Research article

Comparative evaluation of tannin from banana bunch and stem syrup for leather processing

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A R T I C L E   I N F O

A B S T R A C T

Utilization of vegetable tannins in leather processing is one of the convenient solutions to protect the environment pollution. Herein, the banana bunch and syrup of banana stem are utilized to prepare an ecofriendly tanning agent. The yield of banana bunch extraction efficiency is found 69.80 %. FT-IR analysis confirmed the presence of condensed type tanning component owing to the bearing of different polyphenolic groups. The content of tannins in extracted banana bunch and stem syrup is 3.13 % and 2.6 %, respectively. The phenolic content in the banana bunch extract is determined to be 1332.37 mg GAE/100g of dried weight and in syrup was 873.92 mg GAE/100g of dried weight. This makes it possible to be used as vegetable tanners. The extracted bunch and syrup are applied to re-tan leather and compared with conventionally used vegetable tanning agent (quebracho) in parallel. Tensile strength, tear strength and elongation percentage for the extracted banana bunch and syrup are obtained at 23.84 N/mm^2, 68.26 N/mm, 47.07 %, and 22.97 N/mm^2, 68.38 N/mm, 40.70 %, respectively. The softness is found 1.41 for the extracted bunch and 2.01 for the syrup. The grain crack load, distension at grain crack, strength at ball burst, distension at ball burst are 246.86 N, 13.24 mm, 530.77 N, 24.54 mm for banana stem syrup and 338.77 N, 13.42 mm, 460.65 N, 29.08 mm for bunch extract, respectively. The shrinkage temperatures recorded for banana bunch extract, syrup and Quebracho (control trial) tannins tanned leather samples are 76.5 °C, 75 °C and 84 °C subsequently. The flexing endurance of the bunch extract and syrup revealed acceptable values that are less than 4. Moreover, the bunch extract tanned leather shows greater thermal stability and for syrup it is similar with the quebracho tanned leather. All the results are satisfactory compared to the control trial. Finally, tanned leather is evaluated to assess the possibility of the newly developed tannin which proves its efficiency as a potential source of tanning material for the leather industry.

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1. Introduction

Leather making is an ancient art, whereas its manufacturing procedure, the raw hide or skin are converted into leather employing a number of chemical and mechanical operations [1]. There are several tanning methods, such as vegetable, aldehyde, oil, mineral tanning, e.g., Zr, Ti, Al, Cr, Fe, and so on; among them chrome tanning itself accounts for 88–90 % of the entire leather processing in the world [2,3]. Due to the high penetration capability into the inter-fibrillar spaces, chrome tanned hides have several benefits, such as good mechanical stability, excellent dyeing suitability, and comparatively good hydrothermal resistivity [4].

After chrome tanning, a substantial amount of Cr is dispatched which causes environmental pollution [5]. The pollution from Cr can have severe effects for water and the soil environment [6]. Additionally, Cr can induce toxicity and lots of pathophysiological defects in human body, such as allergic reactions, anemia, burning, and sores, particularly in the stomach and small intestine [7,8]. Generally, in the waste effluent of tannery, Cr discharge as trivalent state that can be converted into hexavalent state in the exposure of heat [9]. Both the trivalent and hexavalent Cr can adversely impact the human food chain. To overcome this situation needs a sustainable and alternative source of chrome tanning agents.

Vegetable tanning is one of the best and well suited ecofriendly procedures which results in the discharge of less pollutants to the environment [10]. In this process the tanning refers to the skins or hides applying the tannins found from barks and leaves from green plants. For the extraction of tannins, various parts of plants, such as fruit, seed, pod, stem, leaves, tuber, etc., are used [11]. There are different types of vegetable tannin, including complex tannin, condensed tannin, and hydrolysable tannin [12]. Condensed tannin mainly contains phenolic hydroxyl or catecholic groups (3,4-dihydroxy benzene), which is stable in acid, base, or enzyme, whereas hydrolysable tannin mainly contains pyrogallol group (1,2,3-trihydroxy benzene) that could be hydrolyzed in acid, alkali, or enzyme [12–14].

In the vegetable tanning process, when the hides and skins are converted to leathers the tannin material from vegetable form hydrogen or covalent bond with the collagen functional groups (e.g., –COOH, –NH$_2$) of leather [15]. There are two stages of vegetable tanning, such as fixing and penetration. Penetration implies the diffusion of tannins into the skin whereas fixing causes the penetrated tannins bind with collagen constituting stable material. In this process, to get desired products different components such as temperature, pH, mechanical actions and particle size are involved [14,16,17]. Optimizing of these parameters leads in the production of the most stable and flexible leather which generates less contaminants and save the environment.

Most of the vegetable tannins fail to improve the hydrothermal stability of collagen as offered by the chrome tanning agent. Because of the tanning efficiency, quality, performances, and extraction efficiency issues only a few vegetable tanning agents are commercially suitable for the application in leather processing. Generally, mimosa, quebracho, sumac, tara, valonea, divi-divi, oak, and chestnut tannins are commercially used for chrome-free tanning [18,19]. Among them, mimosa is frequently used as a commercial vegetable tanning material. Mimosa extract mainly contains phenolic substances with sugars, organic acids, and hydrocolloids contaminants those are refines before using [20]. The Mimosa tenuifora (mimosa tannin) is grown in South America and Eastern Africa and the tannery in Bangladesh imported mimosa commercially from Brazil and Eastern Africa [21,22].

Bangladesh produced 826151.76 metric tons of bananas and planted an area of around 49449.42 acres. A banana tree stems fruit only once in its lifetime. When it sprouts fruits, the stem will necessarily rot, catch a virus, or farmers cut it down so that a new stem can emerge from the root again. It is estimated that, a banana plantation produces around two tons of debris for the production of one ton of fruit. A study showed that the banana bunch had a tannin content of 4.1 % [23]. Moreover, the collection of fiber from the waste banana bunch is started in our country and fiber from the waste banana bunch is now exported. After collecting the fiber, the liquid portion (syrup) has no use still. This study aims to extract and assess the tanning efficiency of extracted tannin from banana bunch and syrup as a source of vegetable re-tanning material. The tannin was confirmed by qualitative test using FeCl$_3$, HCl, gelatin and ammonia. FT-IR analysis confirmed the presence of condensed type tanning substance owing to the presence of different phenolic groups in its chain. The phenolic content in banana bunch extract and syrup was determined quantitively by spectrophotometer using the Folin-Ciocalteu reagent at the wavelength of 765 nm. Moreover, the tannin content of both extracted bunch and syrup was quantified by the hide powder method. Thermal stability was checked through thermogravimetry (TG) and differential scanning calorimetric (DSC) analyses. The mechanical performances such as tensile strength, tear strength, elongation, flexing endurance, strength at ball burst, distension at ball burst, resistance to grain cracking, and distension at grain crack, and softness were conducted on the experimental leather re-tanned by banana bunch and syrup and they were compared with the leather re-tanned by commercial quebracho tannin.

2. Materials and method

2.1. Materials

Hide powder was purchased from BLC Leather Technology Center Ltd., England. Chrome Alum, FeCl$_3$, Methanol (99.5 %), HCl, Acetone, Ammonia, Gallic acid, Sodium carbonate, Glycerin were bought from Merck, India and Folin-Ciocalteu reagent was purchased from Sigma Aldrich.

Banana bunch and syrup were collected from Anik Enterprise, Jamalpur, Bangladesh. The banana syrup was obtained while the factory made banana fiber from waste stems to export. After collecting the syrup, it was filtered, concentrated through a rotary evaporator and stored in airtight containers. Following the chopping of the banana bunch into small pieces, it was dried in the sun, then ground into powder using an analytical grinder, and finally it was stored in an airtight glass container at room temperature for

subsequent usage. The chromed-tanned leather was obtained from our Leather Processing Division. All of the compounds in this study were analytical grade and were utilized without any additional purification.

2.2. Extraction of tannin

For each extraction process, 20 g powdered bunch was immersed in a round bottom flask containing 400 mL of distilled water (DW) and it was set with a condenser. The processes were conducted at 80 °C with stirring at 200 rpm for 4h by DW. Following the filtration of sample with a 0.45 μm pore size filter membrane, each of the residual materials was rinsed out for 4 h with extra 300 mL DW and then filtered accordingly. The extracted banana bunch was evaporated under vacuum conditions by rotary evaporator at 60 °C and 110 rpm for 6h. Moreover, after the collection of the banana stem syrup sample, it was also filtered and concentrated by a rotary evaporator in the same condition. The extraction process of tannin from the banana bunch is represented in Fig. 1.

2.3. Characterization

2.3.1. Extraction efficiency of tannin
The water content of the banana bunch extract and syrup was determined by using Volumetric Karl Fischer Titration (Metrohm Karl Fischer Titrator, Switzerland) [24]. The water content was deducted from the weight of the extracted banana bunch to measure the percentage yield of extraction. The yield of the bunch extract was calculated by following the equation:

$$\text{Yield (\%) of extraction} = \frac{\text{Weight of banana bunch solute}}{\text{Weight of dried banana bunch}} \times 100$$

2.3.2. Determination of tannin content
Tannin content was quantified by the hide-powder method (SLC117) as stated in literature [25] and is described as the extent to soluble solids of tannin extract are absorbed by standard hide powder. The difference between the total soluble solids (%) and the soluble non-tannins (%) was used to compute the tannin content (%).

2.3.3. Determination of total phenolic content
Total phenolic content were measured by the Folin-Ciocalteu method29 according to the literature with slight modification [8]. The total phenolic content of the extracts was determined on the basis of standard curve using Gallic acid as standard (0–100 ppm). Exactly 0.2 mL Folin-Ciocalteu reagent, 3.16 mL distilled water, 0.6 mL of 7.5 % (w/v) sodium carbonate (Na_2CO_3) and 40 μL of each concentration of Gallic acid was mixed in their respective test tubes. Later, the mixture was left to stand for 2 h in dark place at room temperature. The absorbance was measured against blank sample at the wavelength of 765 nm using UV-VIS light spectrophotometer

Fig. 1. Schematic extraction diagram of banana bunch tannin.

(Lambda 365, PerkinElmer). Then the results were expressed in mg gallic acid equivalents (GAE) per gram of fresh weight.

2.3.4. Qualitative analysis

In accordance with the published method, a qualitative analysis of the tannin in the extracted banana bunch was conducted [26]. In brief, 1 mL of the extracted banana bunch was poured into each of the three test tubes, and then 10 mL of distilled water and two drops of $FeCl_3$ were added to each tube. The presence of tannins was revealed by the green color that initially emerged and then faded upon standing. One milliliter of the extracted banana bunch was placed into each of the three test tubes, and 1 % gelatin solution was mixed and diluted with distilled water to carry out the fundamental procedures of the gelatin test for tannin quality. The presence of tannins was detected by sediment formation. In addition, 1 mL of the extracted banana bunch was added into each of the three test tubes in order to conduct the tannin test with ammonia. Ammonia was added and then left out in the air. The presence of tannins was indicated by the appearance of green colour that faded after standing. Following that, the HCl test for tannin quality was performed by placing 1 mL of banana bunch extract into each of the three test tubes, followed by 3 drops of concentrated HCl added to each tube and heated [27]. Similarly, these four tests were performed for the banana stem syrup.

2.3.5. FT-IR analyses

By utilizing a Fourier-transform infrared spectrophotometer (FT-IR) (PerkinElmer, Frontier, United Kingdom) combined with Universal Attenuated Total Reflectance Accessory (UATR), the infrared spectra of the extracted banana bunch and syrup were obtained. For each sample, absorbance and FT-IR spectra were obtained. Initially, the FT-IR spectrometer was calibrated against a pure KBr sample for background scanning signal. In the frequency bands 4000-600 cm^{-1}, each spectrum was collected after an average of 20 scans with a resolution of 4 cm^{-1}.

2.3.6. Re-tanning process of leather

The re-tanning processes of wet blue goat skins (chromed tanned leather) was executed by applying banana syrup and extracted bunch as experimental trial and commercial *quebracho* tannin as a control trial. Table 1 shows the re-tanning process used in this study. In both trials, 6 % tannin (based on dried weight of wet blue material) and 1 % syntan were used [7].

2.3.7. Physical-mechanical characteristics of re-tanned leather

In terms of tensile strength, tear strength, percent elongation at break, softness, flexing endurance, strength at ball burst, distension at ball burst, resistance to grain cracking, and distension at grain crack, the physical-mechanical performances of experimental and conventional leather were analyzed. For these tests, the leather samples both experimental and conventional were conditioned for 48 h at 25 ± 2 °C and 50 ± 2 % relative humidity. Following the sample location and specific measurements, the experimental and conventional tanned leather was cut into 3 pieces (for both parallel and perpendicular to the backbone for each test). By following the SATRA TM43 [28], a computer-controlled universal testing machine (UTM) (STM 566, United Kingdom) was used to determine the tear strength, tensile strength, and percent elongation at break. The test speed was set at 100 mm/min, and the extensometer gauge length was 50 mm. The load cell was kept at 1 kN, and each type specimen was 90 mm in length and 10 mm in width. In this study, all experiments were performed 3 times and the average value with standard deviation was given.

Table 1
Technological parameter in re-tanning process of goat skins.

Process	Materials	Dosage (%)	Temp. (°C)	pH	Time (min)
	Water	100			
Neutralization	Neutralizing syntan	3		5.0–5.2	60
	Sodium formate	2			
Retanning	**Treatment-1:**	6	50		60
	Banana bunch extract	1			
	D*1202				
	Treatment-2:	6			
	Banana stem's syrup	1			
	D*1202				
	Treatment-3:	6			
	Quebracho	1			
	D*1202				
Dyeing	Black dye	10			
Fat liquoring	Water	100	60		75
	MSG	2			
	D*1202	3			
	SWR	5			
	HQ	2			
	LQ	2			
	Busan	0.2			
	Formic acid	3			
Wash	Water	150			15 + 15+30
	Cationic fat	1			
	Cr-syntan	1			

In compliance with established procedure SATRA TM 162 [29], the softness of both conventional and experimental leather was evaluated using a ST 300 digital leather softness tester. According to ISO-3378/IUP-12 [18], a computer-controlled universal testing machine (UTM) (STM 566, United Kingdom) was used to assess the resistance to grain cracking, distension at grain crack, strength at ball burst, and distension at ball burst of both conventional and experimental leather. Flexing endurance was measured in this experiment based on the standard method SATRA TM 25 using STM 601 VAMP FLEXER and IUP 2 was used to cut the samples [30].

2.3.8. Hydrothermal property

Shrinkage temperature (Ts) illustrates the hydrothermal characteristics of hides and skins. The Ts equipment was utilized for estimating the hydrothermal properties of both conventional and experimental leather. The test was conducted employing the standard method IUP-16 [31], and the leather samples were cut (50 mm × 12 mm) from the sampling area. After being hooked up to the holder of the Ts apparatus, test samples were then submerged in a bath that included a mixture of water and glycerin in the proportion of 70:30. In step with the pace of increase in heat, the temperature was progressively raised. The temperature at which the shrinking began was recorded as the temperature at which that specific skin shrank. For this investigation, three replicates were examined, and the study's mean has been provided.

2.3.9. Simultaneous thermal analyses (STA)

The thermogravimetric (TG) analysis of the various leather samples tanned with bunch extract, syrup, and quebracho was performed using STA (STA 449 F3 Jupiter®). In a nitrogen atmosphere, the thermal characteristics were recorded from room temperature to 600 °C, with a heating rate of 10 °C per minute. Additionally, the thermal properties were examined using differential scanning calorimetry (DSC) measurement using the same apparatus. Nitrogen was present and the temperature was raised from room temperature to 600 °C at a steady rate of 10 °C/min for the DSC measurement.

3. Results and discussion

3.1. Design concept

In order to better understand, the cross-linking mechanism and to find novel vegetable tannin sources, researchers have been studying the interaction among plant tannin and collagen from hide for over fifty years [15]. In the case of condensed tannins, hydrogen bonds are formed amongst the –OH groups of the tannin polyphenols and the collagen molecules' peptide oxygen and –NH$_2$ groups [32]. In this study, Fig. 2 depicts a possible condensed tannin-collagen reaction scheme. The amino acid side chains –COOH and –NH$_2$ group of the collagen molecules might form hydrogen bonds with the phenolic hydroxyl groups of the extracted tannin (Fig. 2). The other researchers have observed an analogous reaction mechanism for the condensed tannin [12,32].
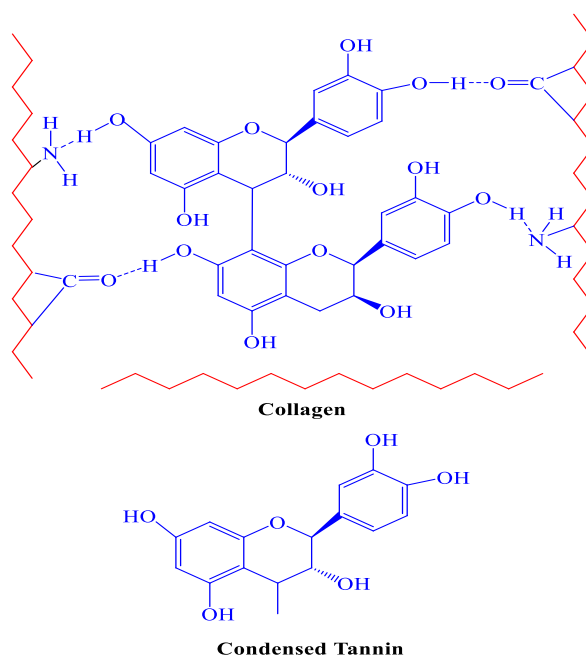

Fig. 2. Schematic reaction of the condensed tannin with collagen.

3.2. Physical properties of extracted tannin

The water content for banana bunch and syrup was found 86.04 % and 91.46 %, respectively. The yield percentage of tannin extraction was 69.80 % for the banana bunch. Moreover, the pH of the extracted banana bunch and syrup was 4.34 and 6.60, respectively.

3.3. Qualitative identification of tannin

Table 2 displays the outcomes of the tannin qualitative analysis. This qualitative investigation was the first step in identifying tannin characteristics in natural materials like banana bunches and stems syrup (Table 2). When $FeCl_3$ was added, the color changed from brown to green, indicating that the tannin was presented. It was hypothesized that the green color came from the interaction between the phenol group in tannins and $FeCl_3$. According to Ezeonu et al. [26], tannin forms complex compounds with Fe^{3+} ions when the extract turns green or dark green after the addition of ferric chloride in it. The experiments were carried out by adding a gelatin solution, which resulted in the sediment. Moreover, it has been noted by Thomas et al. [33] and Zhang et al. [34] that tannins have the ability to precipitate proteins, like gelatin. Reddish-brown color was generated by heating up with adding concentrated hydrochloric acid mixed with banana bunch extract and stem syrup tannin, containing condensed tannins or catechol. When heated in an acidic solution, the catechol tanning agent enlarges its molecules and turns reddish-brown [35,36]. Fig. 3, displays the color change during the addition of HCl. At first, the banana bunch and stem syrup display brownish (Fig. 3a) and black (Fig. 3b) colors, respectively. After treating with HCl the colors of banana bunch and stem syrup changed to Brown-soft orange (Fig. 3c) and Brown-dark orange (Fig. 3d), respectively [27].

3.4. FT-IR analysis

Figs. 4–6 show the FTIR spectra of the tannin in banana bunches, stem syrup, and quebracho (the control trial), respectively. When compared to the commercial standard tanning materials from Quebracho, the extracted sample revealed the existence of O–H stretching, C=O stretching, aromatic C–H stretching, C=C ring stretching, C–H bending, C–O stretching, and out-of-plane C–H bending. In accordance with prior studies [37,38], the FTIR spectra of bunch extract and stem syrup revealed a relatively broadband at about 3251 cm^{-1} and 3352 cm^{-1}, indicating the existence of –OH groups of polyphenols such as tannin and flavonoids. Furthermore, quebracho, a well-known vegetable tanning agent, demonstrated broadband at 3253 cm^{-1}, which is nearly identical to this study [37, 38]. Furthermore, the extracted sample exhibited a medium band at 2988 cm^{-1}, while the quebracho sample showed a band at 2948 cm^{-1}, suggesting the presence of aromatic C–H stretching. A prominent peak was observed at 1606 cm^{-1} for bunch extract and at 1607 cm^{-1} for syrup. Meanwhile, quebracho displayed peaks at 1610 cm^{-1}, suggesting the presence of C=O and C=C ring stretching with substituted benzene ring. A significant, intense peak in the region of 1620–1610 cm^{-1} could be observed in condensed tannin, indicating a high degree of polymerization [38].

Consequently, a high and intense peak at 1606 cm^{-1} & 1607 cm^{-1} (Figs. 3 and 4 respectively) suggests that the extracted samples could be categorized and considered as condensed tannins. Furthermore, aromatic ring vibration was seen in the peaks located between 1000 and 1300 cm^{-1} [35]. Furthermore, out-of-plane deformation causes the absorption of hydrogen atoms from aromatic rings in procyanidins (condensed tannin, catechin) between 780 and 770 cm^{-1} and prodelphinidin (gallocatechin) at near 730 cm^{-1} [39]. Quebracho tannin exhibits a peak at 773 cm^{-1} in the control trial. In both extracted samples, a peak at 777 cm^{-1} was identified, suggesting the presence of a condensed tannin group. Because of the presence of numerous polyphenolic groups in its chain, the extracted tannin demanded the presence of condensed type tanning material-rich compounds.

3.5. Determination of total phenolic content

The calibration curve of gallic acid showed a strong linear relationship between absorbance and concentration (y = 0.0021x + 0.0113, R^2 = 0.991, where y is the absorbance of the sample and x is the sample concentration) within the range of 0–100 mg/L (Fig. 7). Based on this calibration curve, the phenolic content in the banana bunch extract was determined to be 1332.37 mg GAE/100 g of dried weight and in syrup was 873.92 mg GAE/100 g of dried weight. The result suggests that banana bunch is a promising candidate as a tanning agent.
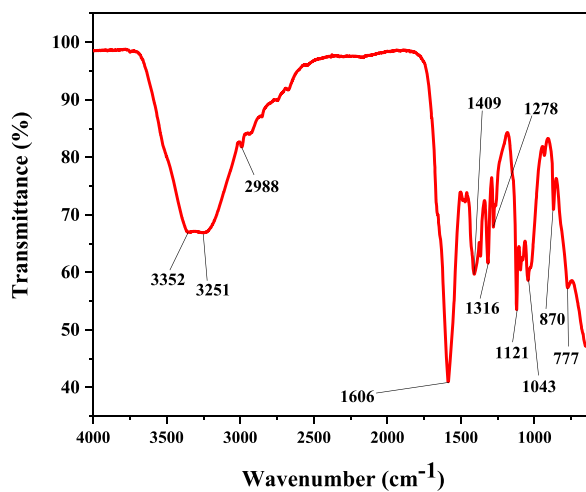
Table 2
Qualitative identification of tannin in the extracted banana bunch and syrup.

| Indicator	Extracted banana bunch	Banana syrup	Conclusion
$FeCl_3$	Green	Green	+
Gelatin	Sediment	Sediment	+
Ammonia	Green	Green	+
HCl	Brown-Soft Orange	Brown-Dark Orange	+

Note: + is for containing tannin.
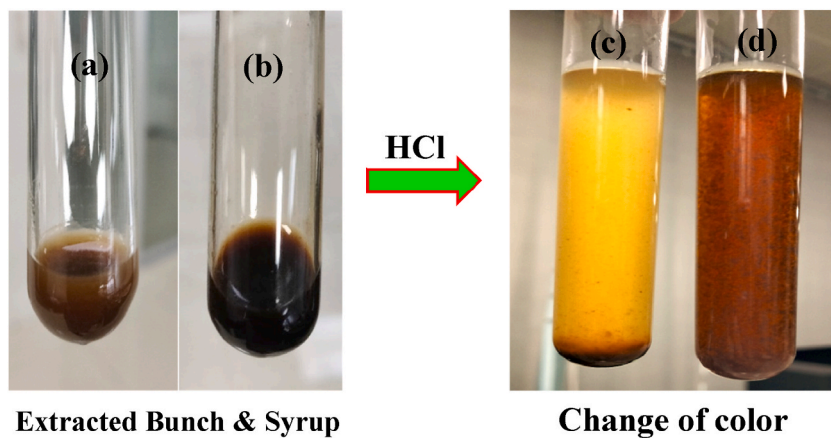
Fig. 3. The initial color of the banana bunch (a) and syrup (b) tannin and color changes to Brown-soft orange (c) and Brown-dark orange (d) after treatment with HCl. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 4. FT-IR spectra of banana bunch.
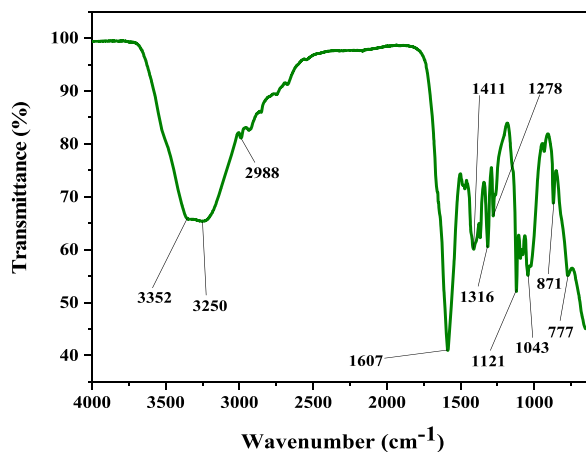
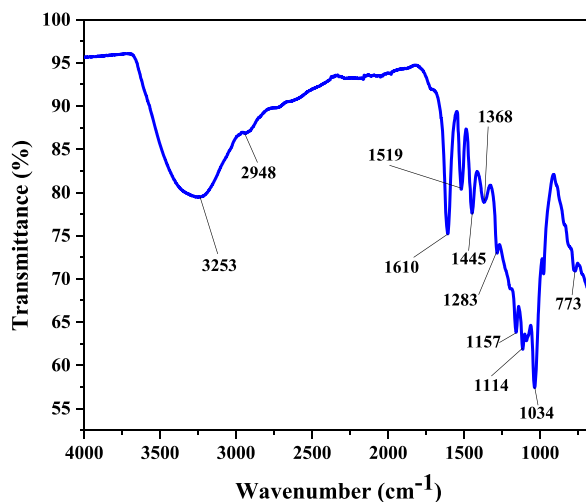**Fig. 5.** FT-IR spectra of banana syrup.
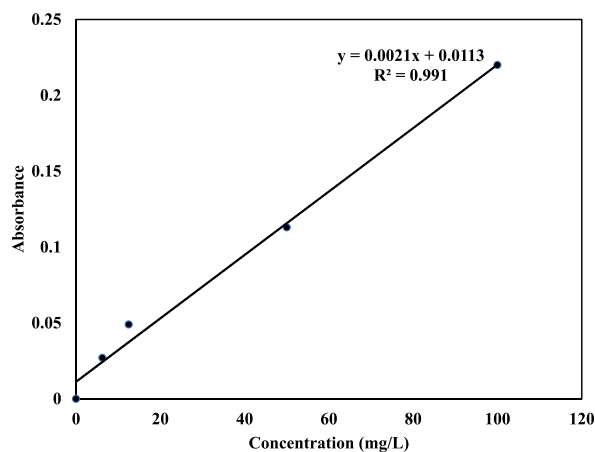
Fig. 6. FT-IR spectra of Quebracho.

Fig. 7. Calibration curve of gallic acid.

Table 3
Physical-Mechanical performances of leather tanned by conventional tanning agent, syrup and extracted tannin from banana.

| Parameter	Re-tanning agent			
	Alignment	Banana Syrup	Banana Bunch	Control Trial
Softness (mm)	–	2.01 ± 2.28	1.41 ± 2.38	1.54 ± 1.22
Tear Strength (N/mm)	Along	64.28 ± 2.35	65.11 ± 2.44	65.97 ± 1.58
	Across	72.49 ± 2.56	71.41 ± 1.75	72.44 ± 1.64
	Average	68.38	68.26	69.20
Tensile Strength (N/mm^2)	Along	22.05 ± 2.52	21.48 ± 1.82	22.26 ± 2.20
	Across	23.89 ± 1.98	26.21 ± 2.24	27.05 ± 1.45
	Average	22.97	23.84	24.65
Elongation (%)	Along	57.52 ± 2.26	60.21 ± 1.80	61.73 ± 1.74
	Across	23.89 ± 1.92	33.94 ± 2.36	34.09 ± 2.02
	Average	40.70	46.07	45.91
Grain crack load (N)	–	246.86	338.77	315.93
Distension at grain Crack(mm)	–	13.24	13.42	15.44
Strength at ball burst (N)	–	530.77	460.65	628.16
Distension at ball burst (mm)	–	24.54	29.08	21.73
Shrinkage temperature (°C)	–	75	76.5	84

3.6. Tannin content

The purpose of the quantitative tannin analysis was to assess and confirm the tannin content of natural components. The content of tannins in syrup of banana stems and the extracted bunch was 2.6 % and 3.13 %, respectively; which makes it possible to be used as vegetable tanners. Different ratio of extracted bunch and stem syrup was also mixed to quantify their percentage of tannin. The ratio of 80 % extracted bunch and 20 % syrup shows the highest value of tannin content (3.09 %) among those different mixtures. As stated by Maryati, the tannin content of a tanning agent is regarded good if it is greater than 0.4 %, hence the tannin content in the banana bunch and stem syrup was suitable for usage as a novel vegetable tanning agent [23].

3.7. Mechanical properties of re-tanned leather

The experimental leather was re-tanned with banana bunch and syrup and a control trial using a conventionally used vegetable tanning agent (quebracho) was tested in parallel. Table 3 and Fig. 8 provide demonstrations of the mechanical characteristics that were examined in this study. The tensile strength of the experimental leather was 22.97 N/mm^2 and 23.84 N/mm^2 for syrup and bunch tannin, respectively; which is pretty similar (24.65 N/mm^2) to the commercial quebracho tanned leather (Fig. 8b). Furthermore, compared to conventionally tanned leather, the experimental leather displayed a very high percentage of elongation, which was 40.70 % for syrup and 47.07 % for bunch (Fig. 8c). As a result, in comparison with conventional vegetable-tanned leather, the experimental leather may be able to stretch and hold up heavier loads. Furthermore, tear strength was found 68.38 N/mm, 68.26 N/mm and 69.20

(a)

(b)

(c)
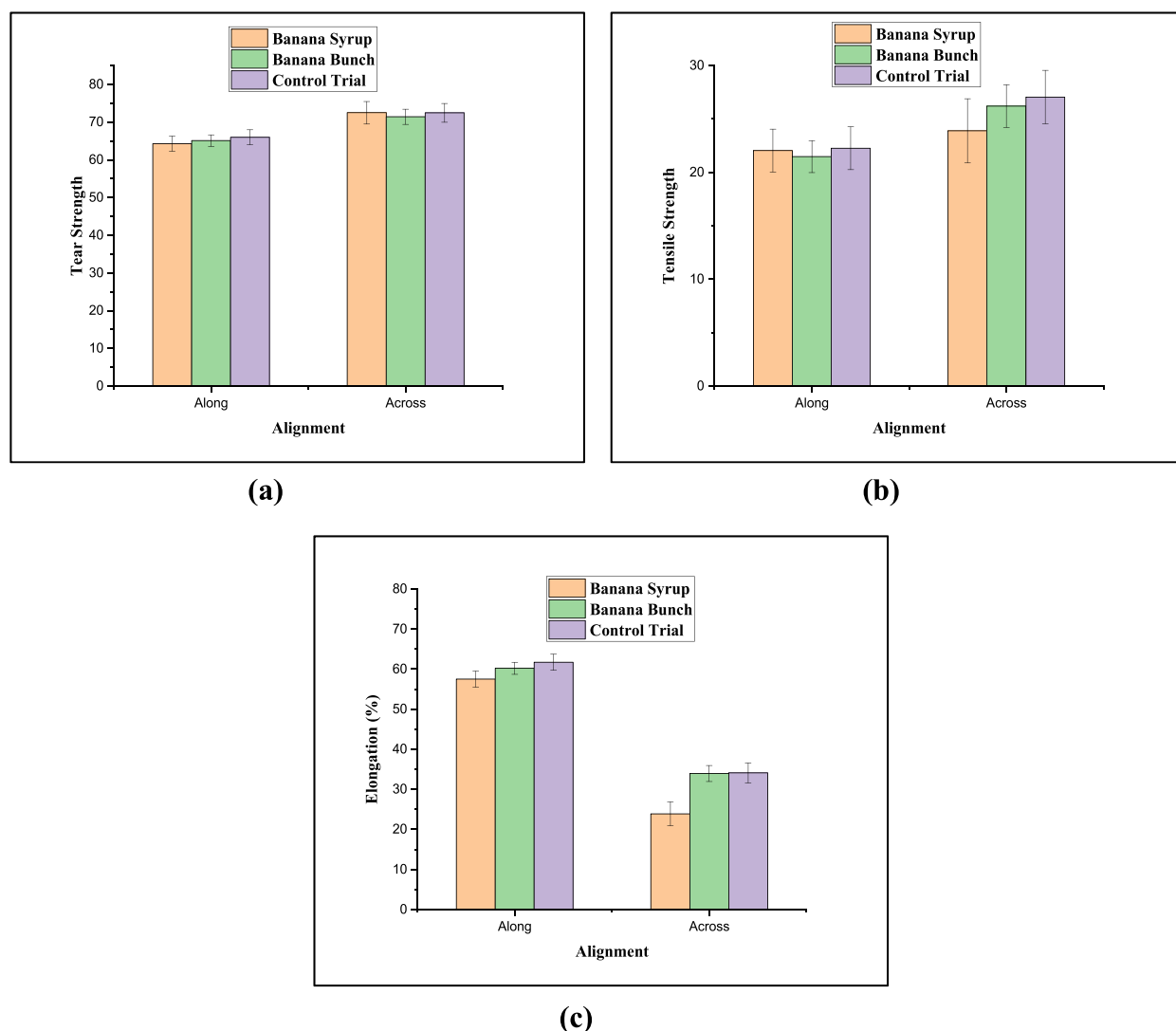
Fig. 8. Tear strength (a), tensile strength (b) and % of elongation in different alignments of leather after re-tanning with extracted banana bunch and syrup and compared with commercially available vegetable tanning.

N/mm for banana syrup, bunch and quebracho tanned leather, respectively (Fig. 8a). There was no noticeable difference in the tear strength of leather that had been tanned conventionally versus experimentally. Softness was also comparable to leather that has been conventionally and experimentally tanned. According to United Nations Industrial Development Organization (UNIDO) tensile strength, tear strength and percentage of elongation should be $\geq$ 22.56 N/mm^2, $\geq$29.4 N/mm and 30–45 % respectively [40].

The lastometer test is a significant another physical examination to assess the overall quality of leather and it measures the force required to cause cracking and bursting while subjecting the material to stretching or distension. In this study, the loads of grain cracking were 246.86 N and 338.77 N for syrup and bunch respectively; similarly, loads of ball bursting was 530.77 N and 460.65 N (Table 3). On the other hand, the distention at grain crack and ball burst for syrup were 13.24 mm and 13.42 mm; for bunch 24.54 mm and 29.08 mm subsequently. The outcomes closely resembled those observed in commercially tanned leather using quebracho, with values of 315.93 N for grain crack load, 15.44 mm for distension at grain crack, 628.16 N for strength at ball burst, and 21.73 mm for distension at ball burst (Table 3). These values significantly exceed the minimum recommended standards proposed by UNIDO ensuring that leather do not crack or burst under stress which is essential for the durability and comfort of consumers. Grain crack load should be $\geq$ 196 N and Distension at grain Crack should be $\geq$ 7 mm in accordance with UNIDO [40] for any types of leather. Several researchers found distention at grain crack 6.74 mm/9.9 mm, and distention at ball burst 7.72 mm/10 mm for different sheep leather [41]. Furthermore, the levels of tensile strength, tear strength, and other strength-related characteristics exhibit fluctuations depending on factors such as the composition of tanning agents, the type and quantity of tannin used, the management of beam-house operations, pre-tanning and tanning processes, post-tanning treatments, and the specific methods employed during the tanning process [42].

3.8. Flexing endurance

The degree of looseness is assessed using the flexing endurance test by looking at the wrinkles or breaks that appear where the leather flexes. This process is usually used for the upper leather of shoes and is rarely applied to the lining. The break Pipiness Scale, which has a scale from 1 to 8, is used to measure the wrinkles or break on the grain side of the leather specimens. A score of 1 indicates the nicest break or wrinkles, and a score of 8 indicates the coarsest break or wrinkles. Samples in the current study (Table 4) demonstrated acceptable results because ratings above 4, are typically regarded as unacceptable [43]. Moreover, Fig. 9 showed that the leather tanned by bunch extract (B) had less wrinkles compared to the banana syrup (S) and quebracho (Q) tanned leather.

3.9. Hydrothermal stability of tanned leather

Shrinkage temperature (Ts) is among the most important leather testing parameters which illustrate thermal stability of tanned leather collagen. Ts is the temperature at which leather starts shrinking in hot water [44]. Thermally stable leather withstands shrinkage even at high temperature. This is due to the formation of cross-links and a variety of strong bonds between the tannin components and the leather collagen. The process of Ts measuring is shown in Fig. 10. According to IULTCS/IUP 16, stating the Ts of tanned leather should not be below 75 °C [45,46] confirmed that the leather samples tanned under this study are hydrothermally stable. The Ts recorded for banana bunch extract, syrup and Quebracho (control trial) tannins tanned leather samples were 76.5 °C, 75 °C and 84 °C, respectively [45].

3.10. TG analysis

The TG curves of leathers tanned with syrup, quebracho, and bunch extract are displayed in Fig. 11. According to the literature [47], all of the samples exhibited three stages of degradation (Fig. 11). The residual mass of the samples at different stages of decomposition has been represented in Table 5.

The initial stage was between 30 and 150 °C. At this stage, residual mass for bunch extract (Fig. 11b) tanned leather (96.59 %) was higher and for syrup (Fig. 11a) was similar (93.44 %) with control trial quebracho (Fig. 11c) tanned leather (93.52 %). In this initial stage, the leather went through an endothermic phase [48], evaporating moisture and small molecules [47,48]. Thermal stability in leather is an effect of the interfibrillar water content, and a prior study by Carşote et al. [49] found that the loss of water during the initial stage of the process could impact cross-linking, which in turn increases thermal stability. In order to stabilize the collagen in leather throughout the tanning process, tannin molecules filled the empty space of collagen and displaced water molecules [50].

The most significant phase occurred in two stages, at temperatures ranging from 188-295 °C to 295–485 °C. Those stages are more complicated than the previous stage. Collagen breakdown was the cause of the mass loss at this point. T_{max} indicates how thermally stable leather collagen is [49], with more residue at T_{max} indicating greater collagen stability. At the second and third stage (Table 5), the bunch extract tanning agent had also the higher residue at the maximum degradation than quebracho, but syrup was similar with

Table 4
Flexing endurance in terms of Break Pipiness Scale rating (1–8) of the leather samples.

Cycles	50,000	1,00,000	2,00,000	3,00,000	Required Value [43]	Remarks
Banana Syrup	1	1	1	2		Acceptable
Banana Bunch	1	1	2	2	Maximum 3/4	Acceptable
Commercial Product	1	2	3	3		Acceptable

Fig. 9. Wrinkles development after flexing endurance testing of bunch extract (B), syrup (S), and quebracho (Q) tanned leather.

Fig. 10. Shrinkage temperature testing.

the quebracho. At these stages, thermo-oxidation and pyrolytic breakdown occurred [51]. Leather is both an amorphous and crystalline material that can exhibit thermal properties because of its well-defined amino acid residue sequences and disordered areas [52]. This final phase denotes the melting crystalline area of leather or the evaporation of residual strongly bind water, as well as the ongoing structural changes of the collagen super helix [48]. Finally, at 595 °C, the final residue of bunch extract (Fig. 11b), syrup (Fig. 11a) and quebracho (Fig. 11c) tanned leather was 59.24 %, 45.06 % and 46.97 %, respectively (Table 5). As a result, the bunch extract exhibited superior leather thermal stability and has a significant potential to prevent decomposition of leather to a great extent.
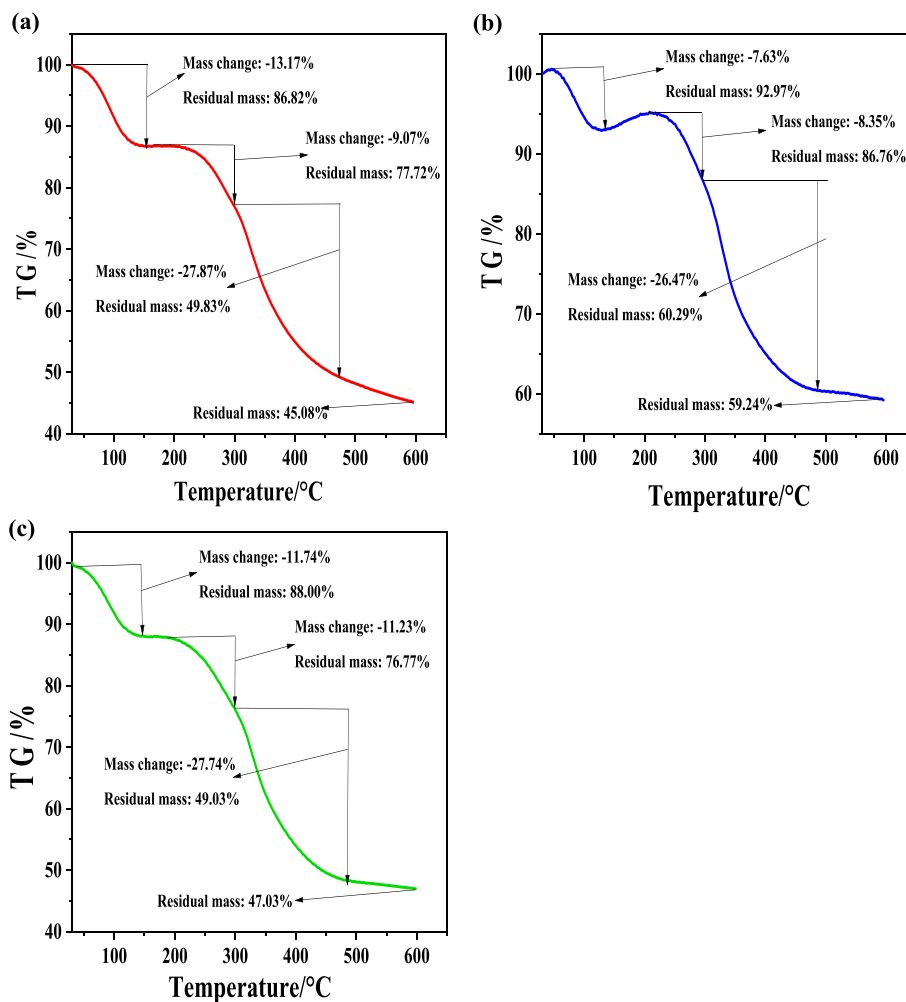
Fig. 11. TG curves of Syrup (a) Bunch extract (b), and Quebracho (c) tanned leather.

Table 5
Different decomposition stages of the samples.

Sample	Index	Initial stage	2nd stage	3rd stage	Final stage
Bunch extract tanned leather	Temperature (°C)	30–135 °C	205–295 °C	295–462 °C	595 °C
	Residue at T_{max} (%)	96.59	93.79	76.80	59.24
Syrup tanned leather	Temperature (°C)	30–150 °C	193–295 °C	295–485 °C	595 °C
	Residue at T_{max} (%)	93.44	85.54	68.13	45.06
Quebracho tanned leather	Temperature (°C)	30–145 °C	188–296 °C	296–462 °C	595 °C
	Residue at T_{max} (%)	93.52	85.56	67.26	46.97

3.11. DSC analysis

The phase transition and denaturation temperatures were determined with DSC. DSC curves (Fig. 12) indicated that leather tanned with bunch extract, syrup and quebracho respectively have two endothermic processes [47]. Bunch extract, syrup, and quebracho-tanned leather displayed endothermic peaks at 90.84 °C, 98.34 °C, and 93.34 °C, accordingly, at the first process, as demonstrated in Fig. 12. Concurrently, the denaturation endothermic peak was discovered for bunch at 328.34 °C, syrup at 328.20 °C, and quebracho at 325.84 °C. These findings closely corresponded to the TG analysis, which identified two processes: first was for the phase in which all of the water in the leather was lost and second was for the decomposition of the materials [9,47].
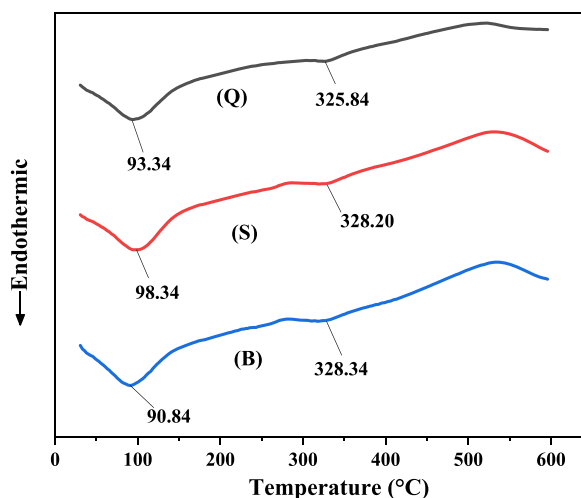
Fig. 12. DSC curves of leather tanned with banana bunch extract (B), syrup (S) and quebracho (Q).

4. Conclusions

Banana bunch and syrup tannin were shown to be prospective novel sources of vegetable tanning agents based on the extraction, characterization, and comparative outcomes of this study. In comparison to commercial vegetable tannins, the extraction yield and total tannin content are within the recommended range. The extraction yield of banana bunches was determined to be 69.80 %. Due to the detection of different polyphenolic groups, FT-IR analysis established the presence of condensed type tanning material in the banana bunch and extract. The content of tannins in banana bunch extract and stem syrup was 3.13 % and 2.6 %, respectively; which makes them possible to be used as vegetable tanners. The phenolic content was found to be 1332.37 mg GAE/100 g of dried weight in the banana bunch extract and 873.92 mg GAE/100 g of dried weight in the syrup. It could be a potential vegetable tannin for the re-tanning process in the leather manufacturing process. Furthermore, the physical-mechanical characteristics of experimental leather were competitive with conventional vegetable (quebracho) tanned leather and far superior to previous studies of vegetable tannin. For the extracted banana bunch and syrup, the tensile strength, tear strength, and elongation percentage are 23.84 N/mm^2, 68.26 N/mm, 47.07 %, and 22.97 N/mm^2, 68.38 N/mm, 40.70 %, correspondingly. Softness was found to be 1.41 for the extracted bunch and 2.01 for the syrup. The bunch syrup had the values: 246.86 N, 13.24 mm, 530.77 N, 24.54 mm; the bunch extract had these values: 338.77 N, 13.42 mm, 460.65 N, 29.08 mm; for the grain crack load, distension at grain crack, strength at ball burst, and distension at ball burst, respectively. The tanned leather samples with banana bunch extract, syrup, and Quebracho (control trial) tannins showed shrinkage temperatures of 76.5 °C, 75 °C, and 84 °C, subsequently. Flexing endurance of the bunch extract and syrup showed the acceptable values which were below 4. Moreover, the bunch extract tanned leather showed higher thermal stability and for syrup it was comparable with the quebracho tanned leather. There are currently no vegetable tannin resources in Bangladesh, yet banana is locally available, therefore exploring this tannin may reduce vegetable tannin import dependency of this country. As an alternate to commercial vegetable tannin, the extracted tannin from banana bunch and stem syrup may be preferred as a potential vegetable tanning material in the leather-processing industry.

Abbreviations

Abbreviation	Commercial name	Generic name
MSG	Lipsol MSG	Combination fat (Synthetic and natural)
DX1202	CORIPOL DX-1202	Synthetic fat
SWR	**NEOPRISTOL SWR**	Semi-synthetic Fat (Sperm oil based)
HQ	PERFECTOL HQ	Waterproof fat (Paraffin oil and hydrophobic emulsifiers)
LQ	Lipsol LQ	Lecithin-based natural fat
Busan	Busan 30	Fungicide (Preservative)
SATRA	–	Shoe and Allied Trade Research Association
IUP	–	International Union for Physical Testing

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Data availability statement

All data presented or analyzed during this study are included in this article.

CRediT authorship contribution statement

Khandoker Tahmina Tasnim: Writing – original draft, Methodology, Formal analysis, Conceptualization. **Akash Debnath:** Writing – original draft, Methodology, Formal analysis, Conceptualization. **Md. Tushar Uddin:** Writing – review & editing, Data curation. **Md. Ashraful Alam:** Formal analysis, Data curation. **Md. Abdur Razzaq:** Formal analysis, Data curation. **Sk Zubaer Zaman:** Formal analysis, Data curation. **Md. Aftab Ali Shaikh:** Writing – review & editing, Validation, Supervision. **Ajoy Kanti Mondal:** Writing – review & editing, Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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