



## Research Article

## Minimization The Chemical Oxygen Demand (COD) Content in Tannery Wastewater Using Activated Carbon from Spent Tea Leaves

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### Abstract

Water pollution from tannery wastewater is a serious environmental issue. This study aimed to investigate the potential of spent tea leaves as activated carbon (AC) to minimize chemical oxygen demand (COD) of tannery effluent. To determine the best conditions for minimizing COD, a batch adsorption process was conducted, involving various factors such as different adsorbent dosages (ranging from 1 to 11 gm L<sup>-1</sup>), contact time (30 to 150 min), and pH values (ranging from 3 to 11). The characterization was done by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM). The outcomes of this study demonstrated that using 1.5 M H<sub>2</sub>SO<sub>4</sub> as activating agents resulted in iodine values of 750.52 mg g<sup>-1</sup>. Employing a higher concentration of H<sub>2</sub>SO<sub>4</sub> had several positive effects, such as minimizing total dissolved solids (TDS) and turbidity, increasing dissolved oxygen (DO), and lowering COD in tannery wastewater. The most significant COD reduction, reaching 96.16%, was achieved with a dosage of 5 gm L<sup>-1</sup>. Furthermore, the data collected from these experiments were analyzed using the Langmuir isotherm model, which provided an excellent fit ( $R^2 = 0.9837$  and  $q_{max} = 5.186 \text{ mg g}^{-1}$ ). Based on these results, it can be concluded that 1.5 M H<sub>2</sub>SO<sub>4</sub> is the optimal choice for developing activated carbon from spent tea leaves. Additionally, the resulting activated carbon proves to be an effective adsorbent for minimizing COD from tannery wastewater.

### Introduction

Environmental degradation and human safety are major challenges for developing countries, mainly because industries release a variety of harmful chemicals and heavy metals. Toxic metals such as Cr, Hg, Cd, As, Ni, and Pb are present in high concentrations in industrial wastewater resulting from different manufacturing processes [1–2]. These metals accumulate in the environment and are passed through the food chain, posing a severe health risk to both humans and animals. The tannery industry in Bangladesh is considered one of the most harmful industries to the environment because it produces a lot of waste, both in liquid and solid forms [3]. Leather processing is the process of

transforming unfinished animal hides and skins into finished leather through a series of chemical and mechanical operations. This includes pre-tanning, tanning, and post-tanning stages. From 1000 kg of raw hides and skins, approximately 150 kg of leather is produced, leaving behind 850 kg of solid waste consisting of 450 kg of collagen and 400 kg of fleshing waste, along with 30 m<sup>3</sup> of effluent. Pre-tanning and tanning stages consume around 57% of the water used in leather processing, while washing accounts for 35% of the total water consumption [4]. At present, there are two popular methods of tanning: chrome tanning and vegetable tanning. Chromium tanning involves the use of chromium salts and tanning liquors, while vegetable

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tanning involves the use of tanning materials derived from natural sources [5].

United Nations Industrial Development Organization (UNIDO) has stated that tanning processes involve the use of 175 different chemicals. Whether partially treated or not, the release of these effluents during the process has caused significant environmental pollution [6]. The use of adsorption methods has been recently introduced to remove from wastewater any organic or inorganic contaminations, and due to its great properties, carbon is a preferred material for producing porous adsorbents. Activated carbon (AC) is a commonly recognized substance that functions as an adsorbent and has numerous beneficial features, including stability at high temperatures, a high ability to adsorb, a substantial specific surface area, and a well-formed system of pores [7]. The process of adsorption can be categorized into two types: chemical adsorption and physical adsorption. Physical adsorption, also known as physisorption, is a reversible process that involves weak Van der Waals forces. On the other hand, chemical adsorption, also known as chemisorption, is an irreversible process that involves chemical bonding between the sorbet and sorbent molecules [8]. A variety of carbonaceous materials, including nut shells, charcoal, wood, lignite, peat, fruit pits, and paper mill waste (lignin), can be found in activated carbon, which can be derived from animal, plant, or mineral sources [9]. Activated carbon that is available commercially can be quite costly. As a result, it is crucial to search for cheaper and more easily obtainable sources to create adsorbents [10].

It is considered that tea is one of the most widely consumed beverages globally after fresh water, and in 2021, the worldwide production of tea reached 28 million tons [11]. In Bangladesh, tea is the second largest cash crop after jute, contributing approximately 1% to the country's GDP. Tea has been produced in Bangladesh for more than 180 years. According to the Bangladesh Tea Board, in 2021, Bangladesh produced a record 965 million kg of tea and exported 680,000 kg globally [12]. Tea possesses antioxidant properties that have health-promoting effects such as antivirus, antidiabetic, antihypertensive, anti-inflammatory, and anticancer properties. Due to these benefits, the consumption of tea is increasing steadily [13]. Significant quantities of used tea leaves are produced and disposed of into the environment without appropriate processing. A small tea stall in Bangladesh could generate around 230 kg of tea waste per year and may vary depending on the specific circumstances of each tea stall [14]. Therefore, the disposal and utilization of this waste has become a significant concern. Researchers have recently shown interest in finding ways to make use of the spent tea

waste. The tea waste comprises a variety of compounds, hemicellulose, cellulose, lignin, theanine, tea protein, polysaccharides, polyphenols, colors, saponins, vitamins and caffeine [15]. Tea waste also contains functional groups like aromatic carboxylate, hydroxyl, oxyl, amino, sulfonic, and phenolic groups that can cause physico-chemical interactions for sorption [16]. The preparation of activated carbon involves two fundamental methods (1) physical or gas activation and (2) chemical activation. Physical activation involves the carbonization of the raw material followed by in the presence of  $\text{CO}_2$ , steam, or air. On the other hand, chemical activation occurs simultaneously with the use of activating agents such as  $\text{ZnCl}_2$ ,  $\text{KOH}$ ,  $\text{NaOH}$  or  $\text{H}_2\text{SO}_4$  during the carbonization and activation process. Both physical and chemical activation methods introduce surface oxygen functional groups to the carbon [17].

Earlier studies have investigated the use of tea waste for producing activated carbon. For example, Gurten et al. [18] created and analyzed activated carbon from tea waste using  $\text{K}_2\text{CO}_3$ , Fadhil et al. [19] produced activated carbon using spent tea waste for purifying biodiesel, Auta and Hammeed [20] used  $\text{CH}_3\text{CO}_2\text{K}$  (Potassium acetate) to create activated carbon from tea waste for adsorbing Acid Blue 25 dye, and Malhotra et al. [21] worked on adsorbing sodium dichlofenac from waste water using tea waste activated carbon with activating agents such as  $\text{H}_2\text{SO}_4$ ,  $\text{KOH}$ ,  $\text{ZnCl}_2$ ,  $\text{K}_2\text{CO}_3$ . Those studies also have proposed that tea waste has potential as an adsorbent to decrease chemical oxygen demand (COD) in tannery wastewater. For this, in this work, black spent tea waste was used as base material for producing activated carbon due to three primary reasons. Firstly, it is readily available, secondly, it is cost-effective, and thirdly, it can be prepared without the use of any harmful chemicals. The present research endeavors to create an economical and effective form of activated carbon by chemically activated spent tea waste. From the best of author knowledge, no investigation has been made on used tea leaves derived AC for COD minimization applications were not performed particularly in Bangladesh. Thus, the goal is to utilize the tea waste as activated carbon to minimize COD load from the tannery wastewater by manipulating the dose of  $\text{H}_2\text{SO}_4$ .

## Material and methods

### 1) Chemicals and materials

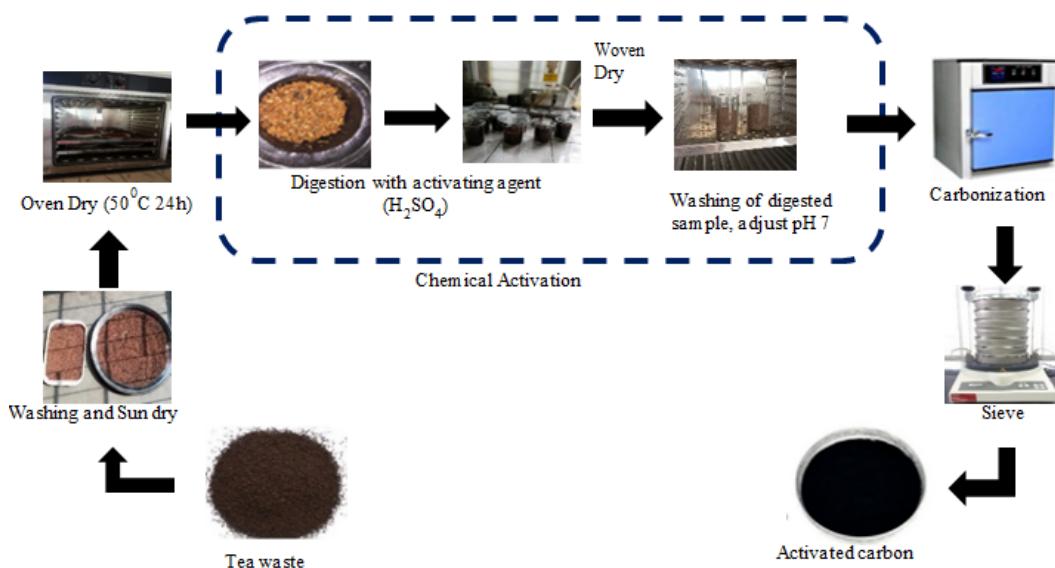
All chemicals were bought from Central Drug House Ltd. (India), and Sigma-Aldrich (Singapore) via local distributors in Dhaka, Bangladesh. Tap and distilled water was used at different stages of the experiments. Tannery wastewater was collected from the tannery

located at Hemayetpur Tannery State in Savar, Dhaka, Bangladesh [Sample 1: Tannery outlet Sample (S1), Sample 2: Inlet water in CETP Sample (S2) and Sample 3: Treated water from CETP (S3)]. To avoid the breakdown of organics prior to analysis, the effluent was kept refrigerated until it was analyzed. Used tea leaves from black tea were collected from five tea stalls in Savar, Dhaka, Bangladesh.

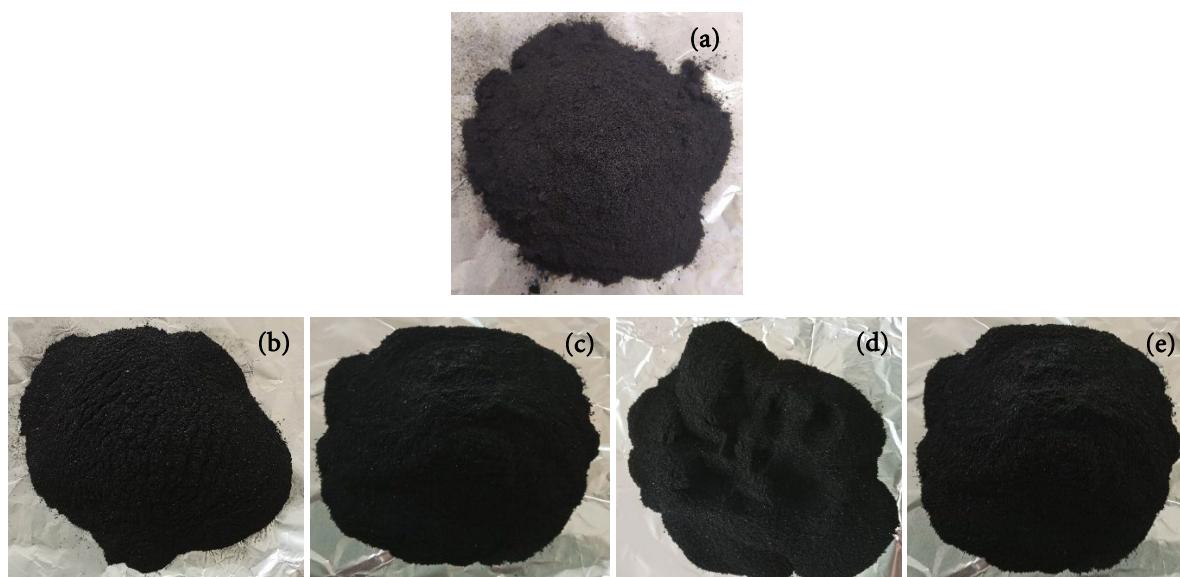
## 2) Preparation of AC

To originate activated carbon (an adsorbent material), black tea waste is boiled in water at temperatures exceeding 1,000°C. Then the tea waste was washed multiple times with tap water to eliminate any color or flavors. First, the tea waste samples were dried in the sun on a steel tray for five days. Next, they were oven-dried at 50°C for 24 h. In a total of 12 experiments, 50 g of the dried sample was taken and placed separately

into various beakers. Each beaker contained a known amount of dilute activating agent ( $H_2SO_4$ ) with concentrations ranging from 0.25M to 1.5M in a 1:2 ratio. The contents in the beakers were thoroughly mixed, creating a paste that was then wrapped in aluminium foil and baked in an oven at 40°C for 12 h. The resulting paste was washed with distilled water to adjust the pH to a range of 6–7, and then dried in an oven at 105°C for 24 h to remove any remaining moisture. The dried sample was transferred to pre-weighed crucibles and positioned in a muffle furnace, where it was heated at 550°C for 15 min. The end product obtained after this process was activated carbon. This activated carbon was collected and finally stored in airtight polyethylene bags. For a visual representation, please refer to Figure 1 for the step to step procedure and Figure 2 for the prepared activated carbon from tea waste with various molarities of sulfuric acid.



**Figure 1** Schematic diagram of the study design.



**Figure 2** Prepared activated carbon from spent tea leaves at various concentrations of  $H_2SO_4$ : (a) control (without acid), (b) 1.5 M, (c) 1.0 M, (d) 0.50 M, and (e) 0.25 M.

### 3) Method for minimizing COD from tannery wastewater

To avoid the need for volume correction, it was decided to use a batch process for each step [22]. For each experiment, 250 mL of the collected wastewater sample was used and a fixed amount of adsorbent was added to a 500 mL beaker stirred with 100 rpm speed. After varying duration, the sample was finally filtered for measuring COD. The concentration of COD was determined by dichromate method (Hanna Model no. H1839800). In this method, a heated digestion is required to oxidize organic matter in the sample. During the digestion, hexavalent chromium in the reagent is minimized to trivalent chromium. The amount of minimized chromium is then measured colorimetrically. The intensity of color is determined by a compatible photometer and the COD concentration is displayed in mg L<sup>-1</sup> (ppm) O<sub>2</sub>.

#### 3.1) Adsorption dose

Various quantities of activated carbon ranging from 1 to 11 g L<sup>-1</sup> were utilized in the study. To treat 250 mL of tannery water, different amounts and concentrations of activated carbon were applied.

#### 3.2) Contact time

For each experiment, a beaker containing 250 mL of sample was used, with the appropriate amount of adsorbent added. The samples were stirred for different durations between 30 to 180 min. Once the set time had elapsed, the sample was filtered and analysed.

#### 3.3) pH value

The effect of pH on the system was examined by keeping the concentration, contact time, and amount of AC constant, while modifying the pH level between 3-10 using different quantities of either NaOH or HCl solution. After a specific time period, the mixture was filtered and analyzed.

### 4) Characterization of prepared activated carbon and tannery wastewater

The evaluation of prepared activated carbon involved assessing various properties including iodine number, moisture content, ash content, pH and yield percentage [23]. Surface morphology analysis was carried out using scanning electron microscopy (SEM) images were used (Model 6490 JEOL JSM) and FTIR analysis (Perkin Elmer Frontier) was conducted to identify functional groups. Regarding tannery wastewater, several properties were examined, such as pH value, total dissolved solids (TDS), total suspended solids (TSS), dissolved oxygen (DO), electrical conductivity (EC), salinity, turbidity and COD.

### 5) Adsorption isotherm

To enhance the design of an adsorption method for equilibrium studies, it is necessary to determine the most suitable correlation. Experimental data and equilibrium adsorption are commonly analyzed using the Freundlich and Langmuir isotherms. These isotherms are widely employed in adsorption studies to recognize the adsorption behavior and optimize the design of adsorption processes. To plot the adsorption isotherm, the solid phase ( $q_e$ ) is plotted against the liquid phase concentration ( $C_e$ ).

The following Eq. 1 represents the linear form of Freundlich model

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (\text{Eq. 1})$$

where,  $q_e$  = the amount of the adsorbate adsorbed (mg g<sup>-1</sup>),  $C_e$  = equilibrium concentration (mg L<sup>-1</sup>),  $K_f$  = the Freundlich isotherm constant (L mg<sup>-1</sup>) and  $n$  = Freundlich adsorption intensity.

The Langmuir isotherm model, on the other hand, implies that there would be non-ideal adsorption on heterogeneous surfaces with a multilayer coverage. It implies that more powerful binding sites are used first, then less powerful binding sites. In other words, the binding strength diminishes as site occupation increases.

The Langmuir isotherm model is described by the following Eq. 2:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} k_1 C_e} \quad (\text{Eq. 2})$$

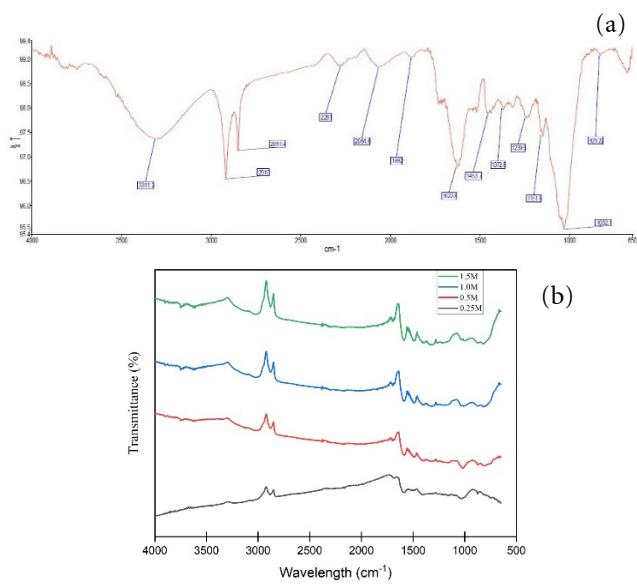
where,  $q_e$  = the amount of the adsorbate per unit mass of adsorbent (mg g<sup>-1</sup>) at equilibrium,  $q_{\max}$  = the maximum monolayer adsorption capacity of the adsorbent (mg g<sup>-1</sup>),  $K_l$  = the Langmuir isotherm constant (L mg<sup>-1</sup>) and  $C_e$  = the equilibrium concentration of the adsorbate in the solution (mg L<sup>-1</sup>).

## Results and discussions

### 1) Fourier transform infrared spectroscopy (FTIR)

The functional groups that are present on the surface of the derived adsorbent were identified using the FTIR spectrum. FTIR spectra of the adsorbent (Figure 3), were measured within the range of 500–4,000 cm<sup>-1</sup> wave number. Figure 3(a) illustrates the presence of alcohol and polyphenols on the adsorbent surface through the O-H group at 3311.3 cm<sup>-1</sup>. On the other hand, Figure 3(b) presents the weak bands in the 1.5 M and 1.0 M H<sub>2</sub>SO<sub>4</sub> spent tea leaves AC at 3,031.43 cm<sup>-1</sup> and 3,014 cm<sup>-1</sup>, respectively. The peaks observed at approximately 2,881 cm<sup>-1</sup> and 2,882.3 cm<sup>-1</sup> showed distinctive cha-

racteristics of the stretching vibration of aliphatic C-H groups in all four molarities of AC whereas for without treatment at  $2,919\text{ cm}^{-1}$  and  $2,851.4\text{ cm}^{-1}$ .



**Figure 3** FTIR spectra of spent tea leaves AC; (a) without treatment and (b) treated with different  $\text{H}_2\text{SO}_4$  concentrations.

Additionally, the peaks at around  $1,622.8\text{ cm}^{-1}$  for AC without treatment and at  $1,591\text{ cm}^{-1}$  and  $1,587.6\text{ cm}^{-1}$  might be attributed to the stretching of C-C bonds in aromatic compounds for all four molarities [24]. But due to interference of moisture content there is a drop in initial T% 0.25 M  $\text{H}_2\text{SO}_4$ .

## 2) Scanning electronic microscope (SEM) analysis

SEM analysis was conducted to investigate the surface characteristics of activated carbon derived from spent tea leaves, with the aim of assessing the formation of pores following the activation process (Figure 4). Before treatment the surface of spent tea waste exhibits smooth and uniform microporous structure. After adsorption, the surfaces of activated carbon with concentrations of 1.50 M and 1.0 M  $\text{H}_2\text{SO}_4$  were found saturated as most of the available pores were covered by the organic molecules. On the other hand, the surfaces of AC with concentrations of 0.50 M and 0.25 M  $\text{H}_2\text{SO}_4$  were observed to be rough and not uniform. The analysis leads to the conclusion that the concentration of the activating agent used for the activation process can affect the surface structure of the AC.

## 3) Determination of iodine number of prepared AC

The iodine number reflects the porosity of activated carbon, defined as the quantity of iodine adsorbed by 1 g of carbon at the milligram scale. The iodine number serves as an estimate for the surface area and micro-porosity of effective carbons with notable accuracy. It

quantifies the amount of microspores (0-200A) present in the activated carbon by measuring the adsorption of iodine from solution. The typical iodine number range of AC falls between 500–1,200 mg g<sup>-1</sup> [25]. In our experiment, the iodine numbers, moisture content, ash content, percent of yield, and pH of AC at concentrations of 1.5 M and 1.0 M  $\text{H}_2\text{SO}_4$  are within the range specified in Table 1.

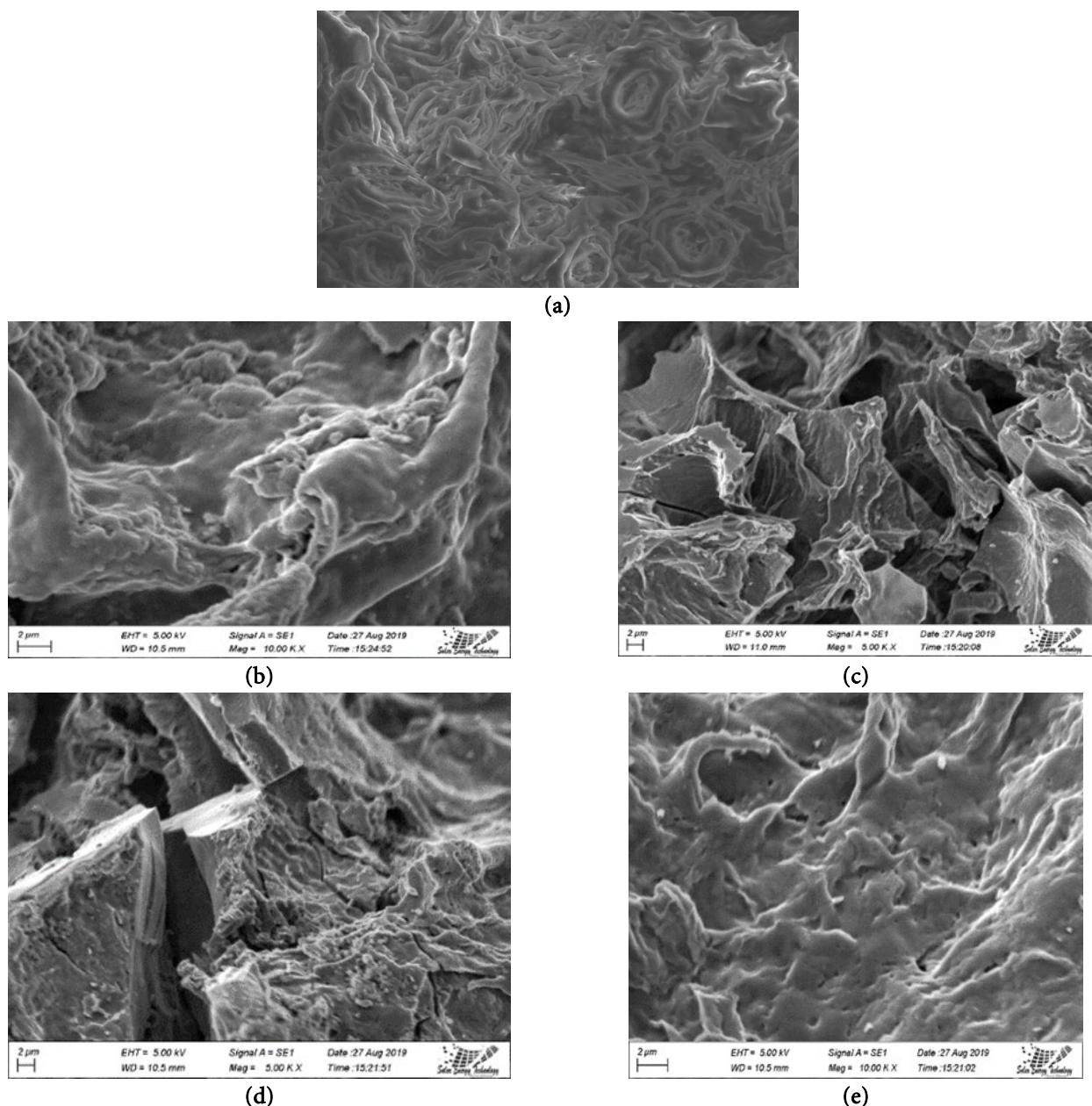
The normal range for iodine numbers is not met by AC treated with 0.50 M and 0.25 M  $\text{H}_2\text{SO}_4$ , indicating that the adsorption capacity is impacted by molarity. In comparison, activated carbon treated with 1.5 M and 1.0 M  $\text{H}_2\text{SO}_4$  has a higher adsorption capacity than that treated with 0.5 M and 0.25 M.

## 4) Determination of the moisture and ash content in the derived activated carbon

The moisture contents of all four samples were examined and found to be higher than the typical range reported for activated carbon, which is usually between 3–6%. This was due to the absence of a moisture-free environment during the production and storage of the ACs in this study. Minimizing ash content could further enhance the adsorption ability of the ACs. Here 0.50 M AC has lower ash content than 1.5 M AC and leads to better adsorption capabilities for AC. The neutral pH value was obtained for 0.25 M and 1.0 M sample while for 0.50 M and 1.5 M AC, it was slightly alkaline [26]. Water parameters, pH, TDS, DO, salinity, TSS, COD of tannery wastewater were studied before and after treatment, depicted in table 2 and 3.

## 5) Effect of adsorbent dose

The data presented in Figure 5 illustrates how varying the amount of AC affects the reduction of COD. The AC dose for the four different molarities ranged from 1 to 11 gm L<sup>-1</sup>, and the samples were run for duration of 90 min. The reduction percentages of COD are seen to be increased with the increase in spent tea leaves dosage and the results show that 5 g L<sup>-1</sup> of AC was the best dosage for minimizing COD across all samples. In 1.5 M AC, S1, S2, and S3 exhibited COD reduction of approximately 92.05%, 96.16%, and 78.01%, respectively. For 1.0 M AC, S1, S2, and S3 showed COD reduction of about 87.68%, 93.79%, and 74.90%, respectively. In 0.5 M AC, S1, S2, and S3 demonstrated COD reduction of roughly 61.53%, 67.19%, and 58.78%, respectively. In 0.25 M AC, S1, S2, and S3 showed COD reduction of approximately 56.19%, 63.89%, and 46.15%, respectively. Beyond the optimal dose, the percentage of COD reduction in all sample considerably declined. COD decrease at 1.5 M and 1.0 M AC ranging from 70% to 96%. However, COD decrease at 0.5 M and 0.25 M AC was between 50% and 60%.



**Figure 4** SEM images of spent tea leaves AC using (a) without treatment, (b) 1.5 M, (c) 1.0 M, (d) 0.50 M, and (e) 0.25 M of  $\text{H}_2\text{SO}_4$ .

**Table 1** The properties of the derived activated carbon

Molarity of $\text{H}_2\text{SO}_4$ (M)	Iodine number ( $\text{mg g}^{-1}$ )	Moisture content (%)	Ash content (%)	Percentage yield (%)	pH value
0.25	273	12	18.7	25.4	6.9
0.50	420	14	17	27.9	6.8
1.00	560	14	18.1	25	6.4
1.50	750.52	15	22.8	20.4	6.1

**Table 2** Water parameters prior to treatment

Water Sample	Water parameters							
	pH value	EC ( $\mu\text{s cm}^{-1}$ )	TDS ( $\text{mg L}^{-1}$ )	DO ( $\text{mg L}^{-1}$ )	Salinity (ppt)	Turbidity (NTU)	TSS ( $\text{mg L}^{-1}$ )	COD ( $\text{mg L}^{-1}$ )
S1	5.2	8530	19520	2.5	7.5	722	10.9	6,220
S2	2.1	43350	21700	8.31	14.3	665	13.1	23,700
S3	9.39	1550	2062	0.48	2.8	520	8.6	2,542

**Table 3** Post-treatment water parameter values

Molarity of H <sub>2</sub> SO <sub>4</sub>	Water Sample	Water parameters					
		pH value	EC (μs cm <sup>-1</sup> )	TDS (mg L <sup>-1</sup> )	DO (mg L <sup>-1</sup> )	Salinity (ppt)	Turbidity (NTU)
1.5 M	S1	7.9	8110	12.69	5.2	19.7	43
	S2	7.1	40120	15.60	7.17	14.2	50.6
	S3	6.1	1320	4.79	0.05	2.8	12.3
1.0 M	S1	8.1	8620	15.34	5.2	14.6	47
	S2	7.2	40420	15.79	7.5	14.5	50.09
	S3	8.5	1430	6.8	0.09	3.1	15.41
0.5 M	S1	7.9	8110	12.60	6.1	17.5	46.7
	S2	8.2	42350	12.39	8.1	14.2	56.25
	S3	6.9	1200	4.79	0.06	5.3	14.06
0.25 M	S1	5.6	8620	21.47	5.2	19.6	46.1
	S2	5.9	41000	13.50	7.21	14.2	47.17
	S3	5.1	1480	5.73	0.06	3.6	15.41

### 6) Effect of pH

The effect of varying the initial pH on COD removal efficiency is presented in Figure 6. High pH favours the adsorption of COD onto the AC prepared from spent tea leaves. As the pH increased from 3 to 11, the corresponding COD reduction rate increased from 58.31 to 92.86 %. From the figure it is seen that COD removal is higher at pH values of 6–8. However, when the pH was raised beyond this range, the COD reduction percentage decreased considerably. The (-) charged functional groups of organic molecules connect to the (+) charged adsorbent surface by electrostatic attraction, as a result the reduction increased gradually at higher pH values.

But there is more resistance to the diffusion of organic ions at lower pH levels, there is a drop in adsorption because the quantity of (H<sup>+</sup>)-ions causes repulsion between the organic molecules and the adsorbent surface [27].

### 7) Effect of contact time

The contact time is an important operational factor for affecting COD reduction efficiency. Increasing in time leads to increase in the contact between the solutions to the larger surface area of adsorbent as there are many adsorption sites [28].

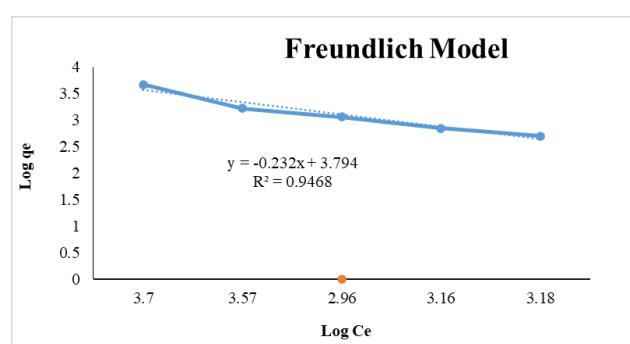
Figure 7 depicts COD reduction as a function of contact time. The graph indicates that the adsorption capacity of the AC increases between 90–120 min of contact time. The AC adsorbent can achieve a COD reduction of 80–90% in 1.5M and 1.0M at a contact time of 90 min. However, for 0.5 M and 0.25 M AC, the optimal COD reduction occurred at 120 min. At

this point, only 70% of the total COD has been adsorbed, as the COD reduction between 90–120 min of contact time is due to the moderate number of active sites available on the AC surface. When the surface-active sites are saturated, organic matters require more time to diffuse through the AC pores and adsorbed on the pore wall. Once the internal and external active sites of the AC are fully occupied, the adsorption rate decrease after 120 min of contact time.

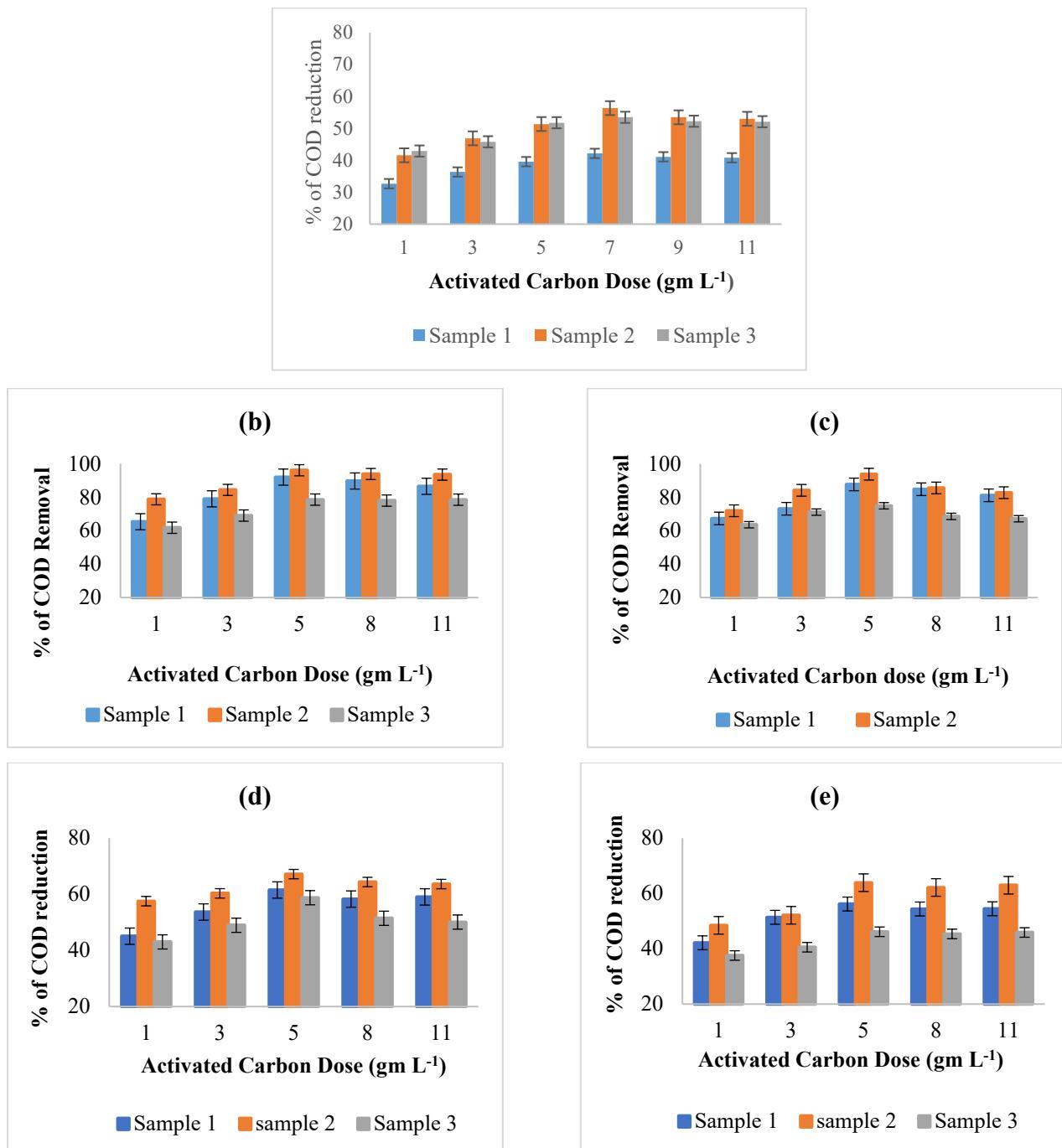
### 8) Adsorption isotherm

The data of adsorption equilibrium for S2 (1.5 M) presented in Table 4 were analysed using the parameters of the Freundlich and Langmuir adsorption isotherm models.

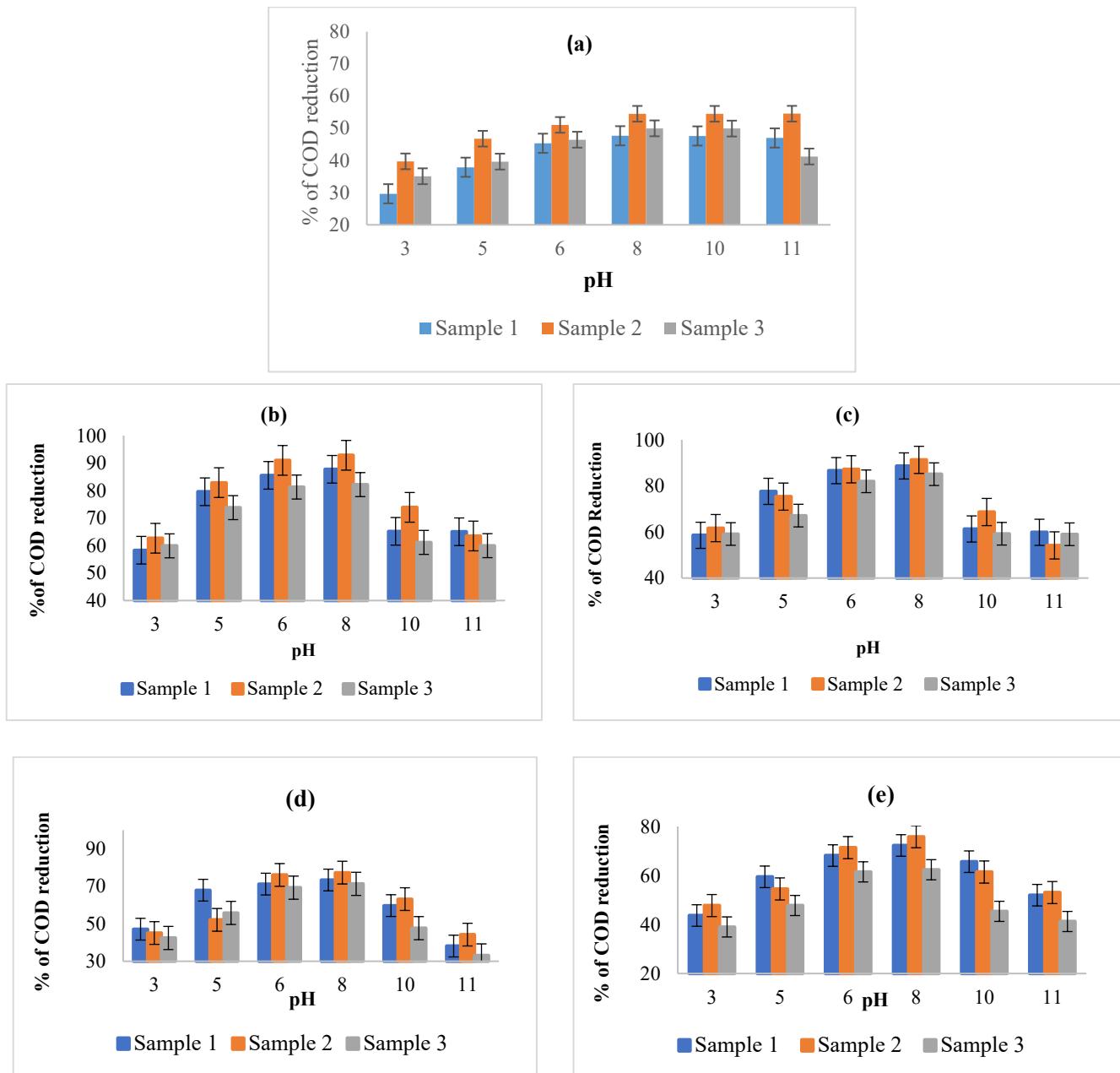
Freundlich isotherm model has been plotted for sample 2 (1.5 M) between log q<sub>e</sub> against log C<sub>e</sub>. According to this isotherm shown in Figure 8, the adsorption capacity, K<sub>f</sub> and adsorption intensity, 1/n, are both 3.794 and -0.232, respectively, the coefficient of regression is 0.947.



**Figure 8** Freundlich isotherm.



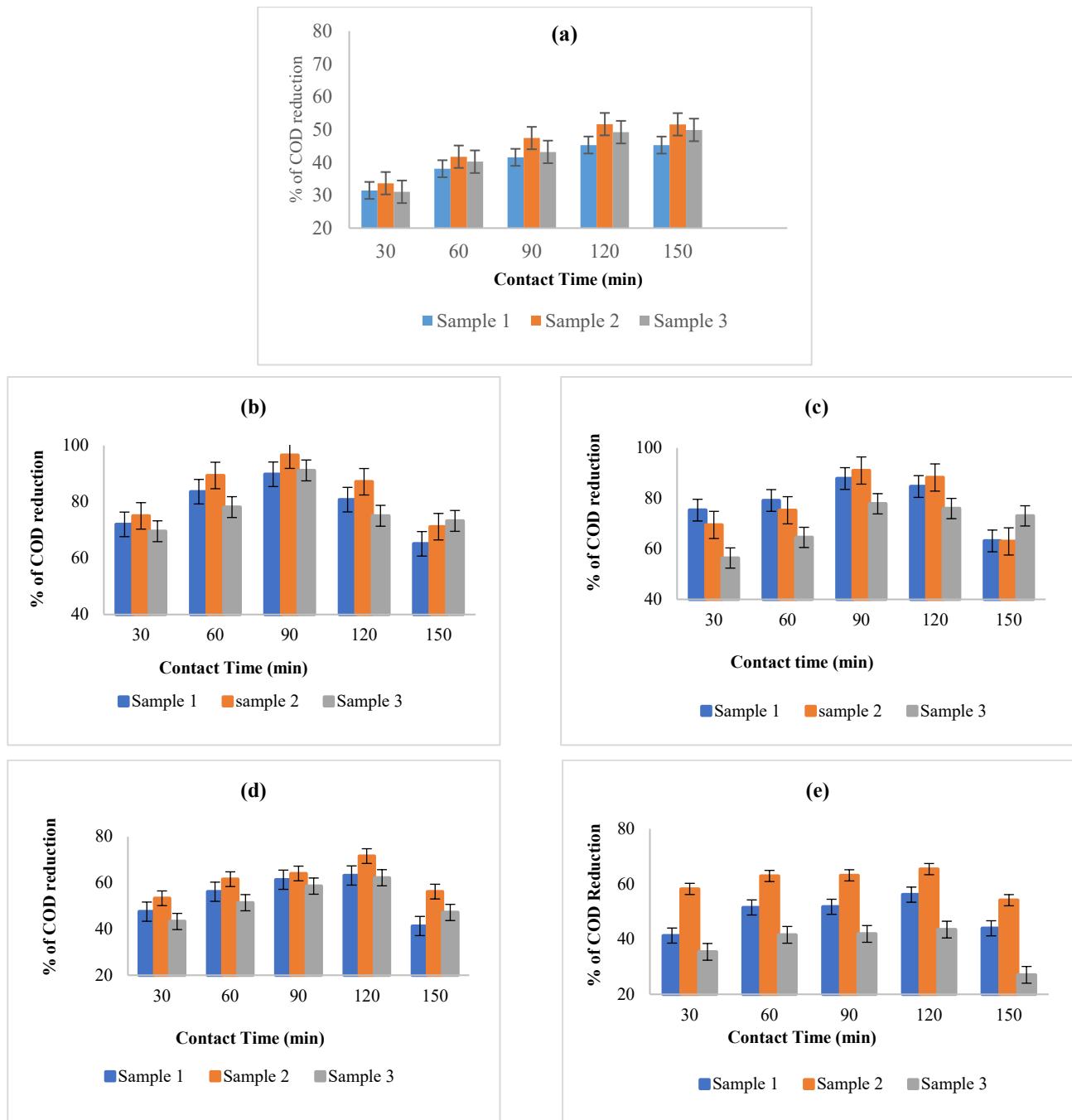
**Figure 5** Effect of  $\text{H}_2\text{SO}_4$  concentration of (a) control (without acid), (b) 1.5 M, (c) 1.0 M, (d) 0.50 M, and (e) 0.25M on COD reduction.



**Figure 6** Effect of pH on COD reduction applying (a) control (without acid), (b) 1.5 M, (c) 1.0 M, (d) 0.50 M, and (e) 0.25M H<sub>2</sub>SO<sub>4</sub>.

**Table 4** Parameters for the Freundlich and Langmuir adsorption isotherm

Ads, m	Raw COD	C <sub>eq</sub> , COD Reading	Rev. x=Co-C <sub>eq</sub> (mg L <sup>-1</sup> )	q <sub>e</sub> =V(x/m), (mg/gm); V=0.25 L	% Rev	Log C <sub>eq</sub>	Log q <sub>e</sub>	1/ C <sub>eq</sub>	1/q <sub>e</sub>
1	23,700	5,027	18,673	4,668.25	78.79	3.70	3.67	0.0002	0.0002
3	23,700	3,697	20,003	1,666.92	84.40	3.57	3.22	0.0003	0.0006
5	23,700	910	22,790	1,139.50	96.16	2.96	3.06	0.0011	0.0009
8	23,700	1,446	22,254	695.44	93.90	3.16	2.84	0.0007	0.0014
11	23,700	1,526	22,174	503.95	93.56	3.18	2.70	0.0007	0.0020

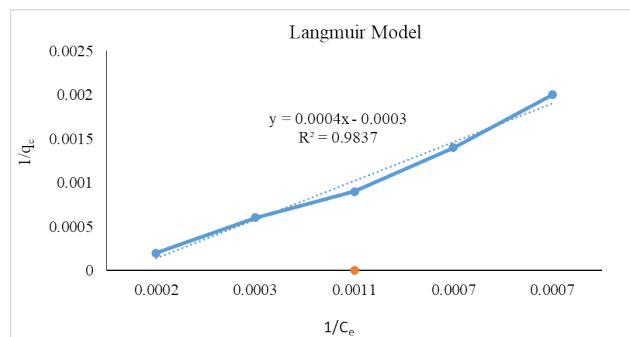


**Figure 7** Effect of activated carbon contact time on COD reduction using (a) control (without acid), (b) 1.5 M, (c) 1.0 M, (d) 0.50 M, and (e) 0.25M  $\text{H}_2\text{SO}_4$ .

**Table 5** Comparison of the maximum monolayer adsorption capacity ( $q_{\text{max}}$ ) of different adsorbent materials

Sl. No.	Adsorbent Maximum	Adsorption capacity $q_{\text{max}}$ ( $\text{mg g}^{-1}$ )	References
1	Rice husk carbon	47.61	[30]
2	Paper mill sludge	23.18	[31]
3	Grafted banana peel	6.17	[32]
4	Walnut shell	40.83	[33]
5	Activated neem leaves	62.97	[34]
6	Chitosan coated fly ash	33.27	[35]
7	Tea waste	5.186	Present study

Langmuir plot of  $1/q_e$  versus  $1/C_e$  depicted in Figure 9. Using the intercept and slope, the values of the maximum adsorption capacity  $q_{\max}$  5.186 mg g<sup>-1</sup> and the Langmuir constant,  $K_L$  -0.0003 were calculated. The coefficient of regression was found 0.984. The  $R^2$  value of Langmuir isotherm was found higher than the  $R^2$  value of Freundlich isotherm. As a result, we can suggest that experimental data was better fitted for Langmuir model [29].



**Figure 9** Langmuir isotherm.

Table 5 presents a summary of the maximum monolayer adsorption capacity ( $q_{\max}$ ) of different adsorbent materials, including tea waste, for COD reduction. The data in Table 5 demonstrates that spent tea leaves has a considerable adsorption capacity for COD reduction.

## Conclusions

Activated carbon, which is prepared from used black wasted tea leaves, can be applied as an entrapment material for COD reduction from tannery wastewater with effectiveness. Morphological observation showed that the surfaces of AC with concentrations of 1.50 M and 1.0 M H<sub>2</sub>SO<sub>4</sub> were distributed over the bead pore. The highest COD reduction (96.16% and 93.79%) was achieved at adsorbent doses of 5 gm L<sup>-1</sup>, pH of 6–8, and contact times of 90 and 120 min. The Langmuir isotherm model afforded the most accurate fit ( $R^2 = 0.9837$ ) when compared to the Freundlich isotherm model ( $R^2 = 0.9468$ ), showing a maximum adsorption capacity ( $q_{\max}$ ) of 5.186 mg g<sup>-1</sup>. This study concluded that 1.5M sulphuric acid was the optimum option for AC from discarded tea leaves. Additionally, the results demonstrated that adsorbents made from tea waste can be effectively utilised for reducing organic matter from tannery wastewater, providing cost effective for the manufacturing industry and benefiting the environment. The study suggests that employing more efficient processing techniques in large-scale treatment systems could further improve COD reduction efficiency, and that low-cost activated carbon produced from renewable resources can be a viable alternative to commercial carbon. Further study on the influence of

operational conditions should be conducted before the activated carbon are used in practically.

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