^{-1})^{1/n}$	N	R^2
Freundlich isotherm	Eggshell [41]	3.45	2.57	0.722
	Powdered marble [41]	5.86	2.99	0.945
	Banana rachis	476.37	3.07	0.9985
		q_e (mg/g)	k_2 (g/mg.min)	R^2
Pseudo-second order	Activated carbon [18]	1.03	0.8333	0.9446
	Biological activated carbon [18]	0.13	0.0519	0.8608
	Banana rachis	2.88	0.0077	0.9996

Treatment Process Efficiency

The results of the treatment process at optimum conditions are presented in Table 7. It shows that after treatment the pH, the BOD and the COD were within the discharge limit. Other parameters, e.g. TDS, the EC and chloride (Cl^-) were higher than the discharge limit, although, after treatment, they were noticeably reduced.

Table 7. Data inspection with standard

Parameters	Raw sample	Treated sample	Removal efficiency(%)	ECR [25]	ISI [43]
Cr (mg/L)	3373.5	12.1	99.64	2.0	0.05
pH	4.5	6.7	-	6-9	6-9
BOD (mg/L)	3197	107	96.65	250	30
COD (mg/L)	4297	293	93.18	400	250
TDS (g/L)	29.83	36.3	21.69	2.1	-
EC (mS)	66.9	81.2	21.38	1.20	0.85
Chloride (mg/L)	17021	6872	59.62	600	600

During the treatment process, the banana rachis adsorbent acts as an adsorbent for the chromium ion, and the chloride ion possibly co-precipitates with it, which might be the reason for chloride reduction. The adsorption of organic and inorganic pollutants at the adsorbent surface is responsible for the BOD and COD reduction. From Table 2 it is clear that the soluble mineral contents might be responsible for the increase in TDS. The rise in the EC might be due to the addition of the -OH group from the adsorbent.

Desorption and Reuse

The chromium-loaded used adsorbent was tried to be used for desorption as an effort to recover and reuse the chromium. A qualitative analysis was performed to ascertain the possibility of chromium recovery. In this case, 1.0 g of chromium-loaded adsorbent was mixed with 50 mL of distilled water at different pH of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 and then left to settle for 24 hours after 5 minutes of stirring.
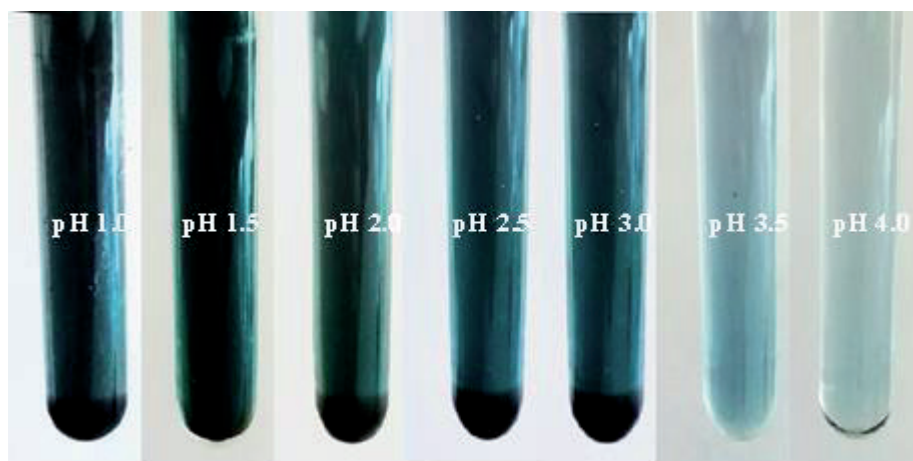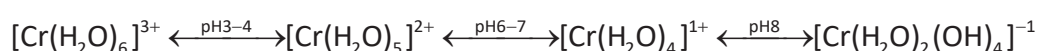
Figure 8. Desorption of chromium-loaded adsorbent at different pH

The result indicates that the lower the pH is, the more chromium is recovered.

The chromium ions exist as hydrated $[Cr(H_2O)_6]^{3+}$ in a solution. As the pH changes, the water molecules can be replaced by the hydroxyl ions. The number of hydroxyls exchanged relies on the pH of the solution [44]:

$$[Cr(H_2O)_6]^{3+} \xleftrightarrow{pH3-4} [Cr(H_2O)_5]^{2+} \xleftrightarrow{pH6-7} [Cr(H_2O)_4]^{1+} \xleftrightarrow{pH8} [Cr(H_2O)_2(OH)_4]^{-1}$$

It shows that a change in the pH can cause changes in the charge on the Cr-ion. Fig. 8 reveals the condition of the filtered water after 24 hours of settling with a unique shade of basic chromium sulphate. Since a quantitative analysis was not performed, it requires further studies to ensure the efficiency of the process.

CONCLUSION

In the batch-wise technique, the chromium-containing wastewater was treated for the removal of chromium by using the banana rachis adsorbent. The removal efficiency of chromium at the optimized condition was 99.64% at 3 g per 75 mL for 15 min at a relative pH of 6.7. The reduction of the BOD, the COD, and chloride was 96.65%, 93.18%, and 59.62%, respectively. The study indicates that the adsorption process follows the Freundlich isotherm for the multi-layer adsorption and the pseudo-second-order kinetics for reaction rate. The FTIR study reveals the associated functional groups for the adsorption process. Several comparisons with other studies in terms of contact time, removal efficiency, isotherm, and kinetic parameters, reveal that it was an effective technique to minimize the pollution load from the spent chrome liquor as well as an efficient approach towards the banana rachis waste management. The desorption study reveals the reappearance of chromium in a solution. Conclusively, the investigation could be helpful to effectively establish the treatment process of the spent chrome liquor in a tannery reservoir before the discharge.

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