

CHARACTERIZATION OF THERMALLY ACTIVATED BIOSORBENT AND USE IN CHROMIUM REMOVAL FROM TANNERY WASTEWATER

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ABSTRACT

The chrome tanning method is extensively used for the development of durable and flexible leather. However, it presents important environmental disadvantages, mainly because there is a discharge of Cr containing wastewater. The removal of chromium from waste leather is critical to the environmental sustainability of the leather industry. In this context, the present study aimed to employ thermally activated waste *Carica papaya* tree (CPT) adsorbent as a cost-effective and alternative method to such modern techniques. The maximum chromium removal efficiency (99.89%) was attained by calcination in a muffle furnace of the CPT adsorbent for 3 h at 600°C, with a dose of 0.25 g per 25 mL solution and a stirring time of 20 min. The adsorbent CPT was characterized by EDX, FTIR, BET surface area, and TEM analysis. The surface charge of the prepared adsorbent was also investigated by doing pH_{pzc} measurement. The Freundlich equilibrium and pseudo-second order model exhibited the highest value of the correlation coefficients; $R^2 = 0.9999$ and $R^2 = 0.9997$, respectively. The adsorption mechanism was found to be chemisorption, confirming the strong affinity between the adsorbent and chromium, along with the pseudo-second order kinetics and the Freundlich equilibrium. The desorption study demonstrated the desorption ability of the CPT adsorbent in both acid and alkali. Other physicochemical properties of the wastewater, including TSS, BOD, and COD, were decreased by 93.28%, 83.57% and 86.87%, respectively. The temperature-governed CPT adsorbent has complete Cr removal and also decreases other wastewater parameters. This is eco-friendly and helps in removing the water pollution from tannery wastewater.

Keywords: Adsorption, Chromium, Pollution, Removal efficiency, Thermal activation.

1. INTRODCUTION

Chromium tanning is normally carried out with the objective of improving the resistance of hides against biodegradation, making coloration easier, ensuring hydrothermal stability, and conferring on final leather products. Under a specific environmental ligand condition, chromium (Cr) exposure can induce apoptosis and change the protein structure (Hashem et al., 2023). The chromium tanning process is necessary for the preparation of hydrothermally stable leather; however, this tannin can be hazardous in some cases owing to its toxicity. In the chrome tanning, only 30-40% of chromium is uptake by the pelt from the effluent (Srivastava et al., 2013). A large portion of the chromium is discharged as such in water without any treatment to the tanning effluent, causing environmental pollution. Effluent from chrome tanning contains chromium in the range of 2656-5420 mg/L, high total solids (TS), and an acid pH of 2.4 -3.0, pointing out severe acidity (Hashem et al., 2021). Highly toxic hexavalent chromium, which is harmful to humans and animals even at low concentrations, is commonly formed during the oxidation of trivalent chromium and released into wastewater. Thus, for its disposal, the efficient removal of chromium in chrome-tanning wastewater is necessary.

Chemical precipitation (Mella et al., 2015), ion exchange (Peng and Guo, 2020), electrochemical precipitation (Hu et al., 2017), membrane processes (Habibi et al., 2015), as well as photocatalytic reduction (Zhao et al., 2019) are alternative methods used for the removal of Cr from tannery wastewater. But these are not affordable solutions because of their high setup and maintenance costs. One or another kind of pre-treatment or processing is needed for different treatments. Adsorption is one of them and can be a simple and economic process without any treatment. Affordable adsorbents are important to realize, as adsorption is an effective method for the removal of heavy metals from wastewater. Chai et al. (2021) have reported that conventional industrial carbons were not fully effective for heavy metal removal.

The microporous structure, high adsorption capacity, and large surface area are the analyses from researchers for cheap waste material-based adsorbents in wastewater treatment (Lan et al., 2022). The characteristics of the end product depend on the properties of the raw materials and the energizing method employed (Tripathi et al., 2016). Of special importance in the use of adsorbents for wastewater treatment are surface area and porosity (Chai et al., 2021). Materials like plant bark (Ighalo and Adeniyi, 2020), brewed tea leaves (Katha et al., 2021), coconut pith (Hashem et al., 2021), and egg casing (Katha et al., 2021) have been successfully transformed into effective, low-cost adsorbents. Branches of these adsorbents were used above all in the elimination of impurities from waste effluents, for example, colorants and heavy metal pollutants, towards a better treatment or control of pollution.

Carica papaya L. is a medicinal plant with nutritious fruits, and it is available in Bangladesh throughout the year. Diverse parts of plants and trees, i.e., fruits, seeds, leaves, and latex, are used in various healing purposes (Sharma et al., 2020). The *Carica papaya* tree (CPT) trunk can be considered as waste when cut down. CPT can be used to fabricate an adsorbent for chromium removal from tannery wastewater. Heat-treatment of the CPT without chemical modifications allows us to prepare an adsorbent that has a high porosity and surface area. Incineration can be one of the thermo-modification processes, but thermal modification is sometimes insufficient; if this has to happen, you need additional processing of chemical saturation, incineration, washing, and pH adjusting (Ahmed et al., 2019). The chemicals applied to treat the adsorbent added not only to its cost but also to the time of contact. The pretreated adsorbent could not be cost-effective. A thermally modified material, on the other hand, is more advantageous since it requires no chemical functionalization and preparation.

In this study, the thermally modified CPT adsorbents obtained from the *Carica papaya* plant waste have been used to remove chromium from tannery effluent. The adsorption performance of the CPT adsorbent was investigated by TEM, EDX, and FTIR according to the literature. Reusability test of thermally activated CPT adsorbent. The reusability performance of the acid and base-treated CPT adsorbent was tested by subjecting them to several adsorption–desorption cycles. The physicochemical characteristics of wastewater were also determined and compared before and after treatment to measure the efficiency of the treatment system

2. METHODOLOGY

2.1 Synthesis of CPT Adsorbent

The trash CPT was gathered from the agricultural area adjacent to Khulna, Bangladesh. Subsequent to collection, the CPT was sanitized, segmented, sun-dried, and subsequently oven-dried for 24 hours at $104\pm 1^\circ\text{C}$. The dehydrated sample was preserved for future research. Approximately 1000 g of ground CPT was subjected to calcination for 3 hours at 600°C to attain adequate thermal activation. The calcined CPT was pulverized.

2.2 Performance analysis of CPT Adsorbent

SAF Leather Limited, a tannery located in Jashore, Bangladesh, supplied the chrome tanning effluent. Chrome tanning wastewater was subjected to filtration using filter paper to eliminate irregular suspended particles. Approximately 25 mL of wastewater was utilized to assess the efficacy of the CPT adsorbent. The beaker was subsequently filled with 0.05, 0.1, 0.15, 0.20, 0.25, 0.30, and 0.35 grams of the CPT adsorbent. A magnetic stirrer was subsequently employed to continue stirring for 20 minutes at 400 rpm. The solution was permitted to stand for 4 hours before filtration. An Atomic Adsorption Spectrophotometer (AAS) and a pH meter were employed to ascertain the chromium concentration and the pH of both the initial and treated solutions, respectively. To calculate the chromium adsorption percentage (R), Equation (1) was employed, where " C_i " represents the starting concentration of Cr and " C_f " signifies the final concentration.

$$R (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Adsorption isotherms were studied using 0.30 g of CPT adsorbent added to 25 mL of chromium wastewater and stirred for 20 min. Origin8 software was used to fit the Langmuir and the Freundlich equilibrium models. The optimal dose of 0.30 g was taken for CPT adsorbent in 25 mL chromium wastewater, and different stirring speeds were used to perform adsorption kinetic experiments during 1, 5, 10, 15, 30, 45, 60, and 90 minutes. The pseudo-first and second-order equations were solved using the obtained data.

2.3 Characterization of CPT Adsorbent and Chromium Wastewater

The CPT adsorbent was also analyzed for chemical functional groups utilizing FTIR spectra (Perkin Elmer, USA) before and after its use. The acquired FTIR data were processed with Origin8 software. The EDX measurements were also made using a Silicon Drift EDS Detector (SDD) with the X-Max EDS system (Oxford Instruments, Oxford, UK) and an accelerating voltage of 80 kV. The TEM analysis of the outer surface of the CPT adsorbent was carried out with a JEOL JEM 1400 Plus TEM (Tokyo, Japan) to gain a photomicrographic image. The specific surface area and pore size distribution of the CPT adsorbent (Quantachrome Quadrasorb Evo, USA) were determined by the Brunauer-Emmett-Teller (BET) analysis. The initial pH of (pHi) was controlled at 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, and 12.0 by adding a few drops of either HCl (0.1 M) or NaOH (0.1 M), post

addition of NaCl solution to each set of ten beakers for determination of pH_{pzc}. Next, the optimum amount of CPT adsorbent was added to each beaker and shaken at 300 rpm using a magnetic stirrer for 24 h. The solution was drained after sedimentation for 4 h, filtered, and a pH meter was used to measure the final pH of the solution (pH_f). The pH_{pzc} was finally calculated by the difference of ΔpH and pH_i. The pH, total dissolved solids (TDS), total suspended solids (TSS), electrical conductivity (EC), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) were used to characterize both raw and treated wastewater.

2.4 Desorption study

The reusability of the CPT adsorbent was tested by desorption of Cr-adsorbed CPT adsorbent. The desorption chemicals Na₂CO₃, NaOH, HNO₃, and H₂SO₄ were studied to estimate the regenerative percentage of the adsorbent.

The Cr-adsorbed CPT adsorbent was treated with 0.1M Na₂CO₃, NaOH, HNO₃, and H₂SO₄ solutions. The suspension was mechanically stirred at 400 rpm for 24 h, at a solid-to-liquid ratio of approximately 2.5 g/500 mL. After stirring, the solution was filtered and washed with distilled water. The adsorbent was then dried in an oven at 104±1°C for 24 h for further use.

3. RESULTS AND DISCUSSION

3.1 Effect of CPT Adsorbent Dose and pH

Fig. 1 illustrates the effectiveness of the CPT adsorbent in chromium removal alongside the associated pH levels. The maximum removal of Cr achieved was 99.88% with an adsorbent dosage of 0.30 g per 25 mL of chromium-containing wastewater. The adsorbent dosage ranges from 0.05 to 0.35 g per 25 mL of wastewater, demonstrating that the efficiency of chromium removal increases progressively with higher adsorbent dosage. The removal efficiency of Cr was 99.88% for 0.30 g and 99.89% for 0.35 g/25 mL of effluent. The optimal dosage was 0.30 g/25 mL of effluent, determined by the adsorbent quantity and removal efficiency. The suspension exhibited pH values of 5.1, 5.4, 5.7, 6.0, 6.4, 6.8, and 6.8, corresponding to adsorbent dosages of 0.05 to 0.35 g for 25 mL of wastewater, respectively. The removal of chromium exhibited a significant increase with the elevation of pH in the suspension.

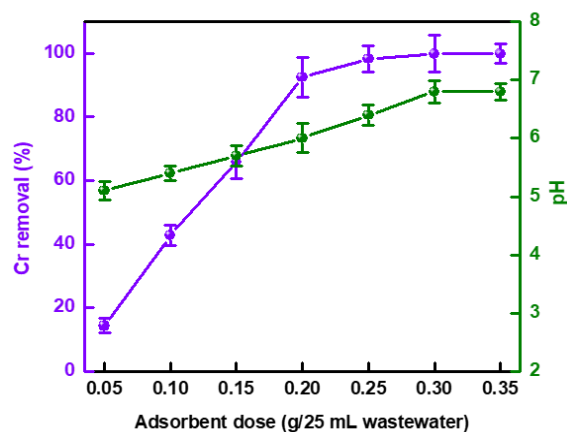


Fig. 1. Effect of CPT adsorbent dose on Cr removal efficiency and pH

3.2 Characterization of Adsorbent

3.2.1 FTIR Analysis

Fig. 2(a) presents the FTIR spectra for the pure and chromium-loaded CPT adsorbent. Table 1 displays the peak wavelengths alongside the associated functional groups prior to and during the adsorption process.

The unique O-H stretching vibrations in the CPT adsorbent spectra are characterized by a minor band at 3697.28 cm⁻¹. The N-H bending vibrations predominantly account for the bands within the range of 3500 to 3300 cm⁻¹. The stretching vibrational modes of C=C (1801 cm⁻¹), =CH₃ (1434.73 cm⁻¹), C-O (ranging from 1188.01 to 1068.76 cm⁻¹), and N-H (ranging from 874.13 to 712.42 cm⁻¹) are evident in the spectra of CPT adsorbents, attributable to the deformation of the carbon structure (Wei et al., 2021). These functional groups mostly represent the CPT fibers' cellulose, hemicelluloses, lignin, and pectin.

The FTIR spectra of the Cr-loaded CPT adsorbent indicated that the adsorption of Cr markedly diminished the intensity of the bands associated with the CPT adsorbent. The removal of Cr ions during adsorption is presumably the reason for this outcome. The N-H bending vibrations predominantly account for the band at 3419.95 cm⁻¹. The spectrum of CPT adsorbents exhibits stretching vibrational modes for hydroxyl O-H (2514.28 cm⁻¹), carboxyl C=C (1802 cm⁻¹), =CH₃ (1438 cm⁻¹), C-O (1091.78 cm⁻¹), and N-H (between 875.20 and 712.48 cm⁻¹) (Wei et al., 2021). The observed shifts are caused by interactions with O-H, C=C, and C-O groups, which greatly contribute to the adsorption of Cr (González-López et al., 2021). The increased number of functional groups in the CPT adsorbent is responsible for the improved Cr adsorption from wastewater. The enhanced functional groups of the CPT adsorbent facilitate the extraction of maximum chromium from wastewater, as evidenced by the EDX analysis.

Table 1. FTIR analysis of the CPT adsorbent before and during the Cr adsorption

Wavelength range (cm ⁻¹)	Before adsorption	After adsorption	Differences	Assignment
3650-3590	3697.28	Absent	-	O-H
3500-3300	3414.25	3419.95	-5.7	N-H
	3229.72	Absent	-	N-H
	2982.84	Absent	-	N-H
	2700-2500	2514.16	2514.28	-0.12
1470-1430	1434.73	Absent	-	=CH ₃
1250-1050	1188.01	Absent	-	C-O
	1092.28	1091.78	0.50	C-O
	1068.76	Absent	-	C-O
900-650	874.13	875.20	-1.07	N-H
	712.42	712.48	-0.06	N-H

3.2.2 TEM and EDX Analysis

Fig. 2(b) presents the pictures of the CPT adsorbent obtained from TEM examination. Fig. 2(b) demonstrates that the TEM image of the CPT adsorbent before chromium adsorption displays a uniform, distinct, and spherical morphology. Spherical adsorbents provide a superior adsorption capability relative to typical adsorbents (Moradi and Sharma, 2021). This adsorbent enhances the interaction between the adsorbent and the adsorbate owing to its high specific surface area (Wang et al., 2018). Therefore, the CPT adsorbent may efficiently remove chromium from tannery wastewater. The CPT adsorbent's chromium adsorption causes the sphere in Fig. 2(c) to agglomerate and lose its clarity. The morphological changes signify the absorption of chromium from the effluent.

The ion exchange mechanism was emphasized by contrasting the peak intensity of interchangeable ions prior to and following Cr adsorption on the CPT adsorbent. As shown in Fig. 2(d), the CPT adsorbent contains the fundamental exchangeable cations K⁺, Ca²⁺, Mg²⁺, and Al³⁺ before Cr adsorption. The CPT adsorbent comprised the following atomic percentages: 51.9% C, 34.1% O, 3.7% S, 3.5% Si, 2.8% Ca, 2.0% Al, 0.9% Cl, 0.5% Mg, 0.4% K, and 0.2% P. The atomic percentages

of C, O, Cr, S, Si, Ca, Al, Cl, Mg, K, and P in the CPT adsorbent during Cr adsorption were 11.6%, 37%, 35.6%, 11.6%, 1.3%, 7.6%, 0.3%, 0.7%, 0.7%, 0.8%, and 1.4%, respectively (Fig. 2(e)). Approximately 35.6% of atomic chromium persists following chromium adsorption, signifying that chromium has been adsorbed onto the CPT adsorbent. The atomic proportion of basic exchangeable cations, such as Ca and Al, diminished due to adsorption (Wang et al., 2018).

3.3.3 pH_{pzc} and BET Analysis

The pH_{pzc} of the CPT adsorbent surface was 8.5 (Figure 2(f)). The chemical and electrical properties of active sites on the adsorbent are responsible for the pH_{pzc} (Saha et al., 2019). The CPT adsorbent surface was positively charged in the experiment as pH_{pzc}. The specific surface area, total pore volume, and the average pore radius for the CPT adsorbent were determined by using BET analysis according to the classical Brunauer-Emmett-Teller (BET) method. As listed in Table 2, the CPT adsorbent has an average pore diameter of 6.865 nm, total pore volume of 0.0075 cm³/g, and surface area of 37.343m²/g; The adsorption capacity value increases with specific surface areas for any adsorbent material in general terms. It was therefore proved that the CPT adsorbent isolated heavy metal adsorption of chromium compared to other adsorbents in terms of surface area, total pore volume, and average pore radius.

3.4 Isotherm and Kinetics Studies

Fig. 3(a) depicts the Langmuir isotherm model. The graphing of 1/Ce and 1/qe values yielded a coefficient of determination, R², of 0.5349. The value of the coefficient of determination appears to be insignificant. Figure 3(b) depicts the Freundlich isotherm model. The Freundlich isotherm had a significant R² value of 0.9999, approaching unity. The R² value of the Freundlich isotherm model surpassed that of the Langmuir isotherm model. Thus, the adsorption mechanism can be clarified by the Freundlich isotherm model.

Plotting the values of t and ln(qe-qt) on the XY-axis yielded a determination coefficient (R²) of 0.8560 for the pseudo-first-order kinetics, as depicted in Fig. 3(c). The t vs t/qe values depicted on the graph along the XY-axis are shown in Fig. 3(d) for the pseudo-second-order kinetics model, with a coefficient of determination of 0.9997. The adsorption process depicting the chemisorption between the adsorbent and the adsorbate (Cr) is more precisely portrayed, as evidenced by the R² value derived from the pseudo-second-order kinetics.

Table 2. Surface analysis of the adsorbents by the BET method

Textural Properties	Value
Surface area (m ² /g)	37.343
Pore volume (cm ³ /g)	0.0075
Pore radius (avg.) (nm)	6.865

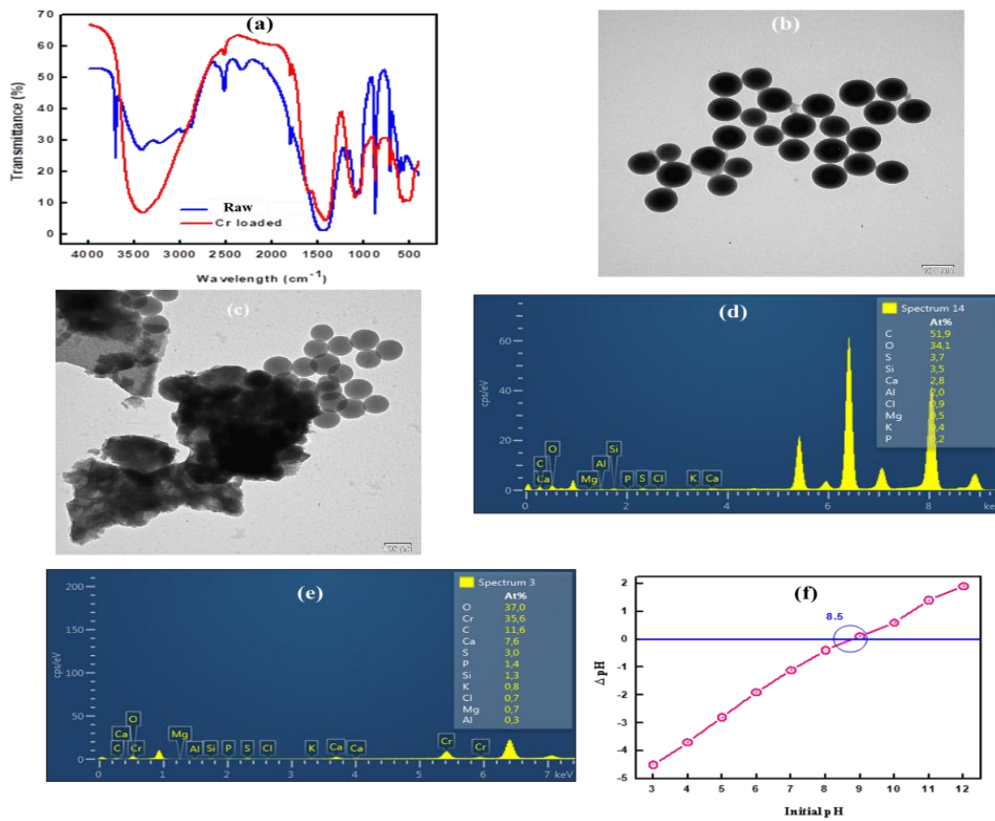


Fig. 2. (a) FTIR analysis of CPT adsorbent and Cr loaded adsorbent, (b) TEM analysis of CPT adsorbent, (c) TEM analysis of Cr loaded adsorbent, (d) EDX analysis of CPT adsorbent, (e) EDX analysis of Cr loaded adsorbent, and (f) pH_{pzc} analysis

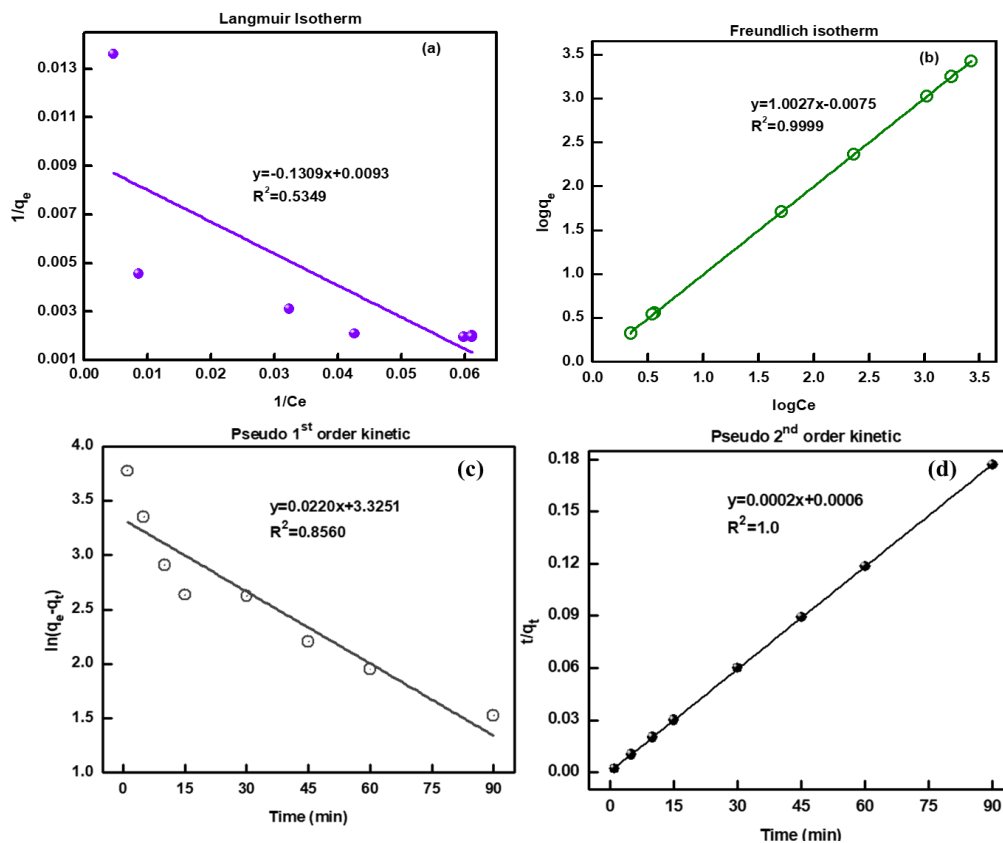


Fig. 3. (a) Langmuir, (b) Freundlich, (c) Pseudo-first-order, and (d) pseudo-second-order model

3.5 Impact of Desorbing Agent

Table 3 shows the effects of various desorbing agents, including NaOH, Na₂CO₃, H₂SO₄, and HNO₃. After the initial desorption cycle, 94.54%, 94.82%, 94.84%, and 94.11% of chromium were desorbed by the agents NaOH, Na₂CO₃, H₂SO₄, and HNO₃, respectively. The results indicate that the Cr absorbed by the CPT adsorbent may be desorbed, allowing for the adsorbent's reuse. Strong acids and bases exhibit distinct behaviors throughout the desorption process, perhaps leading to variations in removal efficacy. The desorbed chromium, however, can be reutilized for additional tanning processes.

Table 3. Impact of various desorbing agents after 1st cycle of desorption

No.	Desorbing agent	1st cycle removal (%)	SD
01.	NaOH	94.54	2.42
02.	Na ₂ CO ₃	94.82	3.58
03.	H ₂ SO ₄	94.84	2.65
04.	HNO ₃	94.11	1.55

3.6 Efficacy of Treatment Process

The physicochemical characteristics of wastewater before and after treatment are represented by Table 4. The untreated wastewater displayed an acidic pH of 4.1, falling below the allowable threshold (ECR, 2023). The pH of the treated wastewater (6.8) is within the acceptable range (ECR, 2023). The treated wastewater reduced BOD, COD, and TSS by 83.57%, 86.87%, and 93.28%, respectively. Both EC and TDS exhibited a slight increase. Accelerated mineral dissolution from the adsorbent may increase TDS and EC. Chromium concentrations were 3084.05 mg/L in the untreated wastewater and 3.60 mg/L post-treatment. The percentage of Cr eliminated was 99.88%.

No.	Parameters	Raw wastewater	Treated wastewater	ECR (2023)
1.	pH	4.1±0.2	6.8±0.31	6-9
2.	TDS (mg/L)	9850 ±5.0	14910±3.0	2100
3.	TSS (mg/L)	6550.0±3.0	440.0± 5.0	100
4.	BOD (mg/L)	3360.0±15	552.0±3.0	150
5.	COD (mg/L)	3724.8±1.2	489.6±5.4	200
6.	EC (mS/cm)	24.29±0.2	31.69±0.2	1.20
7.	Cr (mg/L)	3084.05±2.42	3.60±1.22	2.0

4. CONCLUSIONS

99.88% removal of chromium was obtained by using 0.30 g thermally activated adsorbent from the *Carica papaya* tree per 25 mL effluent. The thermally treated *C. papaya* tree adsorbent was prepared in a less labour and cost-intensive way. Characterization of the thermally activated *C. papaya* adsorbent using FTIR, EDX, and TEM, in addition to surface area and pH(pzc) studies, increased its efficiency for removing chromium from tannery effluent. The thermally activated adsorbent was proven efficient in the adsorption process, and the mechanism of chromium binding to the adsorbent as a stable interaction was verified on the basis of the Freundlich isotherm and second-order kinetics. For the purpose of reducing agricultural solid waste generation and to reduce tannery pollution load,

from *C. papaya* tree may be utilized as an adsorbent. To reduce agricultural waste and to minimize the pollution load on tanneries, the *C. papaya* tree waste can act as an adsorbent.

ACKNOWLEDGEMENTS

The authors thank the Department of Leather Engineering, KUET, for providing the necessary facilities to conduct this research.

AI DECLARATION STATEMENT

The authors confirm that no AI tools were used in the preparation or completion of this assessment. This submission is entirely their own work.

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