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# ADVANTAGES OF UTILIZING MICROWAVE IN SOFT LEATHER DRYING

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**ADVANTAGES OF UTILIZING MICROWAVE IN SOFT LEATHER DRYING**

ABSTRACT. The leather was dried by microwave and compared with the leather dried by oven in mechanical properties, softness, shrinkage temperature, microstructure as well as uniformities of chrome tanning agent, fatliquoring agent and dyestuff as new method for soft leather drying to keep and improve its softness and comprehensive properties. The results indicated that microwave drying would not damage leather collagen structure. Meanwhile, as microwave drying was even and would promote the combinations of collagen with other chemicals, the softness and mechanical properties of microwave dried leather were improved, in addition, the shrinkage temperature and uniformities of chrome tanning agent, fatliquoring agent and dyestuff were also promoted. Moreover, much more orderly and porous arrangement but less adhesion in collagen matrix of microwave dried leather were observed. These phenomena illustrated microwave dried leather could meet the high quality demands of leather better in softness and uniformity. To sum up, microwave has many advantages in drying soft leather products.
KEY WORDS: microwave, garment leather, dry process, softness, uniformity

**AVANTAJELE UTILIZĂRII MICROUNDELOR LA USCAREA PIEILOR MOI**

REZUMAT. Pielea a fost uscată în cuptorul cu microunde şi comparată cu pielea uscată în etuvă în privinţa proprietăţilor mecanice, moliciunii, temperaturii de contracţie, microstructurii, precum şi uniformităţii agentului tanant, agentului de ungere şi colorantului ca o nouă metodă pentru uscarea pieilor moi în vederea menţinerii şi îmbunătăţirii moliciunii şi proprietăţilor acestora. Rezultatele au arătat că uscarea cu microunde nu deteriorează structura colagenului din piele. În acelaşi timp, întrucât uscarea cu microunde este uniformă şi favorizează combinarea colagenului cu alte substanţe chimice, s-au îmbunătăţit moliciunea şi proprietăţile mecanice ale pieii uscate la microunde; în plus, s-au îmbunătăţit şi temperatura de contracţie, uniformitatea agentului de tăbăcire în crom, a agentului de ungere şi a colorantului. Mai mult decât atât, s-a observat o configuraţie mult mai ordonată şi mai poroasă, dar şi o mai mică aderenţă a fibrelor în matricea de colagen la pielea uscată la microunde. Aceste fenomene au ilustrat faptul că pielea uscată la microunde ar putea satisface cerinţele de înaltă calitate ale pieii cu proprietăţi de moliciune şi uniformitate mai bune. În concluzie, microundele au multe avantaje în ceea ce priveşte uscarea produselor din piei moi.
CUVINTE CHEIE: microunde, piele pentru îmbrăcăminte, proces de uscare, moliciune, uniformitate

**LES AVANTAGES DE L'UTILISATION DE MICRO-ONDES DANS LE SÉCHAGE DU CUIR SOUPLE**

RÉSUMÉ. Le cuir a été séché par micro-ondes et comparé au cuir séché en étuve en ce qui concerne les propriétés mécaniques, la souplesse, la température de rétraction, la microstructure ainsi que l'uniformité de l'agent de tannage au chrome, de l'agent de graissage et du colorant, comme une nouvelle méthode de séchage du cuir souple pour maintenir et améliorer sa souplesse et ses propriétés. Les résultats indiquent que le séchage par micro-ondes ne détériore pas la structure du collagène dans le cuir. Dans le même temps, alors que le séchage par micro-ondes est uniforme et favorise les combinaisons de collagène avec d'autres produits chimiques, la souplesse et les propriétés mécaniques du cuir séché par micro-ondes ont été améliorées ; en plus, la température de rétraction et l'uniformité de l'agent de tannage au chrome, de l'agent de graissage et du colorant ont été aussi améliorées. En outre, on a observé un arrangement beaucoup plus ordonné et poreux, mais aussi moins d'adhérence des fibres dans la matrice de collagène au cuir séché aux micro-ondes. Ces phénomènes ont illustré que le cuir séché aux micro-ondes peut répondre aux exigences élevées de cuir plus souple et avec une bonne uniformité. Pour résumer, le micro-ondes présentent de nombreux avantages dans le séchage des produits en cuir souple.
MOTS CLÉS: micro-ondes, cuir pour vêtement, procédé sec, souplesse, uniformité régions importantes.

## INTRODUCTION

Drying is an important process in leather making in which tanning agents, dyestuffs and fatliquoring agents combine with collagen further and water is evaporated to fulfil the demands of final leather product, therefore drying has significant influence on leather chemical and mechanical properties. Hanging, toggling, pasting, vacuum and heat pump are common drying methods, and the basic principles of these methods are to remove moisture through convection, conduction and radiation [1]. Traditional leather drying is time and energy consuming due to poor conductivity of leather. Microwave is a fast, time and energy saving heat resources with the remarkable advantages of selective heating ability, so it has been used to dry leather and leather coat as an efficient power [2-5].

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Microwave dried leather had more uniform water distribution and better feeling, in addition, leather would not harden or shrink in the process, resulting in larger area yield and softer leather product [6, 7]. Moreover, when fatliquored leather was subjected to microwave irradiation, no leather structure damaging but fine fat distribution were observed, in addition, the particle size and viscosity of fatliquoring agent emulsion was decreased at the same time [8]. These advantages of microwave drying are much more suitable for soft leathers like garment and glove which have particular requirements in softness and fine feeling. However, many studies were focused on general leather microwave drying rather than targeting on soft leather [9-12].

In the study, goat garment leather was dried by microwave and compared with oven dried leather in mechanical properties, softness, shrinkage temperature, microstructure as well as uniformities of chrome tanning agent, fatliquoring agent and dyestuff to illustrate advantages of microwave drying for soft leather product. It would provide a new method for soft leather drying to keep its softness and improve microwave utilization in leather making.

## MATERIALS AND METHODS

### Materials

The goat wet blue with thickness of 0.9mm was prepared in the lab and subjected to retanning, neutralizing, dyeing and fatliquoring according to conventional garment leather making process to get wet crust. The chemicals used for leather manufacturing were commercial grade and for analysis were research grade.

### Leather Sampling and Drying Method

The wet crust was divided into two pieces along the backbone after 12h standing. The samples used for microwave drying were cut for 30×30cm from belly and back respectively, the leathers with the same sampling method at symmetric position were used for oven drying.

The weight of each sample before drying was recorded and the water content was 80% (based on the total weight). A MCR-3S microwave reactor (Xi'an Yuhui instrument Co. Ltd. China) was used for drying microwave dried leather (MDL) with 100W heating power, the leather sample was heated 2min every 2min to prevent high temperature at the beginning to damage the leather. The oven dried leather (ODL) was dried in a DHG-9070A drying oven (Shanghai Feiyue Experimental instrument Co. Ltd. China) at 45°C. The drying was ceased when the water content reduced to 20%. Then the MDL and ODL samples were placed into a temperature humidity chamber at 25°C and 65% relative humidity for 24h.

### Test Methods

#### *Physical Properties Measurement*

Both MDL and ODL samples were conditioned according to standard method before mechanical properties testing [13]. The tensile and tear strength were tested by an AI-7000S tensile machine (GOTECH testing Machines Inc. China) following standard [14, 15], and the softness was tested by GJ9E1 measuring apparatus (GOTECH testing Machines Inc. China) [16].

#### *Shrinkage Temperature (Ts) Measurement*

The shrinkage temperature was tested by MSW-YD4 Shrinkage Temperature Tester (China) with 75% glycerine bath. Each value was an average of two samples which were parallel and perpendicular to the backbone. Before testing, the samples were soaked in water for 2h for rewetting.

#### *Chrome Content and Chrome Uniformity Measurement*

The samples were split into 3 uniform layers (about 0.3mm) and cut into about 1×1mm fragments, then dried in 102±2°C for 6h to constant weight. Each sample (about 0.150g) was digested in a flask with 10mL $HNO_3$ and 5mL $H_2O_2$ for 30min at heating condition. After cooling down, the digested solution was dissolved in volumetric flask (100mL). The total chromium content in digestion solution was determined by Optima 2100DV Inductively Coupled Plasma Atomic Emission Spectroscopy (Perkin Elmer, America) following the manufacturer's direction and $Cr_2O_3$ content in leather was calculated. Each value was an average of two tests. The uniformity of chrome distribution was calculated as formula 1.

$$\text{chrome uniformity (\%)} = \frac{2 \text{ x } Cr_2O_3 \text{ in middle layer}}{Cr_2O_3 \text{ in grain layer} + Cr_2O_3 \text{ in flesh layer}} \text{ x } 100\% \quad (1)$$

*Fat Content and Fat Uniformity Measurement*

The samples were split into 3 uniform layers (about 0.3mm) and cut into about 1×1mm fragments. After drying in 102±2°C for 6h to constant weight, fat content was determined by extraction with dichloromethane [17]. The uniformity of fat distribution was calculated as formula 2.

$$\text{fat uniformity (\%)} = \frac{2 \text{ x fat in middle layer}}{\text{fat in grain layer} + \text{fat in flesh layer}} \text{ x } 100\% \quad (2)$$

*Dyestuff Distribution Measurement*

The leather were split into 3 uniform layers (about 0.3mm), and the colour difference between each layers and samples were determined to use X-Rite 8200 chroma colour difference meter (X-rite Company, America).

*Atomic Force Microscope (AFM) Measurement*

A SPM-9600 atomic force microscope (SHIMADZU, Japan) was exploited to observe the microstructure of the collagen fibres in leathers. The AFM images were obtained in ambient conditions at room 20°C with 65% relative humidity. The other testing conditions were as follows: NSG 11 probe with observing size as 0.25μm.

*Scanning Electron Microscope (SEM) Measurement*

A JSM-5900LV scanning electron microscope (Japan Electronic Co. Ltd., Japan) was used for the analysis. The micrographs for the cross sections of leathers were obtained by operating the SEM at low vacuum (10-4Pa) with an accelerating voltage of 20kV at 1000 magnification levels.

## RESULTS AND DISCUSSIONS

### Influence of Microwave Drying on Leather Mechanical Properties and Softness

As shown in Table 1, the tensile strength, tear strength and softness of MDL are slightly better than ODL, indicating leather mechanical properties and softness improved by microwave. Since water could absorb microwave more intensely than leather, leather drying rate under microwave slows down at the end of drying as leather moisture reduces obviously [7]. In addition, there is no temperature gradient in microwave heating, making uniform water evaporation at inner and surface of leather. However, drying rate and temperature of leather would not decrease and the surface would be over-dried in conventional because the drying is outside-in [10]. These characteristics of microwave drying prevent collagen fibre adhesion and stress concentration to improve leather mechanical properties and softness. Since garment leather will be used to make cloth, the improvement in mechanical properties and softness of garment leather is very important to keep flexibility but enhance strength.

Table 1: The mechanical properties and softness of ODL and MDL

| Sample | Tensile strength: MPa | | Tear strength: N/mm | | Softness: mm | |
|---|---|---|---|---|---|---|
| | Back | Belly | Back | Belly | Back | Belly |
| MDL | 25.65 | 21.50 | 56.52 | 38.64 | 6.69 | 8.91 |
| ODL | 23.10 | 20.10 | 55.13 | 36.51 | 6.23 | 8.30 |

## Influence of Microwave Drying on Leather Shrinkage Temperature

Table 2 demonstrated the Ts of MDL back and belly are 1.9°C and 0.9°C higher than ODL respectively, indicating MDL having better hydrothermal stability and better crosslink between collagen and tanning agents. Wang *et al*. [18] found microwave could increase chrome tanned leather shrinkage temperature further. As a consequence, chrome tanning agent cross-links collagen in one step when leather subjected to microwave in drying and higher Ts is obtained just as in microwave assisting chrome tanning process.

Table 2: The shrinkage temperature of ODL and MDL

| Sample | Back Ts: °C | Belly Ts: °C |
|---|---|---|
| MDL | 116.0 | 114.4 |
| ODL | 114.1 | 113.5 |

## Influence of Microwave Drying on Chrome Migration

The chrome uniformity of MDL samples are much more even than ODLs, especially the back is 24.28% higher than the control (shown in Table 3). High chrome uniformity represents low difference of chrome content between inner and surface of leather. As MDL has higher shrinkage temperature, the combination of chromium with collagen in MDL is more stable, leading free and weak combined chromium decreasing to avoid chromium migration in microwave drying. Furthermore, it might be inferred that other tanning agents could combine with collagen firmly as well. More uniform tanning agent distribution benefits for even cross-linkage all over the leather cross section to prevent stress concentration, in addition, it also has positive effect on improving leather mechanical properties and softness.

Table 3: Chrome uniformity of ODL and MDL

| Sample | Chrome uniformity: % | |
|---|---|---|
| | Back | Belly |
| MDL | 80.60 | 85.18 |
| ODL | 56.32 | 82.31 |

## Influence of Microwave Drying on Fat Migration

Table 4 indicates the microwave drying could obtain better fat uniformity leather. Prior study had verified that microwave could reduce the viscosity and particle size of fatliquoring agent to increase the permeability [8], leading fat well distributed in microwave drying. As fatliquoring agent uniform existed in leather, it could lubricate fibres sufficiently and evenly to get better softness and improve mechanical properties of leather.

Table 4: Fat uniformity of ODL and MDL

| Sample | Fat uniformity: % | |
|---|---|---|
| | Back | Belly |
| MDL | 63.04 | 82.32 |
| ODL | 39.75 | 64.61 |

## Influence of Microwave Drying on Colour

The L value represents lightness, L = 0 yields black and L = 100 yields white, so larger L value means whiter colour and less dye stuff on the section. Table 5 shows the L value of ODL middle layer is lower than MDL middle but the grain and flesh layers are higher than MDLs, demonstrating that there is more dyestuff in centre while less on the surface for ODL compared with MDL. As microwave could fix dyestuff further [19], it is difficult to migrate to surface in microwave drying.

Table 5: The lightness (L value) of each layer

| Layer | ODL | MDL |
|---|---|---|
| Grain | 29.3 | 27.8 |
| Middle | 53.8 | 57.1 |
| Flesh | 31.2 | 25.6 |

## Influence of Microwave Drying on Leather Microstructure

The microstructure of the collagen fibres demonstrates in Fig. 1. The collagen fibres have characteristic axial D-periodic cross-striated fibril, which proves that the microstructure of collagen is not damaged during microwave drying. The surface of collagen fibre is not smooth according to the AFM images especially displayed in Figure 4A, and there is some stacking of leather chemicals which should be speculated as tanning agents, fatliquoring agents and dyestuffs. These phenomena demonstrate that microwave will not damage collagen structure but could promote combination of chemicals with collagen.

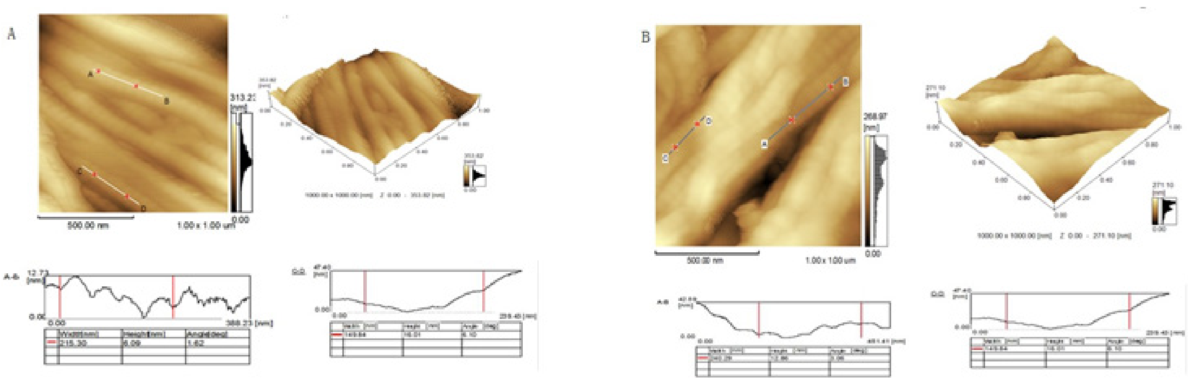


Figure 1. AFM images of MDL and ODL back (A: MDL, B: ODL)

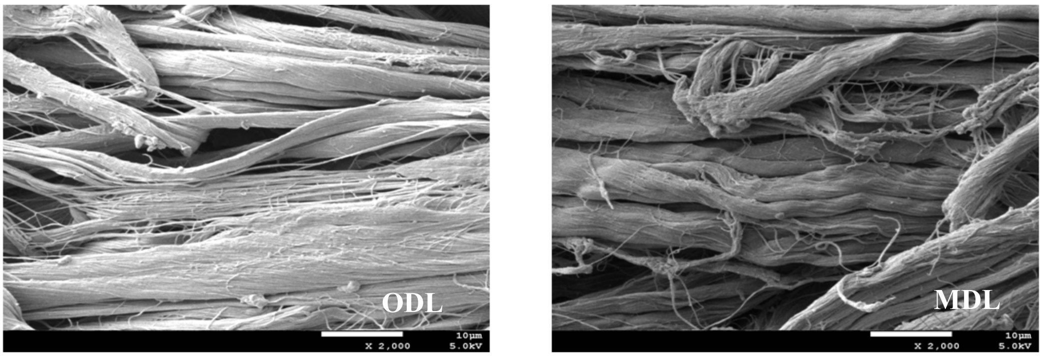


Figure 2. SEM images of MDL and ODL back (A: MDL, B: ODL)

According to Fig. 2, there is no significant difference between ODL and MDL in collagen weaving condition, but collagen fibre of MDL has a slight improvement in porosity and orderliness while adhesion between fibres decreases. It demonstrates microwave could not damage leather matrix too. In addition, because of more porosity but less fibre adhesion, higher area yield and better softness of garment leather are obtained compared with conventional drying.

## CONCLUSIONS

Microwave drying would not damage leather collagen structure. Meanwhile, microwave dried leather has better mechanical properties and softness together with higher shrinkage temperature compared with oven drying; moreover, microwave could improve chrome, dyestuff and fat uniformity and make collagen fibre matrix arrange porously and orderly. These characteristics of microwave drying could not only keep the softness but also improve leather mechanical properties, and leather is more uniform all over the piece. To sum up, microwave has many advantages for drying soft leather products like garment and glove.

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# STUDY ON PLANT GROWTH PROMOTER FROM PROTEINEOUS WASTES FROM LEATHER INDUSTRY

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### STUDY ON PLANT GROWTH PROMOTER FROM PROTEINEOUS WASTES FROM LEATHER INDUSTRY

ABSTRACT. Tanneries generate huge quantities of solid wastes as fleshings. If these bio-waste materials are not utilized properly they are potential source of pollution. So in the present study it has been tried to convert these hide fleshings into NPK fertilizer. During the process of manufacture of NPK fertilizer, phosphorous and potassium were incorporated by suitable chemical reaction under desired conditions of temperature and pressure. The resultant liquid product was converted into pellet form and field tested on horticulture plants (Balsam Plant - Impatiens balsamina).
KEY WORDS: animal fleshings, fertilizers, nitrogen, phosphorus, potassium.

### STUDIU ASUPRA UNUI FERTILIZATOR PENTRU CREŞTEREA PLANTELOR DIN DEŞEURI PROTEICE DIN INDUSTRIA DE PIELĂRIE

REZUMAT. Tăbăcăriile generează cantităţi uriaşe de deşeuri solide sub formă de şeruitură. Dacă aceste deşeuri organice nu sunt utilizate în mod corespunzător, devin o sursă potenţială de poluare. Aşadar, în studiul de faţă s-a încercat transformarea acestei şeruituri în fertilizator NPK. La fabricarea fertilizatorului NPK, s-au încorporat fosfor şi potasiu prin reacţie chimică corespunzătoare în condiţiile dorite de temperatură şi presiune. Produsul lichid obţinut a fost prelucrat sub formă de granule şi s-a testat pe plante horticole (balsamină - Impatiens balsamina).
CUVINTE CHEIE: şeruitură de origine animală, fertilizator, azot, fosfor, potasiu.

### ÉTUDE SUR UN ENGRAIS POUR LA CROISSANCE DES PLANTES À PARTIR DE DÉCHETS PROTÉINES DE L'INDUSTRIE DE CUIR

RÉSUMÉ. Les tanneries génèrent énormes quantités de déchets solides en tant que déchets d'écharnage. Si ces déchets organiques ne sont pas utilisés correctement, ils sont une source potentielle de pollution. Ainsi, dans la présente étude, on a essayé de convertir ces déchets d'écharnage en engrais NPK. Au cours de la fabrication de l'engrais NPK, le phosphore et le potassium ont été incorporés par une réaction chimique appropriée dans les conditions souhaitées de température et de pression. Le produit liquide résultant a été converti en forme de pastille et testé sur des plantes horticoles (la balsamine - Impatiens balsamina).
MOTS CLÉS: déchets d'écharnage, engrais, azote, phosphore, potassium.

## INTRODUCTION

The generation of large quantum of tannery wastes is an environmental threat and their non-utilization or non-treatment would result in health hazards [1, 2]. So in this research work it has been ventured to utilize these solid wastes to produce a value added product viz., NPK fertilizer. Nitrogen (N) phosphorous (P) and potassium (K) are the most important macronutrients required for growth and development of plants. Earlier literature dealt with meat and bone meal (MBM) that contained appreciable amounts of total nitrogen, phosphorous and calcium which were applied as fertilizer for various crops.

In two experiments with spring wheat increased amount of MBM showed linear yield increase related to the N supply. A similar experiment on barley gave positive yield increase for 500 MBM $ha^{-1}$ and no further increase for large amounts of MBM [3]. In another report a screen house study was conducted to evaluate the effect of compound fertilizer (NPK) on the response of cassava (*Manihot esculenta Crantz*) to diseases, pests and mycorrhizal symbiosis. NPK was applied to the soil drenches. Mycorrhizal spores in rhizopore soil and root colonization of cassava by arbuscular mycorrhizal (AM) fungi were estimated after 5.5 months. Incidents of pests-cassava green spider mites (CGM) cassava meelybug (CM), African cassava moossaic disease (ACMD) and cercospora leaf spot disease (CLSD) were rated on varying scales. In this experiment it was found that the mycorrhizal spores and colonization were significantly higher in control experiments. NPK fertilizer significantly increased plant vigour (stem & girth) and also diminished the occurrences of CGM, CM and ACMD [4]. In another report a pot experiment was conducted in the wire house to compare the effects of two precursors (calcium carbide and L-methionine) of ethylene on growth and yield of tomato. This experiment showed that the tomato plants grown in combination with NPK

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fertilizer gave good results in terms of number of flowers per plant, number of fruits per plant, shoot dry weight, fruit dry weight, root dry weight, nitrogen in shoot (%) and nitrogen in fruit (%) [5]. In another report a long term experiment was conducted on Aquic Hapludoll under rice-wheat-cowpea system. It was realized that treatment given with 100% NPK + farmyard manure and 100% NPK fertilizer + Zn gave better results than other treatments [6]. In one more report, the effect of NPK fertilizer on growth and yield of banana has been investigated. The result of the study indicated that vegetative growth parameters (i.e., leaf number, leaf area, stem height and stem circumference) of non-fertilized control plants were neither significantly different nor produced better vegetative growth when compared to NPK fertilized plants [7]. In recent times, protein hydrolysate derived from leather wastes had also been used as biostimulant to activate plant growth thereby increasing the yield of the crops has been reported [8].

In this paper a new process for preparation and application of NPK fertilizer from bio-wastes i.e., tannery fleshings has been reported. In the present investigation phosphorous and potassium were incorporated under suitable experimental conditions with the animal fleshings which are rich source of nitrogen. The obtained NPK product was field tested in horticultural plant (Balsam - *Impatiens balsamina*) and found to give good results in terms of size of the plant, size of the leaf area and dry weight of the plant.

## MATERIALS AND METHODS

### Preparation of NPK Fertilizer

The process of hydrolysis of animal fleshings with strong acids such as hydrochloric acids and sulphuric acid and pancreatic enzymes are already established [9]. In the present work, orthophosphoric acid is used to incorporate phosphorous in the product. 2 Kg of hide fleshings was taken (which was previously washed thoroughly) in the oil sealed high pressure autoclave. 6% orthophosphoric acid (w/v) was added along with 1 liter of water and hydrolyzed in the pressure of 50 Psi for 3 hours. After complete digestion the solution was filtered and the fat content which is settled on the top was removed using a separating funnel. The liquor collected was neutralized to pH 7.0 using 50% Potassium hydroxide solution (V/W) and was concentrated at 80°C for 8 to 10 hours.

The concentrated NPK solution was mixed with known quantity of inert materials like china clay or leaf mould and the mixture was semi dried and converted into pellets for further field experimentation. The obtained NPK pellets are analysed and used for application studies.

## RESULTS AND DISCUSSION

### Characterization of NPK Solution

According to the official procedure [10-13] the total nitrogen, phosphorus and potassium was estimated for the obtained NPK product and is shown in Table 1.

Table 1: Estimation of macronutrients

| S.No | Macro Nutrients | Quantity |
|---|---|---|
| 1 | Nitrogen as N | 1.02±0.01% |
| 2 | Phosphorous as P | 2.38±0.02% |
| 3 | Potassium as K | 2.21±0.02% |

### Infrared Spectroscopy Study of NPK Product

The obtained NPK pellet was analyzed for its nitrogen quantity. The analysis of FTIR spectroscopy reveals the relevant amount of compositional and structural information concerning the subjected sample. The IR spectrum of the sample was taken using Nicolet Impact spectroscopy by preparing a 500 mg KBr pellet containing 2-6 mgs of the sample.

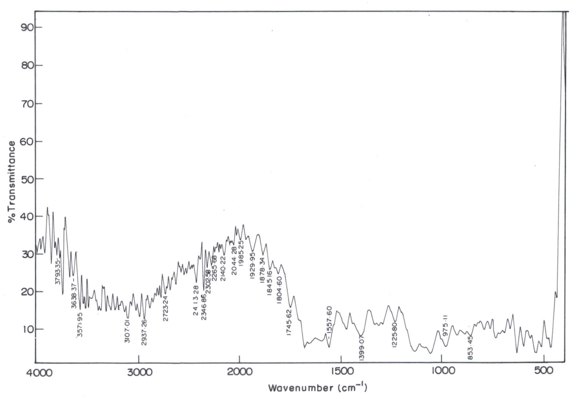


Figure 1. IR spectrum of NPK fertilizer

The IR spectrum of the sample analysed shows the characteristic peaks of collagen. The amide I absorption bands are seen at 1655 $cm^{-1}$ and this band leads to the stretching vibration of the C = O bond of amide group. Amide II absorption bands are seen at 1557 $cm^{-1}$ which leads primarily to bending vibration of the N – H bond [14].

Apart from the above important functional groups of amino acids Aspargin and Glutamin of skin protein, other groups are also seen [15]. Thiocyanate group (SCN) at absorption band of 2140 $cm^{-1}$ amide B (NH stretching) band is seen at 3107 $cm^{-1}$. Carboxylic acid group is seen at absorption band of 2937 $cm^{-1}$. Amines are noticed at 1225 $cm^{-1}$. Hydroxy group (H bonded OH stretch) are seen at 3571 $cm^{-1}$. The above spectral data confirms the presence of nitrogen in the NPK fertilizer taken for study.

## Application of NPK Fertilizer

A different level of standard fertilizers were taken in two batched at the rate of 3 pots per batch. In first batch all the three pots were given red soil, river soil and farmyard manure were taken in 1:1:1 ratio respectively out of which the first two pots were given 100 g of NPK fertilizer each. These two pots were experiment I and experiment II of batch1 and the third pot was control without NPK fertilizer. In the second batch all the 3 pots were taken with red soil, river soil and farmyard manure in the ratio of 1:1:2. Here also the first two pots were given 200 g of NPK fertilizer. These two pots were experiment I and experiment II of second batch. The third pot was without NPK fertilizer and it served as control for second batch.


Figure 2. Experiment plants - Balsam Plant

The plants and soil were irrigated with equal quantity of fresh water as and when required. Plants were monitored for the growth for 20 days to assess the efficacy of the NPK fertilizer on plants. The balsam plants were raised in earthen pots lined with sand at the bottom and filled with 4 kg of different proportions of soils as shown in the Table 2.

Table 2: Application experiments on plants

| Components | Composition | NPK Fertilizer | Pot No. | Batch | Experiments |
|---|---|---|---|---|---|
| Red soil | | 100 g | 1 | | Experiment I |
| River soil | 1:1:1 | 100 g | 2 | Batch 1 | Experiment II |
| Farmyard manure | | 0 | 3 | | Control |
| Red soil | | 200 g | 4 | | Experiment I |
| River soil | 1:1:2 | 200 g | 5 | Batch 2 | Experiment II |
| Farmyard manure | | 0 | 6 | | Control |

## Analysis of Plant Products

In Table 3, though the percentage of dry weight of all the plants of batch 1 and batch 2 seem to uniformly equal, the weight of fresh plants of batch 2 are higher. This is again an indication of the effect of NPK fertilization and manure ratio stated in batch 2.

Table 3: Fresh and dry weights of the plants

| S.No | Description | Soil & Manure ratio | NPK | Weight of the fresh plants | Weight of the dry plants | Dry weight of plants (%) |
|---|---|---|---|---|---|---|
| 1 | | | 100 g | 104.0 g | 15.0 g | 14.4 |
| 2 | Batch 1 | 1:1:1 | 100 g | 120.0 g | 17.0 g | 14.2 |
| 3 | | | 0 | 84.0 g | 12.4 g | 14.8 |
| 4 | | | 200 g | 141.0 g | 20.0 g | 14.2 |
| 5 | Batch 2 | 1:1:2 | 200 g | 158.0 g | 22.7 g | 14.4 |
| 6 | | | 0 | 102.0 g | 15.3 g | 15.0 |

The plants were grown for 20 days in normal condition. From the above experiments it was found that the plants grown in the level of 1:1:2 and NPK fertilizer 200 g gave good result. The plants were bigger with thicker stems and dark green leaves. The dry weights of the plants were also higher compared to control plants.

## CONCLUSION

Bio wastes such as skin and hide fleshings are generated in the tanneries in large quantities during processing all over the world. In the event of non utilization of these materials they may cause environmental pollution. So the present work has been ventured into utilize the waste materials into value added products namely NPK fertilizer. Presently this product has been applied on horticulture plant i.e., Balsam Plant. It has been planned to apply the NPK product in during the cultivation of paddy, corn etc. By this kind of application in the field, it is possible to reduce the commercial synthetic fertilizers.

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# ELECTROCHEMICAL BEHAVIOR OF TANNIN SOLUTIONS UNDER MICROWAVE IRRADIATION

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**ELECTROCHEMICAL BEHAVIOR OF TANNIN SOLUTIONS UNDER MICROWAVE IRRADIATION**

ABSTRACT. Vegetable tannin extract has an important use as a tanning agent in leather industry. The electrochemical behavior of tannin solutions, as a critical factor, greatly affect vegetable tanning. In this work, we have investigated the particle size, Zeta potential and conductivity of Commercial Acacia Mangium extract solutions (CAME) and Commercial valonia extract solutions (CVE) under water bath heating (WBH) and microwave irradiation heating (MIH). The heating conditions were selected as follows: time, 5 min, 15 min, 30 min, 60 min and 120 min; temperature, 30°C, 40°C and 50°C. It was found that the particle size of both CAME and CVE decreased under MIH while Zeta potential increased compared with WBH. Furthermore, the features become more and more significant with the irradiation temperature and time. And the conductivity of CAME and CVE increased more with the temperature under MIH in comparison to WBH. As a result, in the condition of microwave irradiation, tannin extract can easily penetrate into skins and then crosslink well with the collagen owing to the small tannin particle size and stable solution system, hence microwave may contribute to the penetration of tannin extracts in the skin and the binding properties with collagen in vegetable tanning.

KEY WORDS: dynamic light scattering, electrochemical behavior, microwave irradiation, vegetable tannin extract

**COMPORTAMENTUL ELECTROCHIMIC AL SOLUŢIILOR DE TANIN SUPUSE IRADIEIRII CU MICROUNDE**

REZUMAT. Extractul de tanin vegetal are o utilizare importantă ca agent de tăbăcire în industria pielăriei. Comportamentul electrochimic al soluţiilor de tanin, ca factor critic, afectează foarte mult tăbăcirea vegetală. În această lucrare s-au investigat mărimea particulelor, potenţialul Zeta şi conductivitatea soluţiilor pe bază de extract comercial de Acacia Mangium (CAME) şi extract comercial de vallonia (CVE) la încălzire în baie de apă (WBH) şi încălzire prin iradiere cu microunde (MIH). Condiţiile de încălzire au fost selectate după cum urmează: timp - 5 min, 15 min, 30 min, 60 min şi 120 min; temperatură - 30°C, 40°C şi 50°C. S-a constatat că atât mărimea particulelor de CAME cât şi a celor de CVE a scăzut sub MIH, în timp ce potenţialul Zeta a crescut în comparaţie cu WBH. În plus, caracteristicile devin din ce în ce mai semnificative odată cu temperatura şi timpul de iradiere. Conductivitatea CAME şi CVE a crescut mai mult odată cu temperatura sub MIH în comparaţie cu WBH. Ca urmare, în starea de iradiere cu microunde, extractul de tanin poate pătrunde cu uşurinţă în piele şi apoi se reticulează bine cu colagenul, datorită particulelor de tanin mici şi soluţiei stabile; aşadar microundele pot facilita penetrarea extractelor de tanin în piele şi pot îmbunătăţi proprietăţile de legare cu colagenul în tăbăcirea vegetală.

CUVINTE CHEIE: dispersie dinamică a luminii, comportament electrochimic, iradiere cu microunde, extract de tanin vegetal

**LE COMPORTEMENT ÉLECTROCHIMIQUE DES SOLUTIONS DE TANNIN SOUS L'IRRADIATION DES MICRO-ONDES**

RÉSUMÉ. L'extrait de tanin végétal a une utilisation importante en tant qu'agent de tannage dans l'industrie du cuir. Le comportement électrochimique des solutions de tanin, en tant que facteur critique, affecte grandement le tannage végétal. Dans cet article, on a étudié la granulométrie, le potentiel Zeta et la conductivité des solutions d'extrait commercial d'Acacia Mangium (CAME) et d'extrait commercial de vallonée (CVE) sous chauffage au bain-marie (WBH) et à l'irradiation par micro-ondes (MIH). Les conditions de chauffage ont été choisies comme suit: temps - 5 min, 15 min, 30 min, 60 min et 120 min; température, 30°C, 40°C et 50°C. On a constaté que la taille des particules de CAME et de CVE diminue sous MIH tandis que le potentiel Zeta augmente par rapport à WBH. En outre, les caractéristiques deviennent de plus en plus importantes avec la température et le temps d'irradiation. La conductivité de CAME et CVE augmente davantage avec la température sous MIH par rapport à WBH. En conséquence, dans l'état de l'irradiation par micro-ondes, l'extrait de tanin peut facilement pénétrer dans la peau et ensuite réticuler avec le collagène en raison de la petite taille des particules de tanin et du système de solution stable; par conséquent, les micro-ondes peuvent contribuer à la pénétration des extraits de tanin dans la peau et peuvent optimiser les propriétés de liaison avec le collagène dans le tannage végétal.

MOTS CLÉS: diffusion dynamique de la lumière, comportement électrochimique, irradiation par micro-ondes, extrait de tanin végétal

## INTRODUCTION

Microwave is a kind of electromagnetic wave in the frequency from 300 MHz to 300 GHz. At present, the frequency of microwave equipment used in the industry is 2450 MHz (wavelength, 0.122m) and 915MHz (wavelength, 0.33m). In general, the frequency of household microwave oven is 2450MHz [1]. Since microwave is a novel, mild, environmentally friendly and efficient thermal technology, it is widely used in pharmaceutical chemicals [2], food chemicals [3, 4, 5], life sciences field [6] and so on. And these applications have already achieved fruitful research results. However, little research on the application in leather-making was reported, especially the vegetable tanning, which is the aim of this work.

Vegetable tannin extracts have a very important position in leather-making, such as tanning and retanning procedures. With good knowledge of tannin extract, their solutions are extremely complex whether in physics or chemistry. From the composition point of

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view, tannin extract is a complex mixture of polydisperse colloid, containing tannins, non tannins and insolubles. In chemistry, vegetable tannins are classified into two categories: hydrolysable tannin and condensed tannin. According to the reported research [7], condensed tannin shows different properties and features from hydrolysable tannin. Owing to a reversible equilibrium between the molecular dispersions and colloidal dispersions, tannin extract solution system is often referred to as semicolloid. And the micelle of vegetable tannin extracts is a structure with double electrical layer: adsorption layer directly connected with colloidal nucleus and diffusion layer outside the adsorption layer whereabout colloidal nucleus [8]. In electric field, when the tannin molecules move toward the anode, the positive ions in the adsorption layer move with the micelles and the positive ions in the diffusion layer are disengaged from the micelles. Meanwhile, the formed potential difference between micelles and the dispersion medium is called Zeta potential [9]. The smaller the colloidal particle size is, the greater the diffusion coefficient is. Therefore, the tannin particles diffuse easily with great diffusion coefficient and it is calculated by the formula (1) as follows [10]:

$$D = \frac{RT}{6\pi\eta\gamma L}$$

In vegetable tanning, the penetration speed of tannin particles is closely related to the size of tannin particles, and small tannin particles are able to penetrate the skins easily. Perhaps, tannin extracts respond to the microwave, resulting in changes in the electrochemical behavior of the solution. According to Brownian motion, dynamic light scattering and electrophoresis properties of the colloid can be used to study the properties of colloidal particles, such as conductivity, Zeta potential and particle size distribution. And these properties are important for evaluating the permeability, filling performance and degree of combination between tannin extract and skin fibers, even beyond the chemical properties of the tannin extract solution itself [11]. In this work, we have investigated the electrochemical behavior of tannin extract solutions and evaluated the stability of the solutions under microwave irradiation. The penetration, filling and bonding performance of the tannin extract were explained, which may provide an experimental basis for revealing electrochemical change in the vegetable tanning.

## EXPERIMENTAL

### Material

Commercial Acacia Mangium extract (CAME) and Commercial valonia extract (CVE) were industrial products, commercially purchased from Wu Ming tannin extract factory in Guangxi, China. Microwave was produced by a Xian Yuhui MCR-3 microwave chemistry reactor. Zeta potential and particle size were measured on a Zetasizer Nano-ZS series equipment (Malvern Instruments, UK). Conductivities were performed on a DDS-307 conductivity meter (Shanghai INESA Scientific Instrument Co., Ltd, China).

### Methods

Original tannin extract solutions (mass concentration, 4g/L) were prepared according to procedure reported in the literature [12]. The solutions were centrifuged at 3000r/min for 30minutes and collected with a clean beaker.

The schematic diagram of the microwave reactor is displayed in Figure 1. 60 mL of the solutions were heated in the condition of water bath and microwave irradiation, respectively. Selected conditions were showed as follows: time, 5min, 15 min, 30 min, 60 min and 120 min; temperature, 30°C, 40°C and 50°C. After that, Zeta potential, particle size and conductivity of the treated solutions were measured, and then ΔAS (average size difference value between microwave irradiation heating and water bath heating) and ΔZP (difference value of the absolute value about Zeta potential between microwave irradiation heating and water bath heating) were calculated.

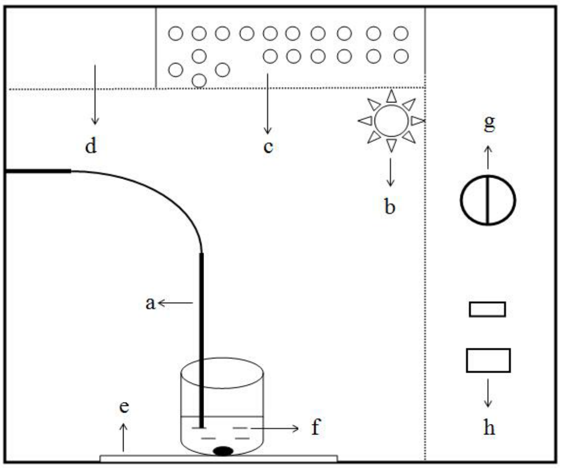


Figure 1. The schematic diagram of the microwave reactor
a: temperature sensor; b: microwave source; c: settings panel; d: display; e: magnetic stirring stage; f: sample; g: magnetic stirring knobs; h: switch

## RESULTS AND DISCUSSION

### Particle Size of CAME and CVE

Known by Stokes-Einstein equation, hydrodynamic diameter of colloidal particles is proportional to the temperature, namely, rising temperature will increase colloidal particle size. Simultaneously, high temperature can accelerate Brownian motion of colloidal particles, and collisions appear more frequently among the particles. Thus, there is a substantial reduction in the stability of the solutions [13]. Nevertheless, in conventional heating process (water bath), thermal energy transfer to the external surface of material by convection, conduction and radiation in the existence of the thermal gradient so that the material is heated slowly and unevenly. But in microwave field, electromagnetic energy directly turns into thermal energy that can generate heat at different depths inside the materials, and the materials are heated more quickly and evenly [14]. Therefore, the average size of tannin extract may change somewhat under microwave irradiation.

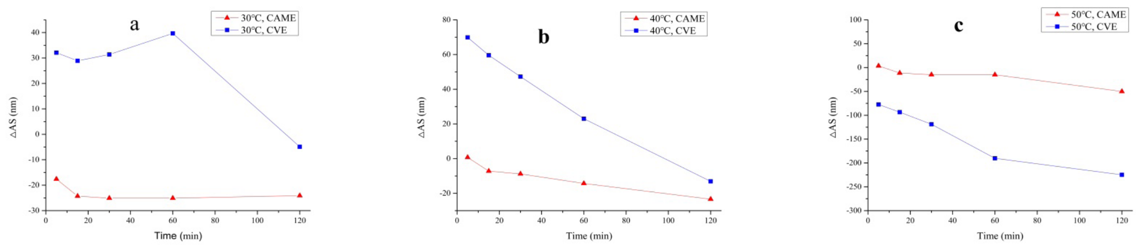


Figure 2. ΔAS of CAME and CVE at 30°C (a), 40°C (b) and 50°C (c)

Figure 2 shows ΔAS of the tannin extract solutions at different temperature (30°C, 40°C and 50°C). Apparently, ΔAS of CAME are all absolutely negative with time, namely, the average size decreased under microwave heating. At 30°C, ΔAS kept essentially unchanged with time while it decreased at 40°C and 50°C. In terms of the level of ΔAS for CAME, microwave effect was more significant with longer heating time under a certain temperature. However, for CVE, there are both positive and negative terms of ΔAS, so the average size increased or decreased as different heating temperature and time were carried out. There is a declining trend for ΔAS of CVE even at different temperature. Obviously, at high temperature (50°C), the particle size of CVE decreased dramatically with time under microwave heating. Contrast to ΔAS of CAME and CVE, different microwave effects occurred between them. For example, microwave irradiation induced the reduction of CAME particle size within 60 minutes under low temperature; but for CVE, it brought the increase of the particle size. However, the effect of microwave related to CAME and CVE particle size was a function of decrease in a similar vein under the high temperature. Although, there is a little different effect on hydrolysable tannin and condensed tannin under microwave irradiation, however, microwave may induce a reduction of tannin extract particle size to some extent.

**Zeta Potential of CAME and CVE**

Zeta potential is an important index to determine whether the colloidal solution is stable. In general, for a stable solution system, the absolute value of Zeta potential is more than 30 mV, on the contrary, the solution is an unstable system. When Zeta potential value is 0, the solution arrives at the isoelectric point, and micelle aggregation and precipitation are most likely to occur.

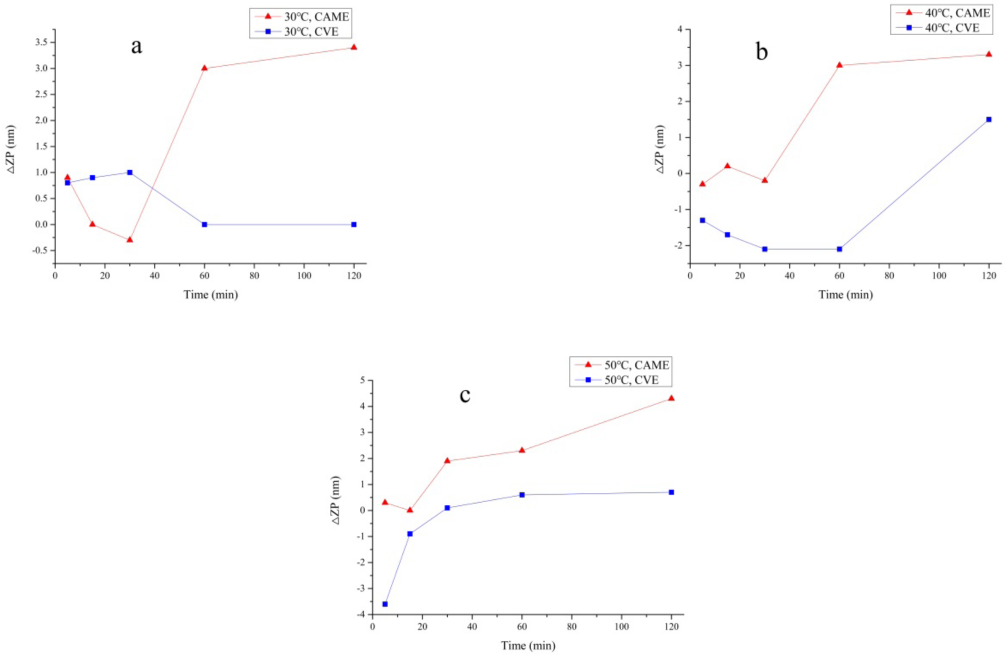


Figure 3. ΔZP of CAME and CVE at 30°C (a), 40°C (b) and 50°C (c)

For the purpose of investigating the stability of tannin extract solutions under microwave irradiation, determination of Zeta potential about the solution was conducted. ΔZP of CAME and CVE at different temperature is exhibited in Figure 3. For CAME, although ΔZP decreases a little within 30 minutes, a rising tendency of ΔZP curve with time emerges visually at 30°C, and it is the same when the temperature is 40°C and 50°C. As the trend is relatively similar, there are some obvious differences about ΔZP between high and low temperature, as well as long and short time. For instance, when the solutions were heated for 120min at 50°C (much more microwave function), ΔZP is 4.3mV which is the biggest different value of CAME in the measured data (seen in Figure 3c). Therefore, with more microwave function, the effect was more significant and promoted the stability of CAME better. As to CVE, ΔZP fluctuates around 0mV at 30°C (Figure 3a), indicating that CVE did not respond well to microwave under the condition of low temperature. Even though ΔZP is negative before heating for 60 minutes, there is an obvious upward trend about ΔZP curve with time at 40°C and 50°C (Figure 3b, 3c). Apparently, ΔZP starts to increase when the time exceeds 30 minutes, hence a more stable solution may be in the treatment of microwave irradiation. As a result, the absolute value of Zeta potential of both CVE and CAME increases, and both of them show a more stable solution system under microwave irradiation. However, compared with CVE, there is an augment of ΔZP for CAME. Therefore, from the variation trend point of view, microwave irradiation is better for CAME to maintain a high degree of stability.

**Conductivities of CAME and CVE**

In order to study the electrolyte content in tannin extract solutions under microwave irradiation heating, the conductivity measurements were carried out. The results are presented in Table 1, where it can be seen that the conductivity always increases with time when the temperature is constant and it also increases with temperature when the time is fixed. However, it shows an increasing trend of the conductivity for both CAME and CVE at a low temperature level (30°C) under microwave irradiation heating, but as temperature rises (especially at 50°C), there is a little change between the two heating methods (microwave irradiation heating and water bath heating) in terms of conductivity. Since conductivity is proportional to electrolyte content which determined by the content of the materials dissociated from non tannins, it is obvious that the temperature plays a decisive role on electrolyte content dissociated from non tannins, nevertheless, microwave can promote the increase of the electrolyte content at the low temperature level.

Table 1: The conductivities of tannin extract solutions under MIH and WBH

| Tannin extract | Temperature (°C) | Heating methods | Conductivities (μS/cm) | | | | |
|---|---|---|---|---|---|---|---|
| | | | 5min | 15min | 30min | 60min | 120min |
| CAME | 30 | MIH | 0.757 | 0.756 | 0.755 | 0.763 | 0.807 |
| | | WBH | 0.746 | 0.748 | 0.752 | 0.758 | 0.767 |
| | 40 | MIH | 0.867 | 0.877 | 0.894 | 0.931 | 1.010 |
| | | WBH | 0.868 | 0.875 | 0.876 | 0.892 | 0.914 |
| | 50 | MIH | 0.957 | 0.980 | 1.000 | 1.000 | 1.02 |
| | | WBH | 0.934 | 0.975 | 0.994 | 1.000 | 1.02 |
| CVE | 30 | MIH | 0.535 | 0.549 | 0.552 | 0.566 | 0.575 |
| | | WBH | 0.541 | 0.550 | 0.550 | 0.551 | 0.559 |
| | 40 | MIH | 0.616 | 0.621 | 0.639 | 0.655 | 0.686 |
| | | WBH | 0.615 | 0.618 | 0.632 | 0.635 | 0.642 |
| | 50 | MIH | 0.656 | 0.655 | 0.673 | 0.695 | 0.702 |
| | | WBH | 0.661 | 0.660 | 0.670 | 0.683 | 0.697 |

MIH: microwave irradiation heating; WBH: water bath heating

## CONCLUSIONS

In this work, the electrochemical behavior of vegetable tannin extract solution under microwave irradiation was investigated and characterized by the particle size, Zeta potential and conductivity. The results are showed as follows: (1) There is a different effect on hydrolysable tannin and condensed tannin under microwave irradiation, however, microwave induces a reduction of tannin extract particle size. Moreover, the effect is more significant with high irradiation temperature and long irradiation time. (2) The absolute value of Zeta potential of both CVE and CAME increases, indicating a more stable tannin extract solution under microwave irradiation. However, the microwave effect on hydrolysable tannin and condensed tannin is different, and it is better for CAME to maintain a high degree of stability. (3) Microwave irradiation can promote the increase of electrolyte content at a low temperature level. In conclusion, as a novel and efficient thermal method, microwave irradiation is likely to bring about reduction in the particle size, increase in conductivity and the absolute value of Zeta potential of tannin solutions. Therefore, microwave may contribute to the penetration of tannin extracts in the skin and the binding properties with collagen in vegetable tanning.

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# APPLICATION OF LAC DYE IN SHOE UPPER LEATHER DYEING

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**APPLICATION OF LAC DYE IN SHOE UPPER LEATHER DYEING**

ABSTRACT. Shoe upper leather samples were dyed with the natural lac dyes (byproduct of shellac and shellac products industry) extracted from washings of the stick lac by conventional methods. The aim of this research is to utilize this dye water and reveal the novel natural recipe for eco-friendly dyeing operation of shoe upper leather processing. The extraction of lac dye was carried out by using water at different temperatures. The lac dye was applied on the leather samples with and without using mordants; and three different mordants (CuSO4, FeSO4, [KAl(SO4)2]) were used following metamordanting method of dyeing. Absorbance and λmax of all dye liquors at different time intervals were determined by UV-visible spectrophotometer. The dyestuffs exhaustion and uptake were investigated and results showed that mordanted dyeing increased the dye uptake on leather than unmordanted dyeing. The FTIR analyses samples were carried out and it was found that lac dye could be mainly composed of -OH, -NH, >C=C<, >C=O, -COOH functional groups. The fastness properties such as fastness to washing, rubbing (dry and wet) and light of prepared leather samples were assessed. The results of color fastness of the mordanted and unmordanted leather samples showed excellent (5) and best (4-5) gray scale rating respectively.
KEY WORDS: Shoe upper leather; Natural dye; Lac dye; Stick lac; Eco-friendly; Mordant

**UTILIZAREA COLORANŢILOR PE BAZĂ DE RĂŞINĂ NATURALĂ LA VOPSIREA FEŢELOR DIN PIELE PENTRU ÎNCĂLŢĂMINTE**

REZUMAT. Eşantioanele de piele pentru încălţăminte au fost vopsite cu coloranţi pe bază de răşină naturală (produs secundar al industriei şelacului şi a produselor din şelac) extrasă din spălarea răşinii prelevate de pe scoarţa copacilor prin metode convenţionale. Scopul acestei cercetări este de a utiliza această soluţie de colorare şi de a propune o nouă reţetă naturală pentru vopsirea ecologică pielii pentru încălţăminte. Colorantul pe bază de răşină a fost extras prin utilizarea apei la temperaturi diferite. Colorantul pe bază de răşină a fost aplicat pe eşantioanele de piele cu şi fără utilizarea mordanţilor, utilizându-se trei mordanţi diferiţi (CuSO4, FeSO4, [KAl(SO4)2]) la vopsirea prin mordansare. S-au determinat absorbanţa şi λmax ale tuturor soluţiilor de colorare la intervale de timp diferite cu ajutorul spectrofotometriei în domeniul UV-vizibil. S-au investigat extracţia şi absorbţia coloranţilor şi rezultatele au arătat că vopsirea prin mordansare a crescut absorbţia colorantului pe piele comparativ cu vopsirea fără mordanţi. S-au examinat probele prin analiza FTIR şi s-a constatat că vopselele pe bază de răşină sunt în principal compuse din grupări funcţionale -OH, -NH, >C=C<, >C=O, -COOH. Au fost evaluate proprietăţile de rezistenţă cum ar fi rezistenţa la spălare, frecare (uscată şi umedă) şi rezistenţa la lumină a probelor de piele. Rezultatele testelor de rezistenţă a culorii a probelor de piele vopsite cu şi fără mordanţi au primit calificativele excelent (5), respectiv optim (4-5) pe scara de gri.
CUVINTE CHEIE: feţe de încălţăminte din piele; colorant natural; colorant pe bază de răşină naturală; răşină prelevată de pe scoarţa copacilor; ecologic; mordant

**L'APPLICATION DES COLORANTS À RESINE NATURELLE DANS LA TEINTURE DES TIGES EN CUIR POUR CHAUSSURES**

RÉSUMÉ. Les échantillons de cuir pour chaussures ont été colorés avec des colorants à base de laque (sous-produit de l'industrie des gommes-laques et des produits en gomme-laque), extraite des lavages de laque en bâton par des procédés classiques. Le but de cette recherche est d'utiliser cette eau de teinture et de proposer une nouvelle recette naturelle pour l'opération de teinture écologique du cuir pour chaussures. L'extraction du colorant à base de laque a été effectuée en utilisant de l'eau à différentes températures. Le colorant à base de laque a été appliqué sur les échantillons de cuir avec et sans l'utilisation de mordants. On a utilisé trois mordants différents (CuSO4, FeSO4, [KAl(SO4)2]) suivant la méthode de la teinture mordante. L'absorbance et λmax de toutes les liqueurs de colorants à différents intervalles de temps ont été déterminés à l'aide d'un spectrophotomètre UV-visible. L'épuisement et l'absorption des colorants ont été étudiés et les résultats ont montré que la teinture mordante a augmenté l'absorption de colorant sur le cuir par rapport à la teinture sans mordant. Les échantillons analysés par FTIR ont révélé que le colorant à base de laque sont composés principalement de groupes -OH, -NH, >C=C<, >C=O, -COOH. Les propriétés de résistance telles que la résistance au lavage, au frottement (sec et humide) et à la lumière des échantillons de cuir préparés ont été évalués. La résistance des couleurs des échantillons de cuir avec ou sans mordant a été évaluée comme excellente (5) et meilleure (4-5) en niveau de gris.
MOTS CLÉS : tiges cuir pour chaussures ; colorant naturel ; colorants à base de laque ; laque en bâton ; écologique ; mordant

## INTRODUCTION

Dye is a coloring agent that has an affinity to the substrate and imparts color to the material on which it is applied. Color is one of the most important parameters of leather as it is the first property of the leather to be assessed by consumers. Shoe upper leather is widely used (approximately 60-70%) for the construction of upper parts of the shoe and synthetic dyes are used abundantly in shoe upper leather dyeing. Natural dyes have been known for a long time and these dyes are derived from natural sources like plants, insects, animals and minerals. Natural dyes produce very uncommon, soothing, and soft shades as compared to synthetic dyes. On the other hand, synthetic dyes are widely available at an economical price and produce a wide variety of colors; these dyes however produce skin allergy, toxic wastes and other harmfulness to human body [1]. Therefore, natural dyes could be a potential substitute of synthetic dyes.

Lac is a momentous source of natural dye which is one of the most valuable gifts of nature to human. Brilliant red dye is produced from

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the resinous substance secreted by tiny insects on some selected both wild and cultivated host plants. Lac contains various percentages of physical components such as resin 68-90%, lac dye 2-10%, wax 4-6% and other materials 2-4% [2]. Lac is the parent of modern plastics and the importance of lac in the modern economy, particularly of India and Thailand, is quite considerable. The lac insect basically lives on native forest trees in South China, India, Myanmar, Vietnam, Thailand, Pakistan, Bangladesh and other countries of South-eastern Asia. Lac dye is a red colored natural dye, which is present in the body fluid of lac insect, known as *Laccifer lacca* [3]. This dye is a byproduct of lac industry which is generally lost during washing of sticklac in primary processing of lac.

A recent crucial issue of the leather industry is to reduce environmental pollution caused by leather processing. Different types of natural dyes have been used for leather dyeing from ancient times before the synthesis of the first chemical dye aniline by William Henry Perkin in 1856 [4]. Then synthetic dyes ruined the natural dyes industry. A number of synthetic dyes are used for leather dyeing purposes that are continuously released into the environment and caused great damage to biodiversity due to the release of large volumes of waste water containing high content of organic discharge and strong coloration. Many dyes used in leather treatment can biologically transform to toxic species and cause interference in natural photosynthesis process [5, 6]. The effluent problems of synthetic dyes occur not only during their application in the leather and textile industry, but also during their manufacture and possibly during the synthesis of their intermediates and other raw materials [7]. Recently, most of the commercial dyes, leather and textile export houses have started re-looking to maximum possibilities of using natural dyes for dyeing purposes [8]. The use of eco-friendly and non-toxic natural dyes has become a matter of significant importance due to the increased environmental awareness to avoid some risky synthetic dyes.

Mordant is a substance used to set dyes on fabrics or tissue section by forming a co-ordination complex with the dye which then attaches to the fabric or tissue [9]. Mordanting can be achieved by pre-mordanting, meta-mordanting and post-mordanting methods of dyeing. Different types and selective mordants or their combination can be applied on leather dyeing to obtain varying color or shades, to increase the dye uptake and improve the color fastness behavior of any natural dye [10]. The effect of different natural and chemical mordants like aluminum sulfate, tartaric acid and cetrimide on bleached jute fabric, as the mordant and dye concentration are increased, there is improvement in the light fastness by 1-2 grades [11]. The present study described the extraction and application of natural lac dye in shoe upper leather dying and investigated the fastness properties of dyed leather.

## EXPERIMENTAL

### Materials and Methods

#### *Materials*

The raw material for the extraction of lac dye was twigs lac or stick lac which was found to grow in Chapainawabganj under the division of Rajshahi, Bangladesh. It was plucked and collected from the branches of host tree of Chapainawabganj. A piece of wet blue cow hide was used for the application of extracted lac dye during dyeing operation of shoe upper leather processing.

#### *Chemicals and Instruments*

Potassium aluminum sulfate [$KAl(SO_4)_2$], copper sulfate ($CuSO_4$) and ferrous sulfate ($FeSO_4$) of analytical grade were purchased from Sigma-Aldrich Co., Germany and applied as mordanting agents. Standard soap with optical brightening agent (ISO 105:1989: Co1 to Co5), IR spectroscopy grade acetone (BDH Germany) and potassium bromide (Spain) pellets were used for FTIR spectral analysis. Distilled water was used for lac dye extraction. Launder-o-meter (wash fastness tester), rub fastness tester (model STM 461, SATRA, England), Gray scale for assessing staining (ISO 105-A03:1993; BSEN 20105-A03:1995; BS 1006-A03:1990; SDC standard methods, 5th Edition A03), microprocessor pH meter (pH 213, HANNA instruments), IR Spectrometer (Model IR Prestige 21, Shimadzu Corporation), UV-visible spectrophotometer (Model CPS-240A, Shimadzu Corporation) were used.

*Extraction Process*

Extraction of natural lac dye from stick lac was carried out by using distilled water. Four steps extraction were accomplished with water at different temperatures such as 25-27°C, 35-40°C, 50-55°C and 65-70°C, respectively. In the first step twigs and others extraneous matter were removed by hand picking, dusting and sieving. Further the stick lac was crushed into small pieces with the help of mortar and sieved to remove impurities. 100 g of crushed lac was measured and taken into 1000 mL beaker and then added 700 mL water at room temperature. It was stirred well for 2 to 3 hours then kept it for overnight. It was then filtered with filter paper. The dye containing lac was washed thoroughly until the water soluble dye was completely extracted. In the second step the extracted dark red dye solution was concentrated through evaporation in a water bath. The dried dye was kept in oven for 30 to 45 minutes at a temperature of 40°C to remove damp and moisture. The extraction of lac dye was also carried out at 35-40°C, 50-55°C and 65-70°C, respectively, maintaining the same procedures mentioned above.

*Leather Dyeing*

Dyeing is the process of adding color to leather fibers and other materials in such a way that the coloring materials become an integral part of materials rather than a surface coating. The leather samples were dyed in two ways such as dyeing with lac dye without using mordant and with using mordant (copper sulfate, ferrous sulfate, potassium aluminum sulfate).

Crushed and sieved lac has been mixed with water at the ratio of 1:7 at room temperature. The aqueous dye solution was sieved to remove solid particles. In the second phase a piece of wet-blue cow hide was taken and operations such as acid wash, re-chroming, neutralization, re-tanning were carried out to make the leather appropriate for dyeing. The dyeing operation was carried out by using 150% lac dye solution and 100% water at 45-50°C for 60-90 minutes. Then 1.5% formic acid was added and ran for 30 minutes to fix the dye molecules with leather fibers. The dyed leather sample was washed well with water and fat-liquoring was done. The mechanical operations were carried out according to conventional leather manufacture.

Mordant can be used in three different ways, such as pre-mordanting, when leather is treated with mordant before dying, meta-mordanting in which mordant is added during dyeing of leather and post-mordanting when leather is treated with mordant after dyeing. In this experiment meta-mordanting technique was followed by using three heavy metal mordants such as copper sulfate, ferrous sulfate and potassium aluminum sulfate. 1.5% of each mordant was used during the dyeing process. The similar dyeing procedures were maintained for the three different mordants used.

*Determination of Dyestuffs Exhaustion and Uptakes*

Spectroscopic measurements were carried out using UV-visible spectrophotometer (spectral region 200-800 nm) at Centre for Advanced Research in Sciences (CARS), University of Dhaka, Bangladesh. The dyestuff exhaustions of the dye bath were determined by collecting the dye liquor at different time intervals such as 0, 15, 30, 45, 60 and 75 minutes at dyeing operations of different leather samples. The measurements of used dye liquors were carried out at $\lambda_{max}$ 296 nm and the percentage of dyestuff exhaustions were calculated by the equation $\%E = A_o – A_t/A_o \times 100\%$, where $A_o$ is the initial absorbance (at $\lambda_{max}$) in the dye bath and $A_t$ is the residual dye in the dye bath within a fixed time, respectively [12, 13]. The uptake of dyestuffs by the leather samples was calculated by the equation, A = 100 - Exhaustion (%E).

*IR Spectral Analysis*

IR analyses of powder and liquid lac dye samples were performed at the region of the wavelengths range 400-4000 $cm^{-1}$. A number of peaks were found at different frequencies which helped to analyze functional groups of the dye molecule.

**Quality Assessment of Prepared Shoe Upper Leather**

*Color Fastness to Washing*

The dyed leather samples were cut into 4×10 $cm^2$ size pieces. Each piece of leather sample was covered with multi-fibers (white cotton cloth) by stitching. The standard soap solution was prepared by adding 5 g of soap per litre of water. Weight of stitched leather samples was measured and added to different steel containers then fixed in launder-o-meter having liquor ratio 50:1. Temperature and time were digitally controlled at 50°C and 45 minutes, which were indicated on a digital indicator. The container, in which the test samples and soap solution were, kept rotating about 40 rpm at horizontal axis with the help of electric motor. The color change of leather sample and staining of adjacent multi-fibers were assessed with help of gray scale.

*Color Fastness to Light*

The dyed leather samples were exposed to direct sunlight for 72 hours then with the help of gray scale the change of shade was assessed.

*Color Fastness to Dry and Wet Rubbing*

Wet and dry color rub fastness test was carried out according to the standard method SATRA-PM-08. The cotton felt was prepared by dipping into boiling water for 3 minutes for wet rubbing fastness, then fixed the cotton felt with holder and applied load 1780 g on the machine. The number of cycle was fixed 64, 128, 256, 512 and 1024 then the machine was started. The grain side of the leather samples was repeatedly rubbed by standard cotton felt. The one edge of grain side rubbed up to 512 cycles with standard cotton felt and other adjacent edge of grain side rubbed up to 1024 cycles by reversing the standard cotton felt. The color change was visually assessed by gray scale. The color fastness was evaluated by the numerical values of grey scale as excellent 5, best 4-5, good 4, average 3-4 and poor 3.

## RESULTS AND DISCUSSION

### Effect of Temperature on Dye Extraction

Effect of temperature on the extraction of lac dye was observed and found that the solid content of the lac dyestuffs reduced on increasing of temperatures. The effect of temperature on the extraction of lac dye is shown in Figure 1.

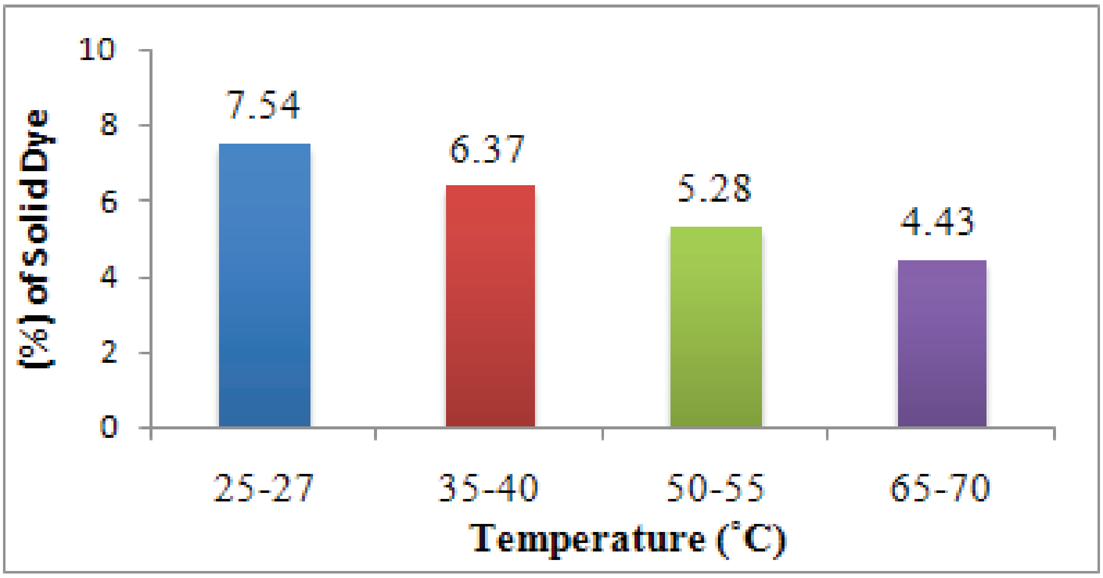


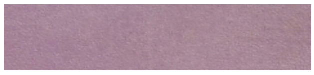
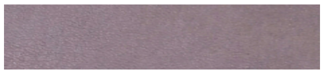

Figure 1. Effect of temperature on the extraction of lac dye

Figure 1 shows that the maximum extraction of lac dye was found at room temperature while at the minimum extraction occurred at the temperature range of 65-70°C. The extraction was also difficult at high temperature due to melting of major component of shellac (Aleuritic acid) present in lac dye. The solid content of extracted dye solution at room temperature was measured to be 7.54% while the solid content was reduced in case of rising temperatures gradually. The solid contents of other extracted dye solutions were 6.37% at 35-40°C, 5.23% at 50-55°C and 4.43% at 65-70°C.

## Effect of Mordants in Dyeing

Various colors were obtained depending on the mordants used which led to change in depth of the shade and produced variation in colors of the leather samples. The color of the lac dyed leather sample without mordant and leather samples dyed with copper sulfate, ferrous sulfate, and potassium aluminum sulfate mordants, respectively, are given in Table 1.

Table 1: Effect of mordants on leather samples

| SL. No. | Mordant used | Color | Dyed leather samples |
|---|---|---|---|
| Leather sample 1 | No mordant | Magenta |  |
| Leather sample 2 | Copper sulfate | Dark pink |  |
| Leather sample 3 | Ferrous sulfate | Light grey |  |
| Leather sample 4 | Potash alum | Purple red |  |

## Dyestuffs Exhaustion and Uptake

At the beginning of dyeing process, the initial dye concentration of dye liquor for all cases was measured to be 6.1 mg/mL and absorbance 1.25 (at $\lambda_{max}$ 296 nm). The results of dyestuffs exhaustion for leather dyeing with only natural lac dye and by using mordants such as potassium aluminum sulfate and ferrous sulfate at the end of 90 minutes of dyeing operation at 45-50°C are shown in Table 2.

Table 2: Dyestuff exhaustions of different dyed leather dye liquors

| SL. No. | Dyeing process | % of Exhaustion | pH |
|---|---|---|---|
| Leather sample 1 | No mordant | 86.42% | 5.7 |
| Leather sample 3 | Ferrous sulfate | 73.88% | 3.21 |
| Leather sample 4 | Potash alum | 77.80% | 3.76 |

The exhaustions of dyestuffs in the dye bath were 86.42% for leather dyed with natural lac dye, 77.80% for leather dyed with lac dye and potassium aluminum sulfate, and 73.88% for leather dyed with lac dye and ferrous sulfate. Comparing the dye liquors from the three different dyeing processes, it was found that the percentage of dyestuff exhaustion of dye liquor without mordanting was the highest whereas dye liquor with ferrous sulfate mordanting showed the lowest percentage of dye exhaustion. The dye liquor with potassium aluminum sulfate mordanting gave moderate dye exhaustion. The percentage of dye uptake of different dyed leather samples are depicted in the Figures 2 and 3.

From Figure 2, it can be observed that the absorbance of dye liquor in dye bath was gradually decreased towards the end of the dyeing operation. It was happened due to the fact that the dyestuffs was gradually taken up by the leather at different intervals of time such as 0, 15, 30, 45, 60 and 75 minutes. The absorbance values were found to be 1.252, 0.568, 0.424, 0.268, and 0.17 for the dye liquor of leather sample-1, 1.252, 0.48, 0.353, and 0.327 for the dye liquor of leather sample-3 and 1.252, 0.392, 0.319, 0.296, 0.278 for the dye liquor of leather sample-4 at the same period of time intervals, respectively. The percentage of dye uptake by the leather was increased with time while decreased the absorbance value in the dye bath liquors. From Figure 3, the reverse phenomenon was observed and it was found that with the increasing of time the dye uptake reached the equilibrium state between the dye concentrations on the leather fibers and in the dye bath. The dye uptakes were increased gradually but in case of leather sample 1 after 30 minutes of dyeing operation, it decreased slightly and then again reached equilibrium state. The dye uptake by the leather sample 4 was higher than that of leather sample 1 and leather sample 3.

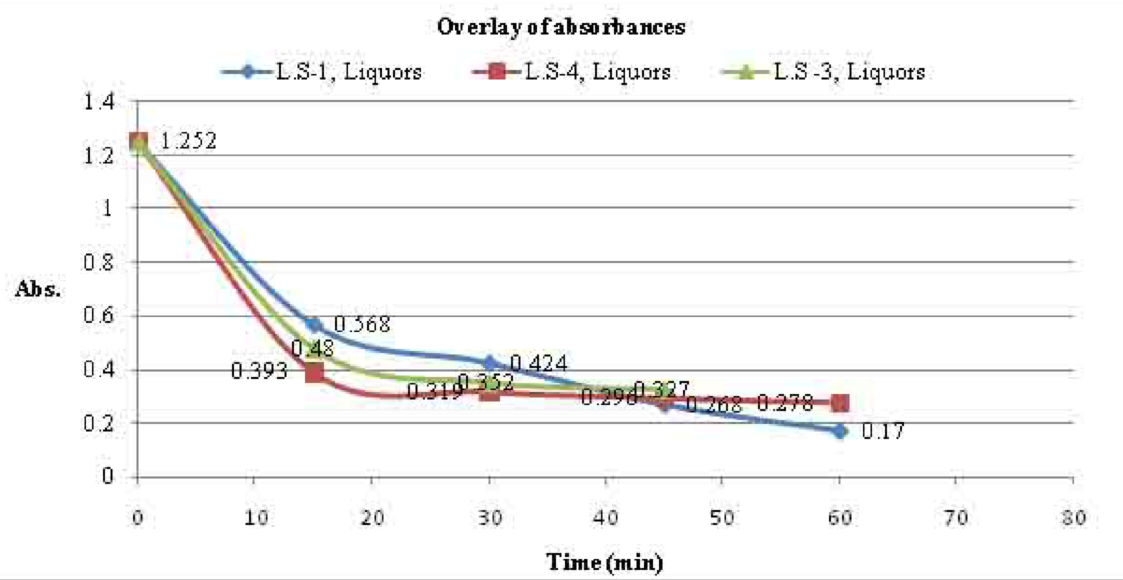



Figure 2. Absorbance peak of dye liquors overlay (L.S-1, L.S-3 and L.S-4)

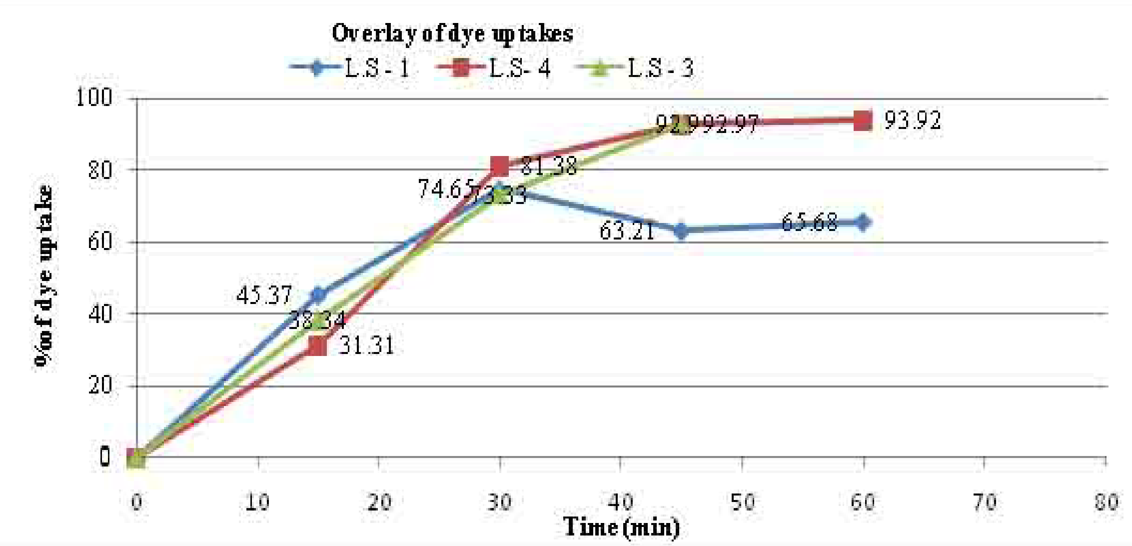



Figure 3. Percentage of dye uptake on dyed leathers overlay (L.S-1, L.S-3 and L.S-4)

## IR Spectral Analysis

Tentative assignments of some IR bands of the studied compounds were carried out on the basis of standard references and those of the molecules are found out. The FTIR spectra of lac dye samples are shown in Figure 4.

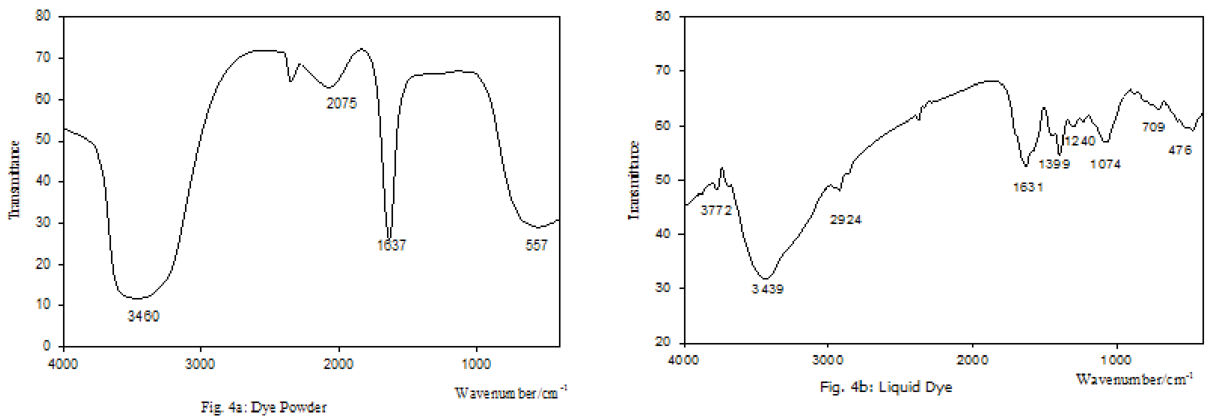



Figure 4. FTIR analysis of extracted lac dye

From the FTIR analysis, a broad peak observed between 3000 $cm^{-1}$ and 3400 $cm^{-1}$ could be assigned to the N-H stretching, phenolic O-H or O-H of the carboxylic acid. The absorption peak observed at 2924 $cm^{-1}$ was assigned to the C-H of aliphatic or aromatic groups. The peak at 1631 was referred to the >C=C aromatic group. The peaks between 1000 $cm^{-1}$ and 1320 $cm^{-1}$ were indicated to the >C-O stretching of primary alcoholic group (-CH2-OH) and COOH group, respectively [14, 15]. The aromatic C-H bending was observed between 675 $cm^{-1}$ and 1000 $cm^{-1}$ peak. The >C=O group appeared between 1630 $cm^{-1}$ to 1680 $cm^{-1}$. From the IR spectral analysis, it was clearly understood that the structure of prepared lac dye could be mainly composed of –OH, -NH-, >C=C<, >C=O, -COOH groups.

## Color Fastness to Washing and Light

The grey scale results of the color fastness to washing and light of leather dyed with lac dye and three different heavy mordants are given in Table 3.

Table 3: Color fastness to washing and light

| SL. No. | Mordant used | Grey scale rating for: Washing fastness – White cotton cloth | Washing fastness – Leather | Light fastness |
|---|---|---|---|---|
| Leather sample 1 | No mordant | 4 | 4-5 | 4-5 |
| Leather sample 2 | Copper sulfate | 5 | 5 | 5 |
| Leather sample 3 | Ferrous sulfate | 5 | 5 | 5 |
| Leather sample 4 | Potassium aluminum sulfate | 4-5 | 4-5 | 5 |

The color fastness to washing of different leather samples dyed with extracted lac dye and different mordants were observed for both leather specimen and white cotton cloth as well. The grey scale rating of leather sample 1 was 4-5 which assumed to be best and the corresponding white cotton cloth rating was 4, i.e. good. The leather samples 2 and 3 which were mordanted with copper sulfate and ferrous sulfate respectively, gave excellent grey scale rating (5) for both leather and cotton fabric while the leather sample 4 which was mordanted with potassium aluminum sulfate showed little lower rating than leather samples 2 and 3 and it was 4-5, indicating best result.

The grey scale rating of the color fastnesses to light of lac dyed leather sample with and without mordants were observed. The leather samples those were mordanted, gave excellent grey scale rating (5) while leather sample dyed only lac dye without using mordant showed best grey scale rating (4-5). Therefore, it can be said that the mordanting of lac dye increased the fastness properties of dyed leather.

**Color Fastness to Dry and Wet Rubbing**

The results of color fastness to dry and wet rubbing of different leather samples dyed with lac dye and with or without mordants are depicted in the Table 4.

Table 4: Color fastness to dry and wet rubbing

| SL. No. | No. of cycles | Grey scale rating for stain | | Grey scale rating for leather | |
|---|---|---|---|---|---|
| | | dry | wet | dry | wet |
| Leather sample 1 | 64 | 5 | 5 | 5 | 5 |
| | 124 | 5 | 5 | 5 | 5 |
| | 256 | 5 | 5 | 5 | 5 |
| | 512 | 5 | 5 | 5 | 5 |
| | 1024 | 4-5 | 4 | 4-5 | 4-5 |
| Leather sample 2 | 64 | 5 | 5 | 5 | 5 |
| | 124 | 5 | 5 | 5 | 5 |
| | 256 | 5 | 5 | 5 | 5 |
| | 512 | 4-5 | 4-5 | 5 | 5 |
| | 1024 | 4-5 | 4 | 5 | 4-5 |
| Leather sample 3 | 64 | 5 | 5 | 5 | 5 |
| | 124 | 5 | 5 | 5 | 5 |
| | 256 | 5 | 5 | 5 | 5 |
| | 512 | 5 | 4-5 | 5 | 5 |
| | 1024 | 4-5 | 4-5 | 5 | 5 |
| Leather sample 4 | 64 | 5 | 5 | 5 | 5 |
| | 124 | 5 | 5 | 5 | 5 |
| | 256 | 5 | 5 | 5 | 5 |
| | 512 | 5 | 5 | 5 | 5 |
| | 1024 | 4-5 | 4-5 | 5 | 5 |

The grey scale rating of lac dyed leather sample 1 as shown in the above table for both stain and leather were found excellent rating (5) up to 512 cycles. After 1024 cycles, the grey scale ratings of stain were found to be best (4-5) at dry rubbing and good (4) at wet rubbing where as best ratings were found for leather at both dry and wet rubbing. On the other hand, color fastnesses to dry and wet rubbing of leather sample 2 was found to be excellent (5) and stain best (4-5) up to 512 cycles. After 1024 cycle the grey scale rating of leather sample 2 was showed excellent (5) at dry condition and best (4-5) at wet condition while stain was found to be best (4-5) at dry rubbing and poor (4) at wet rubbing. It was also noticed that the leather samples 3 and 4 gave excellent (5) gray scale rating for color fastness to both dry and wet rubbing till the end of cycle. The grey scale ratings of dry and wet rubbing fastness for stain were found to be excellent (5) up to 512 cycles but in case of stain sample 3, rating was found to be best (4-5) at wet condition whereas after 1024 cycles, the grey scale rating for stain were showed best (4-5) at both dry and wet condition. All leather samples dyed with lac dye and mordant gave best color fastness to both dry and wet rubbing and samples 3 and 4 which were mordanted with ferrous sulfate and potash alum respectively showed excellent grey scale rating.

## CONCLUSION

The experimental results revealed that lac dyes can be effectively used as a potential natural source of dyes for dyeing of leather. It gave the opportunity to produce different colors on shoe upper leather from the single color extracted lac dye using various mordants. The wash fastness, dry and wet rub fastness and light fastness grades of extracted lac dyed leather with both mordanted and unmordanted were found to be best to excellent in the grey scale rating whereas ferrous sulfate and alum mordanted dyed leather showed excellent grey scale rating. Now fast moving synthetic dyes stand as a big question before natural dyes. But the worldwide concern over the use of eco-friendly and biodegradable materials, the use of lac dyes would make its own way to reach the hearts of health conscious consumers.

The results from this study will help to underpin the future development of leather sector with respect to clean technology and environmental remediation. This may be considered as a co-partner to implement in Bangladesh upcoming government project “Green Tannery”.

*Acknowledgement*

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# EXPERIMENTAL STUDY ON DIFFERENT CHARACTERISTICS OF PLANTAR PRESSURE DISTRIBUTION IN DIFFERENT SPORTS SHOES

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**EXPERIMENTAL STUDY ON DIFFERENT CHARACTERISTICS OF PLANTAR PRESSURE DISTRIBUTION IN DIFFERENT SPORTS SHOES**

ABSTRACT. This paper studies the effects of sports shoes in improving people's exercise capacity and preventing sports injuries, and by performing gait (0.8m/s), jogging (1.5m/s) and moderate-speed running (2.3m/s) tests on athletes, discusses the characteristics of plantar pressure distribution on bare foot or in different sports shoes. According to the research results, when athletes are bare foot and wearing sports shoes, the heel region bears the largest pressure in both cases. When bare foot, the plantar pressure on the first toe region is also large, but when in sports shoes, the plantar pressure in this region is significantly reduced. During bare foot gait, plantar pressure is relatively concentrated in toe, forefoot and heel regions; during gait in sports shoes, plantar pressure is evenly distributed. Shoes are designed to allow the arch region to also bear some pressure so that the whole plantar pressure tends to be even. During jogging and gait, the ground reaction forces given by NIKE sports shoes to the 4 plantar regions are small, indicating that NIKE shoes provide better cushioning effects compared with the other two sports shoe brands; ADIDAS shoes provides the poorest cushioning effects – the pressure is high and concentrated in forefoot, arch and heel regions, bringing more harm to the foot arch region. The pressure brought by these 3 brands of sports shoes does not vary much in the toe bone region, but significantly in the arch region.
KEY WORDS: plantar pressure, pressure distribution, sports shoes, pressure intensity, running

**STUDIU EXPERIMENTAL PRIVIND CARACTERISTICILE DISTRIBUŢIEI PRESIUNII PLANTARE LA PURTAREA DIFERITELOR TIPURI DE PANTOFI SPORT**

REZUMAT. Această lucrare studiază efectele încălţămintei sportive asupra îmbunătăţirii capacităţii persoanelor de a face sport şi asupra prevenirii leziunilor cauzate de sport. În urma efectuării unor teste de mers (0,8 m/s), jogging (1,5 m/s) şi alergare cu viteză moderată (2,3 m/s) se discută caracteristicile distribuţiei presiunii plantare în timpul exerciţiilor cu piciorul gol sau purtând diferite tipuri de pantofi sport. Conform rezultatelor cercetărilor, atât în cazul în care sportivii sunt desculţi, cât şi atunci când poartă pantofi sport, regiunea călcâiului suportă cea mai mare presiune. În cazul mersului desculţ, presiunea plantară în zona degetului mare este de asemenea mare, însă la purtarea pantofilor sport, presiunea plantară în această regiune este semnificativ redusă. În timpul mersului desculţ, presiunea plantară este relativ concentrată în regiunile degetelor, antepiciorului şi călcâiului; în timpul mersului cu pantofi sport, presiunea plantară este uniform distribuită. Pantofii sunt proiectaţi pentru a permite şi bolţii piciorului să suporte o anumită presiune, astfel încât întreaga presiune plantară să fie distribuită uniform. În timpul jogging-ului şi al mersului, forţele de reacţiune ale solului la purtarea pantofilor sport NIKE în cele 4 regiuni plantare sunt mici, ceea ce indică faptul că pantofii NIKE oferă amortizare mai bună comparativ cu celelalte două mărci de pantofi sport; pantofii ADIDAS oferă cea mai slabă amortizare - presiunea este ridicată şi concentrată în regiunile antepiciorului, bolţii şi călcâiului, dăunând mai mult regiunii bolţii piciorului. Presiunea la utilizarea celor 3 branduri de încălţăminte sport nu variază mult în regiunea osoasă a piciorului, însă este semnificativă în regiunea bolţii piciorului.
CUVINTE-CHEIE: presiune plantară, distribuţia presiunii, pantofi sport, intensitatea presiunii, alergare

**ETUDE EXPÉRIMENTALE SUR LES CARACTÉRISTIQUES DE RÉPARTITION DE LA PRESSION PLANTAIRE EN PORTANT DE DIFFÉRENTS TYPES DE CHAUSSURES DE SPORT**

RÉSUMÉ. Cet article étudie les effets des chaussures de sport sur le renforcement de la capacité des individus à faire du sport et la prévention des blessures sportives. A la suite des testes de marche (0,8 m/s), de jogging (1,5 m/s) et de course à une vitesse modérée (2,3 m/s) on a discuté les caractéristiques de répartition de la pression plantaire au cours de l'exercice avec les pieds nus ou avec de différents types de chaussures. Selon les résultats de la recherche, n'importe si les athlètes sont pieds nus ou portent des chaussures, la région du talon porte la plus grande pression. Dans le cas de la marche, la pression plantaire aux pieds nus dans la région du grand orteil est aussi grande, mais aux chaussures de sport, la pression plantaire dans cette région est considérablement réduite. Pendant la marche aux pieds nus la pression plantaire est relativement concentrée dans les régions des orteils, de l'avant-pied et du talon; pendant la marche en portant des chaussures de sport, la pression plantaire est uniformément répartie. Les chaussures sont conçues pour permettre à la voûte du pied de porter une certaine pression, de sorte que toute la pression plantaire peut être répartie uniformément. Pendant le jogging et la marche, les forces de réaction au sol en portant des chaussures de sport Nike dans les 4 régions plantaires sont baisses, ce qui indique que les chaussures NIKE offrent un mieux amortissement par rapport aux deux autres marques de chaussures; ADIDAS offre un amortissement plus faible - la pression est élevée et concentrée dans l'avant-pied, la voûte et le talon, endommageant de plus la région de la voûte plantaire. La pression en utilisant les 3 marques de chaussures de sport ne varie pas beaucoup dans la région de l'os du pied, mais elle est considérable dans la région de la voûte plantaire.
MOTS CLÉS: pression plantaire, répartition de la pression, chaussures de sport, intensité de la pression, course

## INTRODUCTION

Walking and running are the most common ways to travel in people's daily life. Whether during normal walking or vigorous exercise, human foot withstands great impacts. Long-time walking would bring great harm to the plantar arch. Suitable sports shoes can effectively reduce the impacts of exercise on human foot, but unsuitable ones would cause a series of diseases like plantar fasciitis, foot bone spur and foot injuries [1-2].

Plantar pressure is the pressure or pressure intensity that human foot withstands during all kinds of exercises. Plantar pressure can be classified into static and dynamic pressure. Plantar pressure tests include peak plantar pressure and pressure intensity, average pressure and pressure intensity, and foot touchdown speed and pressure change rates under different motions [3-4]. Different ages, sexes and exercise forms will affect plantar pressure distribution. So far, many scholars have studied how to design sports shoes to improve their cushioning and health care effects. Nawata *et al*. analyzed the plantar pressure of 70 students during exercise [5]; Sacco *et al*. analyzed the effects of different types of shoes on the leg muscles and plantar pressure [4]; Mika *et al*. studied the influence of high heels on the spines and plantar arch of women during gait [6]; Nagel and Van *et al*. studied how to modify the structure of shoes to reduce the pressure in forefoot [7-8]; De *et al*. studied the changes in plantar pressure during running on bare foot and in shoes [9]; Henning *et al*. studied the difference in plantar pressure in different kinds of sports shoes [10]. At the same time, some scholars also designed health-care shoes that could help people lose weight, correct posture, reduce injuries during gait and lower plantar loads [11-17].

This paper studies the effects of sports shoes in improving people's exercise capacity and preventing sports injuries, and by performing gait (0.8m/s), jogging (1.5m/s) and moderate-speed running (2.3m/s) tests on athletes, discusses the characteristics of plantar pressure distribution on bare foot or in different sports shoes. Research conclusions can serve as scientific reference for people during selection of sports shoes.

## RESEARCH SUBJECTS AND METHODS

### Research Subjects

The test subjects are 20 male athletes from an institute of physical education. All these test subjects are healthy and have suffered no structural damage in their lower limbs and feet in the recent year. The basic information on these test subjects are listed in Table 1.

Table 1: Basic information on research subjects

| Age/years | Height/cm | Body weight/kg | Foot length/cm | Foot breadth/cm | Foot arch height/cm |
|---|---|---|---|---|---|
| 20±1.95 | 180±4.82 | 76.28±5.39 | 25.79±0.77 | 10.11±0.32 | 5.01±0.85 |

### Test Contents

Test instruments: 2 plantar pressure test plates; 2 cameras; a set of synchronous lamps and synchronizing system; 2 pieces of processing equipment.

Test on the effects of shoes on plantar pressure: the 20 athletes were divided into 2 groups, with one group wearing sports shoes and the other bare foot when running. We collected the data about the characteristics of plantar pressure in these two groups.

Plantar pressure test in different sports shoes: basketball shoes of different brands but with the same sole thickness and all having cushioning effects should be selected. In this test, we selected Lining (LN), ADIDAS and NIKE basketball shoes. Persons to be tested were arranged to walk (0.8m/s), jog (1.5m/s) and run at a moderate speed (2.3m/s) wearing different brands of sports shoes.

Test indices mainly include the peak pressure, plantar contact area and plantar pressure distribution in different parts of the plantar arch. By using the pressure test and analysis software, we exported the data of the different tests mentioned above and used the SPSS software to do statistics.

## TEST RESULTS AND ANALYSIS

### Plantar Pressure Distributions on Bare Foot and in Sports Shoes

Figures 1 and 2 show the pressure distribution in different regions of the plantar arch when athletes are walking on bare foot and wearing sports shoes. From the figures, it can be seen that whether athletes wear shoes or not, the pressure on the heel is the greatest. During gait on bare foot, the maximum pressure in the heel region is up to 622N, and during gait in sports shoes, the maximum plantar pressure is 501N, which also appears in the heel region. In the bare foot case, the plantar pressure in the first toe region is also great, the maximum value of which can be up to 537N. In the sport shoes case, the plantar pressure in this region is significantly reduced, of which the maximum value is only 313N. This indicates that sports shoes can well protect and cushion the plantar arch. It can also be seen from the figure that, in the bare foot case, plantar pressure is relatively concentrated in toe, forefoot and heel regions; in the sports shoes case, plantar pressure is evenly distributed. Shoes are designed to allow the arch region to also bear some pressure so that the whole plantar pressure tends to be even. Therefore, wearing sports shoes while doing exercise can effectively protect the plantar arch.

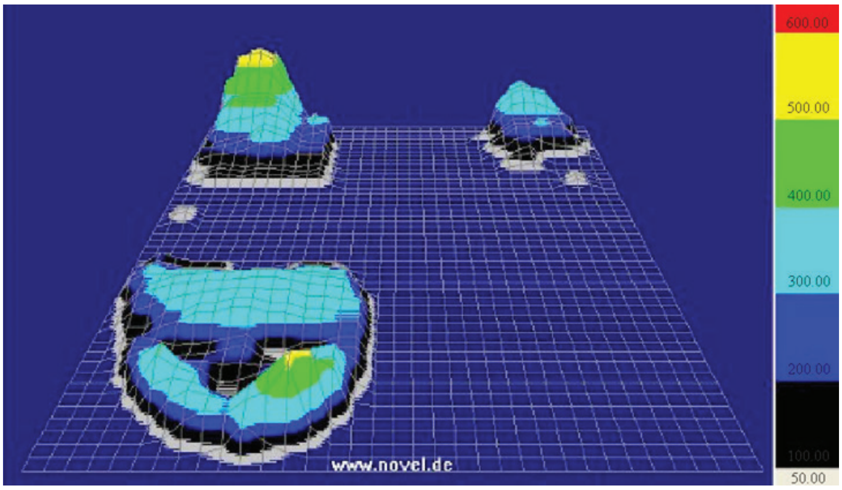


Figure 1. Peak plantar pressure characteristics of bare foot gait

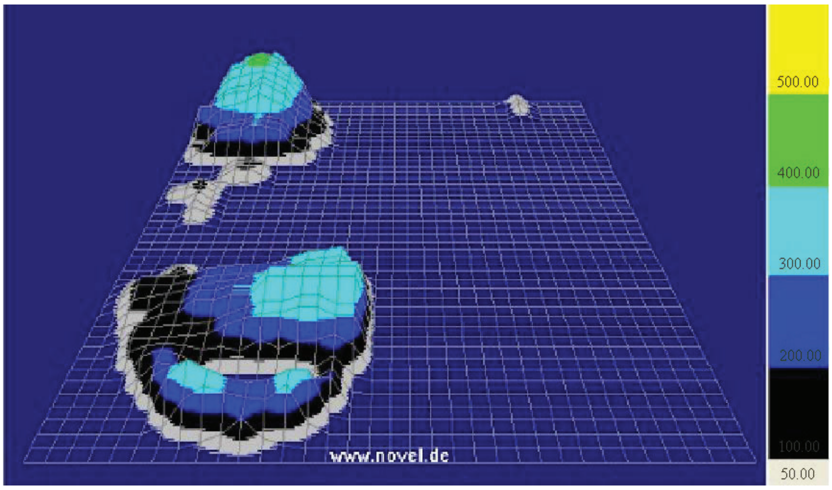


Figure 2. Peak plantar pressure characteristics of wearing sports shoes

## Characteristics of Plantar Pressure Distribution in Different Sports Shoes

Based on the above analysis, we can see that exercising bare foot will cause great load onto the feet, which is not healthy to the human body, while wearing suitable sports shoes in our daily life can effectively mitigate soft tissue injuries in human foot. Therefore, this section studies the characteristics of plantar pressure distribution when athletes are wearing different kinds of sports shoes and analyzes which sport shoes provide better protection for athletes' feet.

In this paper, we divide the plantar arch into 4 regions – toe bone, forefoot, arch and heel, and number them as 1-4 respectively, as shown in Figure 3.

In this test, we used ADIDAS, LN and NIKE sports shoes. We divide 20 persons into 3 groups, with 7 in Group 1, wearing ADIDAS shoes; 7 in Group 2, wearing LN; and 6 in Group 3, wearing NIKE. According to the test results of athletes running at different speeds, we obtain the mechanical parameters of different sports shoes, as shown in Table 2, where force MPP represents the maximum reaction force from the ground; peak pressure MPP stands for the peak plantar pressure; mean pressure MVP stands for the mean plantar pressure; and force-time integral means the force-time integral value.

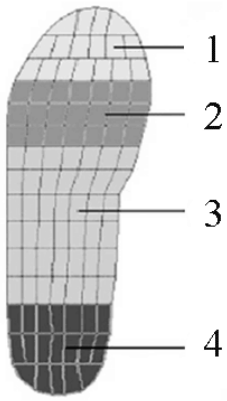

Figure 3. Regional Division of plantar pressure

Table 2: Plantar pressure mechanical parameters of different sports shoes

| Velocity (m/s) | Shoe types | Force MPP/N | Peak pressure MPP/kPa | Mean pressure MVP/KPa | Force time integral/ N-S |
|---|---|---|---|---|---|
| | LN | 760.9±60.3 | 239.1±60.4 | 33.48±2.79 | 421.8±40.7 |
| 0.8 | ADIDAS | 850.7±40.6 | 260.3±55.7 | 37.91±2.36 | 461.3±49.22 |
| | NIKE | 749.0±47.7 | 182.3±20.8 | 31.98±2.47 | 369.1±35.8 |
| | LN | 1302.1±119.6 | 253.8±58.2 | 38.17±2.46 | 324.8±20.4 |
| 1.5 | ADIDAS | 1330.2±90.3 | 279.4±59.9 | 40.11±2.52 | 361.9±24.6 |
| | NIKE | 1189.4±138.6 | 249.1±70.0 | 34.78±3.15 | 299.9±21.3 |
| | LN | 1388.4±200.7 | 287.3±38.5 | 40.27±3.45 | 283.5±14.9 |
| 2.3 | ADIDAS | 1539.6±90.2 | 310.7±38.6 | 45.01±3.68 | 321.7±15.3 |
| | NIKE | 1422.8±108.8 | 273.9±60.1 | 42.16±2.36 | 271.4±11.5 |

From the table we can see that regarding the maximum reaction force from the ground, in the cases where athletes walk (0.8m/s) and jog (1.5m/s), NIKE<LN<ADIDAS; in the case where athletes run at a moderate speed (2.3m/s), LN<NIKE<ADIDAS. Therefore, during jogging and gait, NIKE sports shoes have the best cushioning effects, followed by LN, and ADIDAS shoes provide the poorest cushioning. During running at a moderate speed, LN shoes are the best. When the running speed is gradually increased, the plantar pressure and plantar contact area are both increased, and the ground reaction force is also gradually increased.

Figure 4 shows the changes in the peak pressure in different plantar regions when athletes are walking in these three different sports shoes. The horizontal coordinates 1-4 represent the toe bone, forefoot, arch and heel regions. From the figure, it can be seen that for athletes wearing ADIDAS shoes, the pressure is high and concentrated in forefoot, arch and heel regions, which brings great harm to the foot arch region and can easily cause plantar fasciitis. LN sports shoes give less pressure to the toe bone and arch regions than ADIDAS, indicating that LN shoes protect the arch region better, but as this type of LN shoes are not equipped with separate cushioning materials in the forefoot region, the ground reaction force to the forefoot region is the greatest. The ground reaction forces given by NIKE sports shoes to the 4 plantar regions are small, indicating that NIKE shoes provide the best protection for plantar arch during gait.

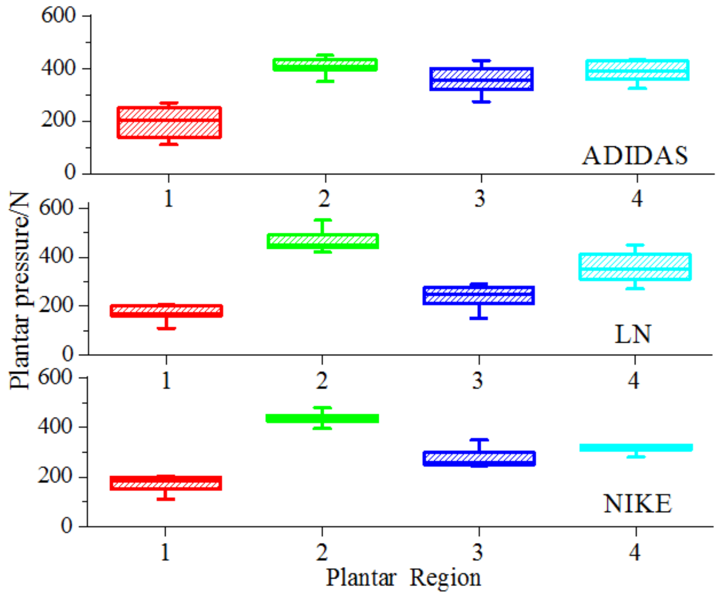


Figure 4. Plantar pressure of different region in different sports shoes

At the same moving speed, the foot withstands the same ground reaction force, but as the shoes are different, different elastic effects will occur when the foot acts on the sole. From the peak plantar pressure listed in Table 2, it can be seen that regarding the peak plantar pressure given by the three kinds of sports shoes in the three exercises is NIKE<LN<ADIDAS; in other words, NIKE sports shoes give the lowest peak plantar pressure, indicating that they provide good cushioning and protection for feet. Figure 5 shows the peak pressure in the 4 plantar regions when athletes are walking in three different kinds of sports shoes. Based on Table 2 and Figure 5, it can be concluded that the pressure in the forefoot given by the three kinds of shoes is: NIKE<ADIDAS<LN; and that the pressure in the heel region is: NIKE<LN<ADIDAS. From the analysis in the previous section, we can see that the forefoot and the heel are the two regions bearing the largest pressure. Compared with NIKE sports shoes, LN and ADIDAS sports shoes do not provide very stable foot protection and can easily cause sport injuries.

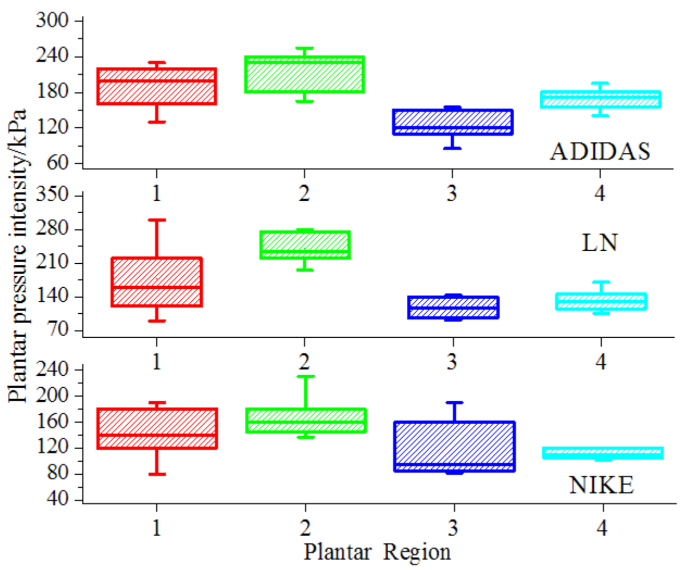


Figure 5. Plantar pressure intensities of different regions in different sports shoes

The mean plantar pressure intensity reflects the average value of the plantar pressure intensity during a certain period. The greater the mean plantar pressure intensity is, the more unsuitable the sports shoes will be in long-time running. From the statistics given in Table 2, it can be seen that during gait and jogging, the mean plantar pressure intensity of sports shoes is NIKE<LN< ADIDAS; and that the mean pressure intensity during the moderate-speed running is LN<NIKE<ADIDAS. From Figure 6, for ADIDAS sports shoes, the toe bone, arch and heel regions bear the largest mean pressure intensity, while for LN sports shoes, the forefoot region bears the greatest mean pressure intensity. Variance analysis results show that there are significant differences between ADIDAS and NIKE. Therefore, during the three exercises, ADIDAS sports shoes are the least comfortable and NIKE ones are the best.

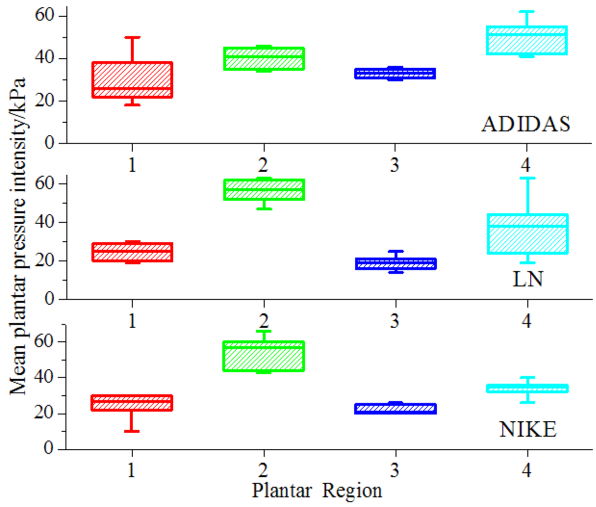


Figure 6. Mean plantar pressure intensities of different regions in different sports shoes

The force-time integral stands for the accumulated effects of pressure in each plantar region after athletes exercise for a certain period. When the speed increases, the average gait cycle is reduced. The plantar pressure is inversely proportional to the force-time integral. From Table 2, it can be seen that the force-time integrals for the three sports shoes are NIKE<LN< ADIDAS. Figures 7 and 8 show the force-time curves of athletes walking and jogging in three different sports shoes. According to these figures, the overall integral performance of ADIDAS is the worst, that of LN is medium and that of NIKE is the best. As the NIKE sports shoes selected in the test are equipped with full-length air cushions, they are the best in terms of comfortableness.

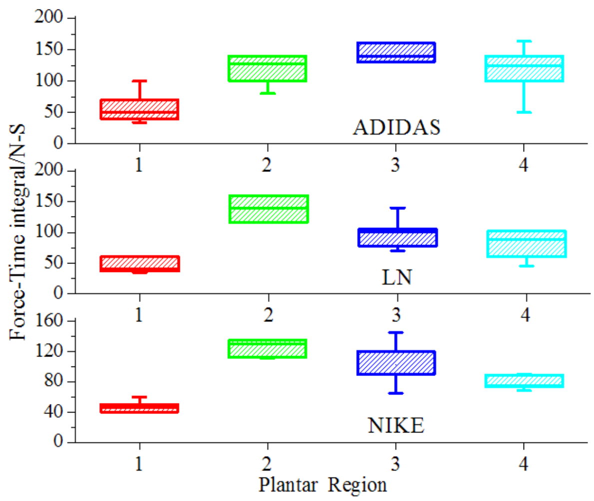


Figure 7. Force-time integrals for different sports shoes during gait at a velocity of 0.8m/s

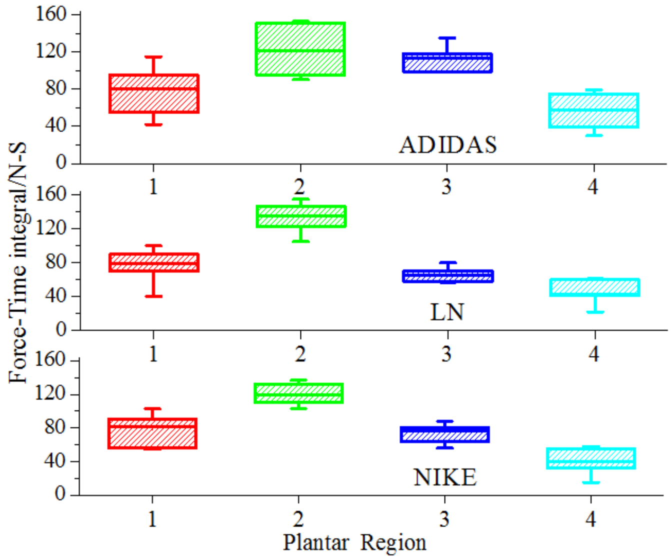


Figure 8. Force-time integrals for different sports shoes during running at a velocity of 1.5m/s

We select one athlete and let him jog at a speed of 1.5m/s wearing NIKE shoes and ADIDAS shoes, respectively. The ratios between the peak pressure of different plantar regions and the weight of the athlete are shown in Table 3. From the table we can see that, when the athlete is wearing the NIKE shoes, the ratios between the peak pressure in the toe tone region and the arch region and the weight of the athlete are higher than those in the ADIDAS case by 12.95% and 7.35% respectively; the ratios between the peak pressure in the forefoot region and the heel region and the weight of the athlete are lower than those in the ADIDAS case by 14.62 and 26.22%.

Table 3: Ratio between plantar pressure and body weight

| Plantar region | ADIDAS | NIKE | Difference | Change percentage / % |
|---|---|---|---|---|
| 1 | 0.121 | 0.139 | 0.018 | 12.95 |
| 2 | 0.345 | 0.301 | -0.044 | -14.62 |
| 3 | 0.416 | 0.449 | 0.033 | 7.35 |
| 4 | 0.621 | 0.492 | -0.129 | -26.22 |

Similarly, the statistics of plantar pressure-time integral when the athlete wears NIKE and ADIDAS shoes are shown in Table 4. From the table we can see that, when the athlete is wearing the NIKE shoes, the ratios between the peak pressure in the toe tone region and the arch region and the weight of the athlete are higher than those in the ADIDAS case by 17.61% and 18.27% respectively; the ratios between the peak pressure in the forefoot region and the heel region and the weight of the athlete are lower than those in the ADIDAS case by 9.42% and 20.62%.

Table 4: Pressure-Time integral for different sports shoes during running at a velocity of 1.5m/s

| Plantar region | ADIDAS | NIKE | Difference | Change percentage/% |
|---|---|---|---|---|
| 1 | 50.48 | 61.27 | 10.79 | 17.61 |
| 2 | 45.29 | 41.39 | -3.9 | -9.42 |
| 3 | 40.98 | 50.14 | 9.16 | 18.27 |
| 4 | 38.79 | 32.16 | -6.63 | -20.62 |

Therefore, from Tables 3 and 4, we can see that compared with ADIDAS, when the athlete wears NIKE shoes, the plantar pressure shifts obviously – the peak pressure in the forefoot and heel regions is allocated to the toe bone and arch regions so that the plantar pressure is more evenly distributed and the foot can be better protected.

## CONCLUSIONS

This paper studies the effects of sports shoes in improving people's exercise capacity and preventing sports injuries, and by performing gait (0.8m/s), jogging (1.5m/s) and moderate-speed running (2.3m/s) tests on athletes, discusses the characteristics of plantar pressure distribution on bare foot or in different sports shoes. The research conclusions are as follows:

(1) When athletes are bare foot and wearing sports shoes, the heel region bears the largest pressure in both cases. When bare foot, the plantar pressure on the first toe region is also large, but when in sports shoes, the plantar pressure in this region is significantly reduced, indicating that sports shoes can protect and cushion the heel well. During bare foot gait, plantar pressure is relatively concentrated in toe, forefoot and heel regions; during gait in sports shoes, plantar pressure is evenly distributed. Shoes are designed to allow the arch region to also bear some pressure so that the whole plantar pressure tends to be even.

(2) Forefoot and heel are the two regions bearing the greatest pressure in the plantar arch. During jogging and gait, the ground reaction forces given by NIKE sports shoes to the 4 plantar regions are small, indicating that NIKE shoes provide better cushioning effects compared with the other two sports shoe brands; ADIDAS shoes provides the poorest cushioning effects – the pressure is high and concentrated in forefoot, arch and heel regions, bringing more harm to the foot arch region.

(3) The pressure brought by these 3 brands of sports shoes does not vary much in the toe bone region, but significantly in the arch region. Compared with NIKE sports shoes, LN and ADIDAS sports shoes do not provide very stable foot protection and can easily cause sport injuries. NIKE sports shoes provide the best protection for plantar arch during gait.

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