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Valorization of sustainable vegetable oil deodorizer distillate as a novel fatliquor

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Abstract

The deodorizer distillate (DD) is a byproduct of vegetable oil processing industry and is rich in functional bioactive components. This study aimed to employ phosphorylation modification for DD to produce a new sustainable fatliquor. The bioactive ingredients in DD, namely fatty acids, sterols, and tocopherols, were determined by using HPLC and GLC. The results revealed that the DD sample contained a high percentage of unsaturated fatty acids (72.3%) and high levels of γ and δ-tocopherols (54.8% and 31.60%, respectively). Mechanical parameters (tensile strength, elongation at break, and tear strength) of leather were improved after being treated with the prepared fatliquor emulsion. Eventually, SEM showed that the texture of the fatliquored leather had been remarkably enhanced. Moreover, the fatliquored leather possessed effective antibacterial effect against the specified +ve, −ve bacteria, and Candida albicans microorganisms. The strength, fullness, soft handle, and elasticity of leather were all improved, and the grain of leather was protected from becoming loose after drying.

Keywords Vegetable oil, Deodorizer distillate, Bioactive components, Fatliquor, Phosphorylation, Chrome tanned leather
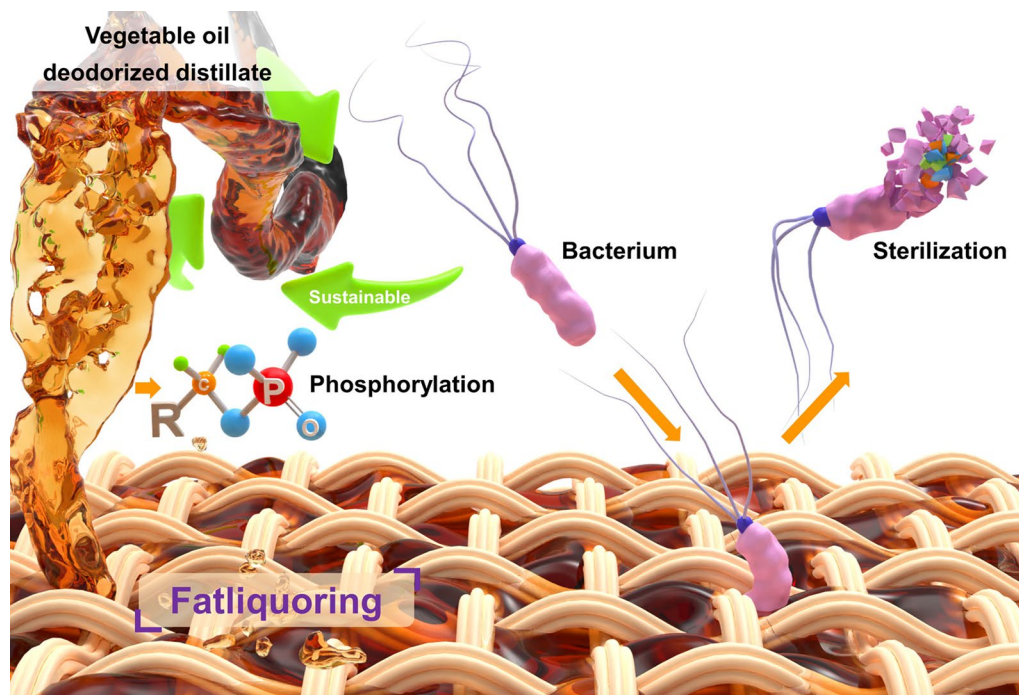
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Graphical Abstract

1 Introduction

Hides and skins undergo a series of chemical and mechanical processes throughout leather production, including soaking, unhairing/liming, deliming/bating, pickling, tanning, neutralization/dyeing, fatliquoring, drying, and finishing. The natural oil that gives animal skins/hides strength, flexibility, and softness is typically removed during the beamhouse process. This is important because it facilitates the penetration of water-soluble tanning chemicals into the hide. Chrome tanning agents, vegetable tannins, or syntans transform the cleaned matrix into a long-lasting, non-rotting substrate throughout the tanning process [1–3]. When leather is processed without adding additional oil after tanning, the finished product will be too stiff to produce leather goods. The cohesion of the fibers without fatliquors occurs during the drying process, making the leather harsh, inflexible, and difficult to rehydrate [4–7] and giving the leather a dark color. As chrome leather lacks the inter-fibrillary "fillers" like vegetable-tanned leather, this tendency is more pronounced. Fatliquoring is to incorporate an oil component into the leather, and thus to obtain a lubricated leather with full, soft handle, flexibility, and suppleness, and simultaneously increase its mechanical properties [8]. For this reason, fatliquoring is an essential

part of leather processing. It aids in achieving not just the features (such as softness, waterproofness, or attractiveness) but also the desired qualities (such as suppleness and aesthetic appeal). The commonly used fatliquors include modified vegetable oils [9, 10], modified animal oils [11, 12], synthetic oils, and oils combined with emulsifiers [13, 14].

Edible oil refineries produce deodorizer distillate (DD) as a byproduct of the deodorization of vegetable oils, which has potential to be developed to be a fatliquor. DD is a low-cost source containing many valuable compounds including tocopherols, sterols, squalene, and free fatty acids (FFA) for medical and commercial applications [15–19], may give leather a higher performance than a common fatliquor. Several byproducts, including soap stocks, deodorizer fatty acid distillates, and acid oil, are produced during the refining process. If these waste products are not used for something productive, they will harm the environment to some extent [20]. Therefore, it is crucial to find suitable approaches to utilize this cheap by-product.

Phosphorylation is one of the most common methods used to modify oils and/or fats by converting them into ester phosphate compounds. Phosphate ester is widely used as a surfactant in various fields, including

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chemical fiber, weaving, spinning, papermaking, plastics, and common chemical goods [21–26]. The phosphorylation mechanism is the esterification reaction between hydroxyl groups and phosphorylated reagents. Phosphorus oxychloride ($POCl_3$), phosphorus pentoxide (P_2O_5), polyphosphoric acid, phosphorus trichloride (PCl_3) are the most commonly used phosphorylation reagents nowadays [27]. Due to the presence of phosphate group that can coordinate with Cr(III) in chrome tanned leather, phosphated fatliquor succeeds as a reactive material suitable for treating leather fibers, and is widely used in leather industry. This implies that phosphorylation modification may be an effective way for DD to be processed as a fatliquor.

Consequently, this work aimed to use phosphorylation to modify and valorize DD to produce phosphorylated DD (PDD) as a leather fatliquor. The bioactive components, structural feature, zeta potential, and particle size of PDD were determined. The stability of PDD towards acids and salts were evaluated. Then, the PDD was used for leather fatliquoring, and the physical properties and antibacterial effect of the fatliquored leathers were investigated.

2 Materials and methods

2.1 Materials
Refineries owned by the Cairo Oil Company in Cairo, Egypt, generously provided a sample of DD. DD was not a single oil, but instead were composites of at least two different oils (soybean and sunflower). Sigma Chemical Company provided a genuine collection of sterols, standard tocopherols, and methyl esters of saturated and unsaturated fatty acids (C_{14}–C_{24}).

2.2 Preparation of DD for chromatographic analysis
DD was first dehydrated by using anhydrous sodium sulphate. Then, the dehydrated DD was dissolved in hexane and titrated to neutral with diluted alcoholic KOH (0.25 mol/L). After distilling the solvent, the organic phase was centrifuged and dried over anhydrous sodium sulphate for further analysis.

2.3 Determination of bioactive components
2.3.1 Fatty acids composition
Transesterification with 5% methanolic hydrogen chloride was used to convert the sample isolated from the residue using preparative thin layer chromatography (TLC) to methyl esters. TLC was used to monitor the transesterification process; silica gel G plates and a developing solvent of n-hexane/diethyl ether/acetic acid (80/20/1, *v/v*) were used. Our previous works discussed the procedure in great detail [28]. The triacylglycerol (TAG) profile (after being isolated from the residue by preparative

TLC) was also measured by HPLC instrument (a Toyo-Soda-CCPM) [28, 29], where 10 μL of the separated TAG solution in chloroform (300 mg/mL) was injected into an ODS Capsel Pak, C_{18}-1 (4.4 mm×10 cm) column. A gradient elution with acetonitrile: dichloromethane from 90:10 to 35:65 (*v/v*) in 150 min was conducted. An FID detector (with a moving band, Tracor 945) was attached to the instrument. The carbon number assignment for the separated peaks was determined using the HPLC chromatogram of soybean oil (SBO) taken as reference, which contained 29 TAG starting with trilinolenin (LnLnLn) and terminating with tristearin (SSS). The eluted TAGs were separated according to their equivalent carbon number (ECN) or critical pairs. The elution sequence was the same as what Hamdy and Perkins [30] reported.

2.3.2 Tocopherols pattern
The tocopherols (T) in the residue (after removal of free acidity from the distillate) were determined according to El-Shami et. al. [29]. HPLC analysis of tocopherols in DD and the standard mixture, was carried out using a Toyo-Soda-CCPM HPLC instrument. A DD sample (10 g) was dissolved in n-hexane to make a 10% solution, and 10 μL of this solution was injected into a silica column (YMC-A-012, silica 6.0×150 mm). Isocratic elution was conducted using n-hexane: isopropyl alcohol (100:0.5, by volume) as a mobile phase at a flow rate of 1–2 mL/min. A Hitachi-650-10S fluorescence detector was used. The spectral absorption was set at excitation and emission wavelengths of 295 nm and 325 nm, respectively. The conditions were optimized to elute delta-T after 10 min; the results were automatically recorded as peak area percentages by the electronic integrator. The total tocopherol content and the percentage compositions were calculated from the peak area and the corresponding weight of each individual tocopherol in the standard and the sample.

2.3.3 Whole sterols
The unsaponifiable fraction was separated from the rest of the mixture using preparative TLC on silica gel G plates with a thickness of 0.5 mm and a developing solvent of chloroform, diethyl ether, and acetic acid in the proportion of 95/4/1 by volume. The sterol zone was located with the help of standard β-sitosterol (R_f=0.16) applied alongside the sample prior to development. The sterol zone was scraped off the plate and thoroughly extracted with moistened diethyl ether, and the solvent was distilled. The sterol mixtures of the sample and the reference were separately converted into trimethylsilyl derivatives (TMS). Hewlett-Packard (HP 5890-A) gas chromatograph was employed for the analysis using the following operating conditions: column, DB-17

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(0.32 mm×15 m, 0.25 μm coating) at 250 °C; detector, FID at 260 °C; carrier gas, helium (8.6 mL/min; and split ratio, 35:1). An automatic integrator was coupled directly to the detector. TMS of the reference sterol mixture (containing known percentages of sterols) were used for identification and quantification of the sterols in DD sample. The automatic integrator measured the area of each peak [28].

2.3.4 Free and acylated sterols (FS and AS), as well as free and acylated sterylglycosides (FSG and ASG)

The isolation of FS and AS as 9-anthroylnitrile (9-AN) derivatives and the procedure of separation of FSG and ASG as 1-anthroylnitrile (1-AN) derivatives from the DD were carried out using HPLC, according to Hassanein et al. [28]. Separation of 9-AN FS and AS derivatives was conducted under the following conditions: reversed-phase column, ODS-1250Y, Senshu Pack (4.6 mm×250 mm); detector, fluorescence; excitation and emission wavelengths set at 360 nm and 460 nm; isocratic elution using acetonitrile/dichloromethane (75/25, v/v) at a flow rate of 1 mL/min. While 1-AN FSG and ASG derivatives were analyzed using an HPLC instrument equipped with UV detectors (Toso, UV 8000), and ODS Wakosil-5, C_{18} (6.4 mm×250 mm) was used for SG-1-AN analysis. Gradient elution with acetonitrile/dichloromethane from 50/50 to 68/32 (v/v) was used, and the absorption was measured at 254 nm. It is noteworthy that this method is sensitive to 0.5 nanograms of SG.

All measurements of the bioactive components were done in three replicates, and the data obtained in the tables were presented as the mean±standard deviation of the three replicates.

2.4 Phosphorylation processes

100 g of DD was phosphorylated in a three-necked flask outfitted with a stirrer, a thermometer, and an inlet to add the chemicals. Orthophosphoric acid (30% of the DD weight) was added dropwise at intervals with slowly stirring and reaction temperature below 30 °C. The reaction took 3 h once the temperature reached 45 °C. Ten percent of sodium chloride was used to wash the PDD at room temperature, and thirty percent of sodium hydroxide was used to neutralize the products. Official procedures were applied to analyse the PDD [31]. The product was prepared at a concentration of about 60–70% prior (pH 7.5–8.0) to its use as a fatliquor.

2.5 Characterization of the PDD sample
2.5.1 FTIR analysis

PDD was washed in a saturated salt solution and chloroform and dried in an oven at 105 °C for 4 h before being examined using IR equipment. Fourier transform infrared (FTIR) spectra was taken with a Nexus 670 spectroscopy (Nicolet, United States) over the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}; the KBr disk technique was applied.

2.5.2 Zeta potential and particle size

The particle size and zeta potential, as two predominant parameters, have been analyzed using a Malvern instrument (model: Zetasizer 3000 HSA). Reference fatliquors (1% solution) were diluted with deionized water to determine how their particle size correlated with emulsion qualities.

2.5.3 Stability of fatliquor towards acids and salts

Sulphuric acid solution (1 mL, 10%) was added to the fatliquor emulsion and boiled for 15 min. The appearance of the emulsion was recorded. The process was repeated with 1, 3, 5, 7, and 10% acidity, and the stability was recorded. The solution of metallic salts (1%) was added dropwise from the Mohr measuring pipette to the fatliquor emulsion until the emulsion became turbid or precipitation occurred. The volume of metallic salt solution was recorded.

2.6 Fatliquoring process

Chrome-tanned cattle leather underwent a 15-min neutralization treatment with 1% sodium formate. After that, 0.5% sodium bicarbonate was added, and the drum ran for another 10 min. Then, the leather was retanned with 4% chrome tanning agent and 4% vegetable tanning agent and colored with 5% acid dye for 30 min. A different percent of fat emulsion (2%-8%) was then added to dye bath at room temperature, and the drum ran for an additional 40 min. The fatliquored leather was rinsed, sammed, and hung to dry at room temperature.

2.7 Characterization of the fatliquored leather
2.7.1 Mechanical and hardness measurements

Dumbbell-shaped leather specimens were used to measure tensile strength and elongation at break (%) according to ASTM D412c [32, 33]. These tests were carried out using Zwick/Roell (Z010) and a 50 mm/min cross-head speed at room temperature. Tear strength was measured according to ASTM D624. The average value for each test was taken for three samples to confirm the results (mean±SD, $n=3$).

Leather samples were sliced with press knives made of special steel at a position perpendicular to the spine. We followed the instructions in the literature and made specimens that were 50 mm in length and 4 mm in neck width. The experiments were conducted at a regulated room temperature (25 °C) with the cross-head speed set at 50 mm/min.

The hardness was measured by a Shore Durometer Rubber Portable Handheld Shore A, Digital Shore Durometer A type LCD Display Hardness Meter Tester, range 0–100 HA, resolution 0.5 HA, (TA 300A), China (Zhejiang).

2.7.2 Scanning electron microscopy (SEM)
The experimental and control specimens received sputter coatings with gold ions to create a conducting medium, and the resulting samples were round and 10 mm in diameter (sputter coater-Edwards-Model S-150 A, Eng.). The microscopic analysis was performed using a Jeol scanning microscope (Japan) [34, 35].

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used for elemental analysis or chemical characterization. It combines with SEM using a Philips Quanta250 electron microscope.

2.7.3 Antimicrobial tests
The best samples in terms of mechanical properties (6% and 8% fat emulsion) were chosen for antimicrobial tests compared with blanks using Nutrient Agar Medium (NA), Nutrient Broth Medium (NB), one set of samples and 100.0 mL sterile conical flasks [36]. A general culture medium for less fastidious microorganisms as well as for permanent cultures was carried out in nutrient broth according to Elsayed et al., [5], Sultan et al., [35] and Barry [37]. The antimicrobial test was carried out via the plat diffusion method according to previous studies [34, 38] with about 0.2 g of fatliquored leather. Five microorganisms are tested against fatliquored leather: Bacillus cereus (ATCC 6629), Micrococcus leutus (ATCC 10240), and Staphyllococcus aureus (ATCC 6538) were used as Gram-positive bacterium, and Escherichia coli (ATCC25922) and Pseudomonas aeruginosa (ATCC27853) were used as Gram-negative bacterium; and Candida albicans (ATCC 10231) was used as an example of the unicellular fungi.

The inoculum should be adjusted to apply 1.5×108 CFU/mL to the plates and flasks. The following procedure describes a method for preparing the desired inoculum by comparison with the 0.5 McFarland standard [39]. The inoculation of pathogenic microorganisms used in this study, which were Gram-positive bacteria [*Bacillus cereus, Micrococcus leutus* and *Staphylococcus aureus*], Gram-negative bacteria [*Escherichia coli* and *Pseudomonas aeruginosa*], and pathogenic yeast [*Candida albicans*], was prepared from fresh overnight broth cultures using nutrient broth medium that were incubated at 37 °C [35]. This pathogenic strain's inoculum was generated and adjusted to a size of around 0.5 McFarland standard (1.5×108 CFU /mL) [38]. Each plate containing 20.0 mL of the sterile nutrient agar medium was inoculated with 25.0 L of the inoculum size of each microorganism strain (NA). After applying the samples, each disc was then put separately on the surface of the infected agar plates after the medium had cooled and hardened -a step called the Disc Diffusion Method [38]. These seeded plates were placed in the refrigerator for one hour for more diffusion of these samples, followed by incubation at 37 °C for 24 h, and zones of inhibition (ZI) were measured in mm [40].

3 Results and discussion
3.1 Characterization of DD
3.1.1 Fatty acids (FA) composition
FA composition shows that DD sample is rich in linoleic, palmitic, and oleic acids (Table 1).

As recorded in Table 1, it can be seen that C16:0 (palmitic acid) is the main saturated fatty acid (SFA), amounting to 24.7%. Where C18:2 (linoleic acid) is the major unsaturated fatty acid (USFA) (49.4%). It is worth mentioning that the total USFA amounted to 72.3%. These results were in consistent with those of El-Shami et al. [29].

As shown in Table 2, 17 kinds of TAGs were found in DD [18]. It can be noticed that the major TAGs were those containing three, two, or one linolyl acyls, namely LOP, LLP, LPP, LLO, and LLL (16.0, 15.8, 14.2, 10.2, and 9.1%, respectively), which constituted about 64% of the total TAGs. Unsaturated acyl glycerols were detected at significant levels and may be useful for producing oleochemicals. (e.g., epoxides, alkanol amides, and fatliquor). The outcomes resembled those of El-Shami et al. [29].

Table 1 FA composition of DD sample

Fatty acids composition (%)							Total	
Myristic acid (C14:0)	Palmitic acid (C16:0)	Palmitoleic acid (C16:1)	Stearic acid (C18:0)	Oleic acid (C18:1)	Linoleic acid (C18:2)	Linolenic acid (C18:3)	SFA	USFA
0.3 ± 0.04	24.7 ± 0.6	0.6 ± 0.04	2.7 ± 0.3	21.8 ± 0.24	49.4 ± 0.3	0.5 ± 0.1	27.7 ± 1.0	72.3 ± 3.0

SFA Saturated fatty acids, *USFA* Unsaturated fatty acids

Data were represented as mean ± standard deviation; Number of replicates for each analysis was 3

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Table 2 HPLC analysis of TAG molecular species of DD sample

TAG	ECN	TAG (%)	TAG	ECN	TAG (%)
LnLL	42	0.35 ± 0.05	OOO	48	3.1 ± 0.4
LLL	42	9.1 ± 1.1	LOS	48	1.9 ± 0.55
LnLp	42	0.59 ± 0.07	OOP	48	0.2 ± 0.06
LLO	44	10.2 ± 1.2	LSP	48	7.0 ± 0.38
LLP	44	15.8 ± 0.5	POP	48	3.5 ± 0.5
LnOP	44	6.1 ± 0.6	OOS	50	0.65 ± 0.08
LOO	46	6.9 ± 0.52	LSS	50	0.75 ± 0.06
LOP	46	16.0 ± 0.46	POS	50	3.3 ± 0.51
LPP	46	14.2 ± 0.56	–	–	–

TAG: triacylglycerol; ECN = Equivalent carbon number; P, S, O, L, and Ln representing palmitic, stearic, oleic, linoleic, and linolenic acyl groups. Data were represented as mean ± standard deviation; Number of replicates for each analysis was 3

3.1.2 Tocopherols composition

The total tocopherol content of DD was found to be 7210 ppm. Figure 1A shows that γ- and δ- tocopherols were the major components in DD (54.8% and 31.6%, respectively), where γ- tocopherol is known to be a more potent tocopherol component that inhibits oxidation in addition to its nutritional importance. While α-tocopherol was found in a reasonable amount (11.8%) and β-tocopherol in a small amount (1.7%). It is worth mentioning that γ- and δ-tocopherol have more potent antioxidant efficiency than α-tocopherol.

Fatliquoring uses different materials to add fatty substances into leather. These materials are more or less sensitive to the oxidation process. The lipid oxidation state may also be related to the fatliquoring process, which occurs at 55–60 °C. Tocopherols, found in DD, are natural antioxidants that can stop or slow down this chemical reaction.
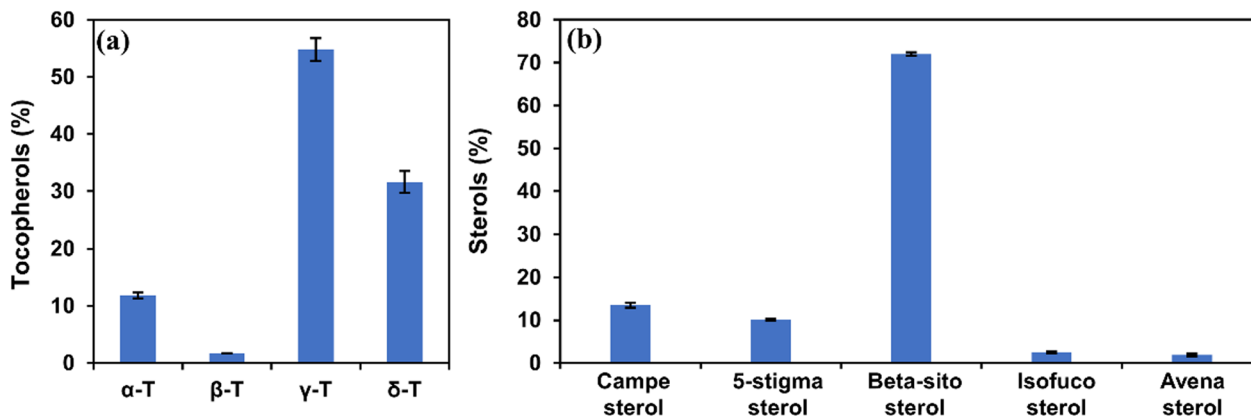
3.1.3 Whole sterols profile

The whole sterol content of DD is shown in Fig. 1B. A total sterol content of 1.35% was measured in DD. The analysis of sterols in DD revealed that β-sito sterol was the most component (72.05%), followed by campe sterol (13.5%) and 5-stigma sterol (10.1%). Avena- and isofuco-sterols were present in small amounts (1.9 and 2.45, respectively). The findings for tocopherols and total sterols are consistent with El-Mallah et al.'s findings [41].

3.1.4 FS and AS, as well as FSG and ASG

FS and AS amounted to 2010 mg/g, in which campe + stigma sterol (unseparable) and β-sito sterol (40.2% and 50.4% respectively), are predominating in DD sample (Fig. 2).
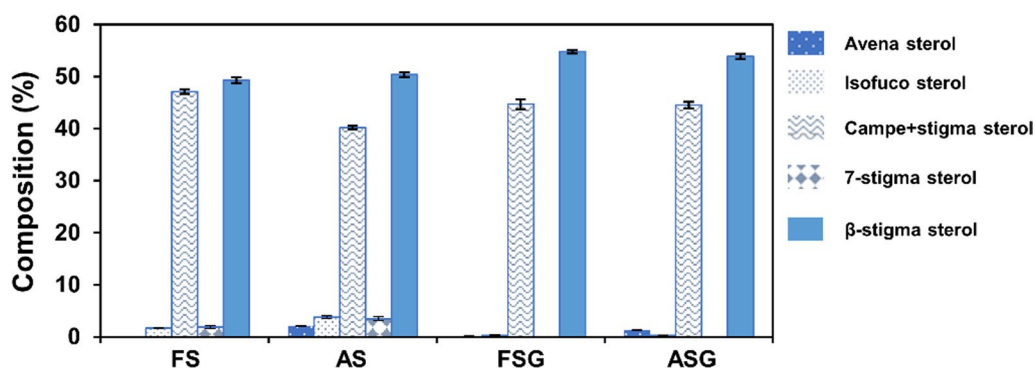
The total content of FSG and ASG in DD sample was 841 mg/g. It appears from Fig. 2 that β-sito sterol and campe + stigma sterol are the most abundant FSG components (54.8% and 44.7%, respectively) and ASG components (53.9% and 44.5%, respectively) [42]. These results agree with those obtained by El-Mallah et.al. [15].

There is a need for soft leather in the leather industry, where affordable and low-polluting fatliquor will open up more opportunities. Pervez et al. [43] found that, based on chemical and physical analysis, the blended oil-based fatliquor was better than the individual oil-based fatliquors (castor or canola). As mentioned above, DD is a natural source of fatty material consisting of two vegetable oils (soybean and sunflower) and is encouraged to be used as a fatliquor.

3.2 Characterization of the PDD sample
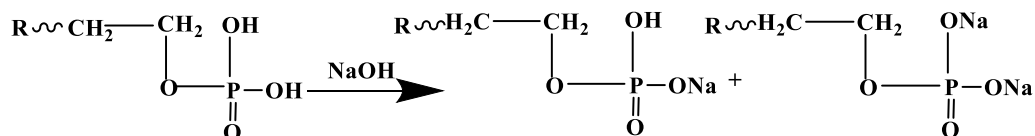### 3.2.1 Phosphorylation reaction of DD

When a phosphating substance is mixed with alcohol, phosphate esters are produced. Alcohols and an activated phosphorous derivative react to create phosphate ester

Fig. 1 Tocopherols (%) (**a**) and sterols (%) (**b**) composition of DD sample (α-T = Alpha-tocopherol, β-T = Beta-tocopherol, γ-T = gamma-tocopherol and δ-T = delta-tocopherol. Data were represented as mean ± standard deviation; Number of replicates for each analysis was 3.)

Fig. 2 FS & AS and FSG & ASG composition in DD sample (FS & AS were determined as 9-anthroylnitrile (9-AN) derivatives, FSG & ASG were determined as 1-anthroylnitrile (1-AN) derivatives. Data were represented as mean ± standard deviation; Number of replicates for each analysis was 3)
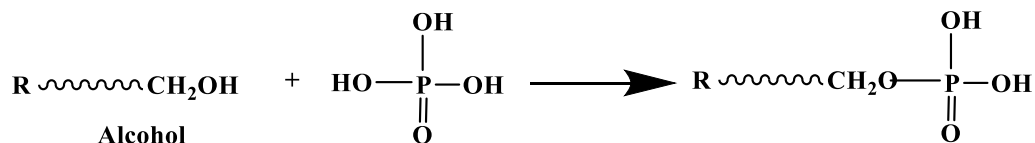
A: Phosphorylation reactions and ester-phosphate products

B: Neutralization of phosphorylated products

Scheme 1: Phosphorylation reaction of DD

surfactants, as shown in Scheme 1. Residual alcohol and phosphoric acid are also present in phosphate ester products, together with monoalkyl phosphate (monoester) and dialkyl phosphate (diester) [44]. Several types of phosphate esters are possible from various starting materials (Scheme 1). It is possible to obtain a succession of items with various characteristics. Changing the base materials, phosphating agents, and reaction conditions can modify the quality and attributes phosphate esters [45]. The phosphorus content of PDD was 5.5%, which was determined by inductively coupled plasma (ICP).

3.2.2 FTIR analysis
FTIR spectra of DD show that a broad absorption peak is observed at 3020 cm^{-1} and 715 cm^{-1}, which are associated with the stretch and bending of the=CH olefinic group, and at 1805 cm^{-1} and 1850 cm^{-1}, which correspond to the C=O of the ester and carboxylic group

stretch, respectively. The bands of CH$_3$ and CH$_2$ groups were seen around 2920 cm^{-1} and 2850 cm^{-1}, respectively.

The spectrum of PDD shows characteristic absorption peaks at 1201 cm^{-1} corresponding to sym. dihydrogen phosphate, and another at 1087 cm^{-1} which is associated with asym. groups. It can also be seen from Fig. 3 that a strong broadband appeared at (3510 and 3450) cm^{-1} and 761 cm^{-1}, which correspond to the hydroxyl groups and mono hydrogen phosphate, respectively. The obtained results were in agreement with those of Megahed and Nashy [9].
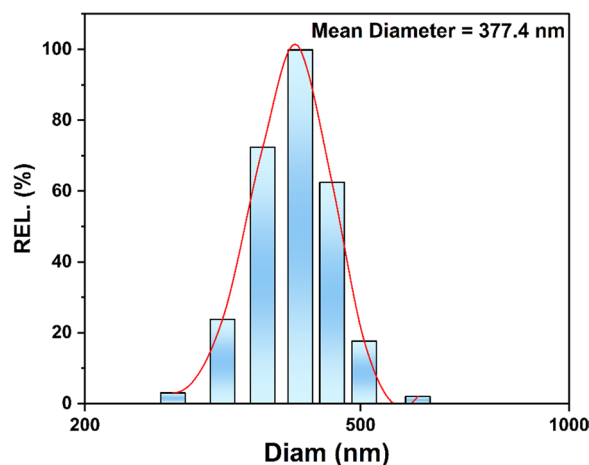
3.2.3 Zeta potential
The electrochemical equilibrium is quantified by zeta potential. It is one of the primary characteristics known to determine the stability of colloidal particles since it indicates the strength of electrostatic

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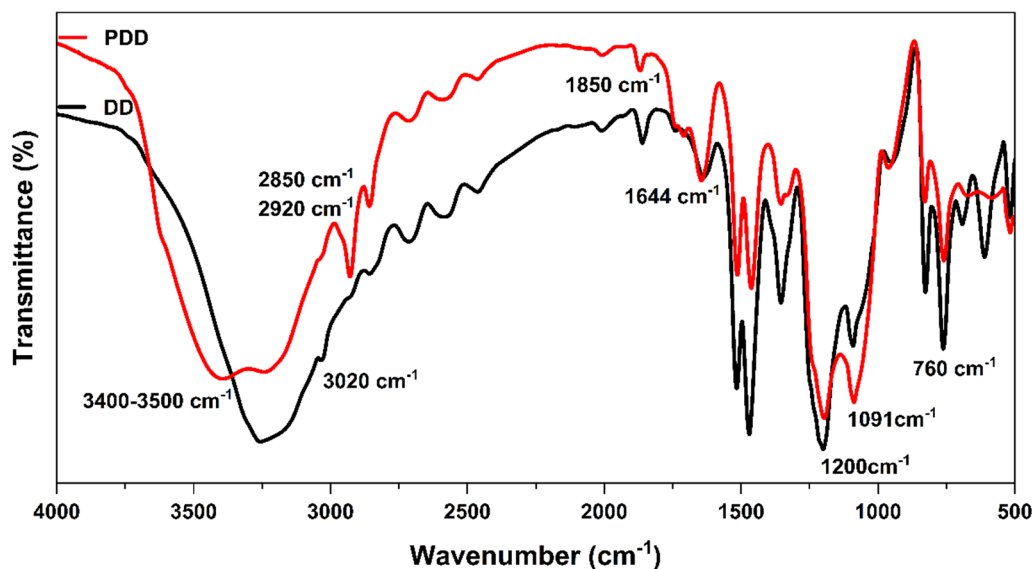
Fig. 3 FTIR spectra of DD and PDD
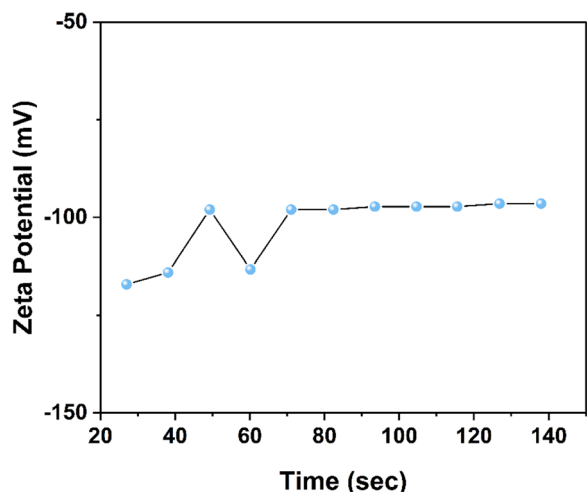
Fig. 4 Zeta potential of (1% solution) PDD

Fig. 5 The particle size of (1% solution) the PDD

repulsion/attraction between particles. It also aids in estimating the long-term stability of fatliquors [46]. As shown in Fig. 4, the zeta potential of PDD was found as − 96.98 mV, presenting excellent stability [47].

3.2.4 Particle size
The leather quality may be influenced by the particle size of the emulsions used. The smaller particle has greater ability to penetrate the material [48, 49]. The grease component of the fatliquor creates an oily film between the fibers, while the polar groups of the emulsifying agent in PDD interact with the active sites of the leather to soften and lubricate the fibers. The fatliquor with small particle size can permeate the leather's hierarchical structure [50]. Microemulsions used for fatliquoring must be 'oil in water', while 'water in oil' can disrupt the fatliquoring system and lead to fat deposition on the leather's surface. Emulsions can be categorised according to the size of the dispersed particles: macroemulsions (droplet sizes of 1.5–100 μm), nanoemulsions (droplet sizes of 50–500 nm), and microemulsions (droplet size 3–50 nm) [51]. The average particle size of the PDD fatliquor is 377 nm, which indicates that it can easily permeate and display a soft grain without forming a fatty spew, as shown in Fig. 5.

3.2.5 Stability of fatliquor

The application of fatliquor in leather industry is based on the stability of fatliquor emulsion. The emulsion of fatliquor must have a stability against acids and metal ions, such as Ca, Mg, Cr, and Fe [52]. It was observed that the prepared emulsion was stable at pH ≥ 3, and it was also stable to salt solution of $CaCl_2$ (18%), $MgSO_4$ (15%), $FeSO_4$ (12%), and chromium sulfate (16%). These results show that PDD had good acid and metal ion resistance stability.

3.3 Characterization of the fatliquored leather

3.3.1 Strength properties

The fatliquoring process was carried out on neutralized leather using 2–8% emulsion. Strength properties are a good indication of fiber lubricity of fatliquored leather. The average value of at least three tests was taken for each item (Table 3).

It was noticed from Table 3 that strength characteristics were enhanced due to the good lubrication of fibers, as shown in SEM images, Fig. 6. It was also observed that the fatliquored leathers with 6% and 8% dosage had a relatively steady state, so they were considered as the suitable usage for fatliquoring. The hardness of the fatliquored leather decreased because of the good lubrication of fatliquors, as shown in Table 3.

3.3.2 SEM analysis

The impact of fatliquor on leather fiber and grain surface may be seen in detail by using SEM, which can evaluate the diffusion of the fatliquor in leather. As shown in Fig. 6a, b, e and f, fatliquored leather exhibited a soft grain without any fatty spew. While from the cross-section micrographs in Fig. 6c, d, g and h, fatliquored fibers showed obvious lubrication of fiber bundles. It refers to the coating or deposition of fatliquor on leather fibers

Table 3 Mechanical properties and hardness of fatliquored leather

Fatliquored leather	Tear strength (N/m)	Strain at rupture, (R%)	Tensile strength (N/mm^2)	Hardness (0–100) HA
Chrome tanned leather	7.82	40.65	16.75	95
2%	8.59	48.88	19.68	91
3%	8.80	53.15	20.09	88
4%	9.38	52.36	22.04	85
6%	10.15	60.56	26.74	77
8%	10.56	62.08	28.69	75
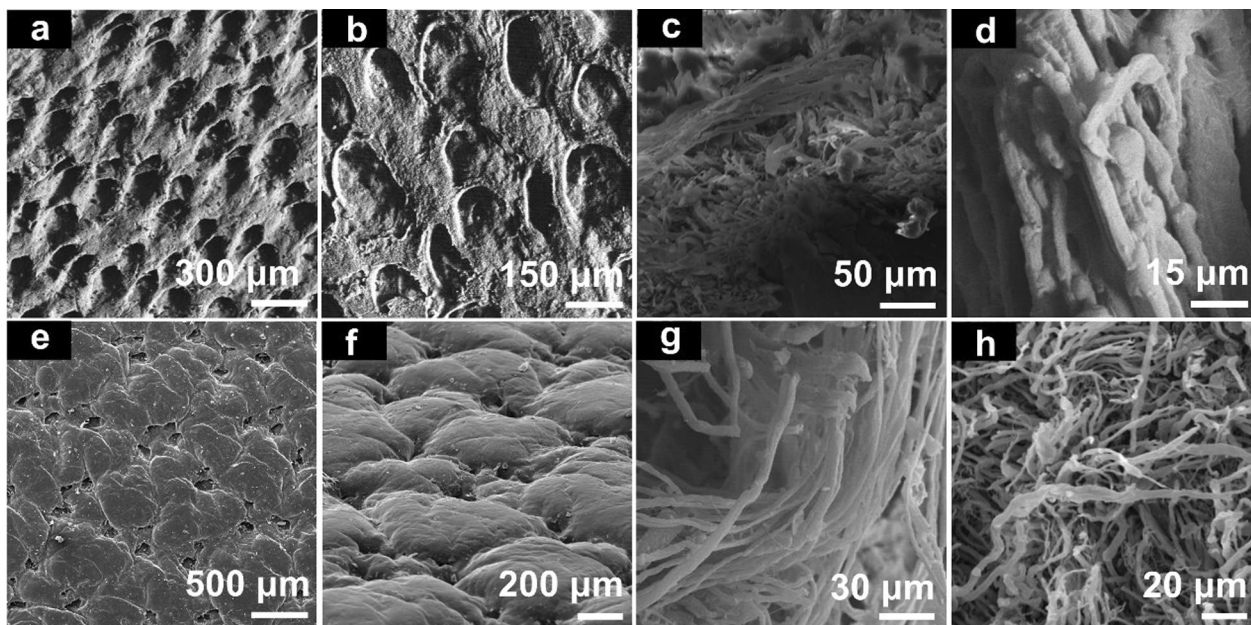
Fig. 6 SEM images of the grain surfaces and cross sections of chrome-tanned leather samples **a**–**d** without treatment by fatliquor, **e**–**h** treated with fatliquor
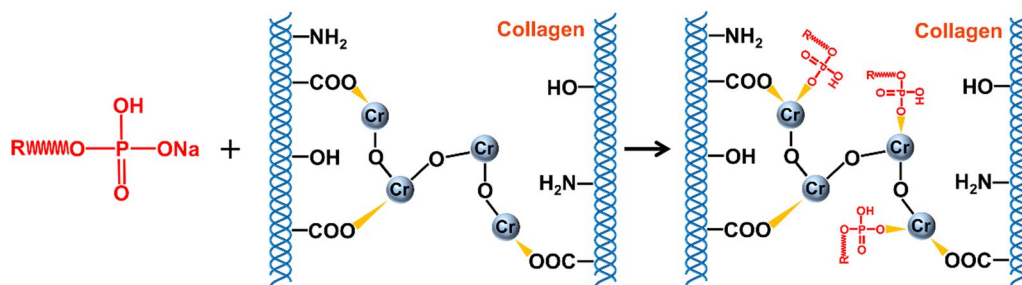
Scheme 2: Suggested lubrication mechanism of the PDD for the leather

Table 4 Elemental analysis of leathers fatliquored by 6% and 8% PDD

Element	6% PDD		8% PDD	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	75.14	80.17	57.13	70.73
O	19.44	15.96	15.17	14.10
N	0.6	1.11	4.44	4.71
P	1.18	1.90	1.18	3.90
Cr	0.74	0.19	9.65	2.76
Na	0.53	0.3	7.69	4.97

through interaction with the active groups of leather. On the other hand, the fatliquored leather has more smoothness and flexibility than the chrome-tanned leather without fatliquoring. These results indicate the obvious lubrication of fiber bundles and the fine-grain surface of leather benefitted from fatliquoring. Schematic diagram 2 shows a suggested lubrication mechanism of PDD micelles for the leather.

3.3.3 EDS analysis
The presence of phosphorus was confirmed in the fatliquored leather using EDS, as shown in Table 4 and Fig. 7 and Additional file 1: Figures S1, S2.
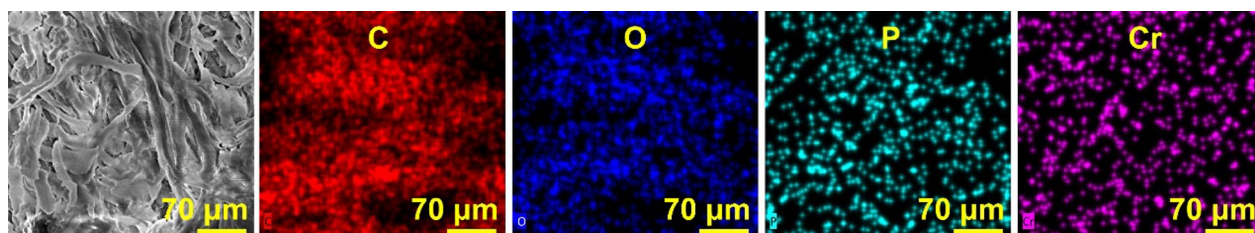
3.3.4 Antimicrobial activity
In the current study, the antimicrobial activity of leather treated by the prepared PDD against Gram-negative bacteria (*E. coli*), Gram-positive bacteria (*Pseudomonas aeruginosa, Bacillus cereus* (+), *Micrococcus leucos* (+), *and staphyllococusaureus* (+), *and non-filamentous fungi (Candida albicans*) was investigated using two different dosages of fatliquor (6% and 8%) by calculating the growth inhibition zone around the agent's discs in millimeters shown in Table 5. As can be seen in Fig. 8, the microbial growth was reduced. In this connection, the sample exhibits the preferred antimicrobial activity towards *E. coli* (19 mm), *Micrococcus leutus* (+), (12 mm), and *Candida albicans* (22 mm).
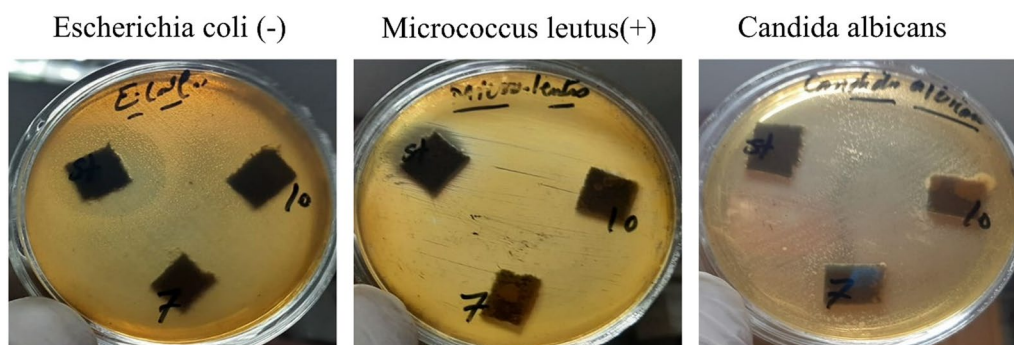
Table 5 Inhibition zone diameter (millimeter) of the fatliquored leather samples

Test bacteria	Blank	6%	8%
Escherichia coli (−)	19.0	NiL	NiL
Pseudomonas aeruginosa (−)	NiL*	NiL	NiL
Bacillus cereus (+)	NiL	NiL	NiL
Micrococcus leutus (+)	12.0	NiL	NiL
Staphyllococus aureus (+)	NiL	NiL	NiL
Candida albicans	22.0	10.0	11.0

*NiL No antimicrobial activity recorded

Fig. 7 SEM image of leather fatliquored by 6% PDD and EDS images of the corresponding area for carbon, oxygen, phosphorus and chromium

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Escherichia coli (-)   Micrococcus leutus(+)   Candida albicans

Fig. 8 Photograph of the inhibition zone diameter (millimeter) of the samples

In general, antimicrobial activity of the fatliquored leather may be attributed to the tocopherols in DD.

4 Conclusions

The sustainable development of industry requires increased attention to the environment, in which effective utilization of industrial by-products is important. The oil industry's byproduct DD is rich in fatty acids, determining its potential use as a fatliquor in leather industry. The fatliquor developed from phosphorylation of DD has excellent stability to acids and metal ions, and suitable particle size to permeate the leather fiber, which endows leather with a softer grain and higher mechanical strengths. In addition, the powerful antioxidants γ- and δ-tocopherols in DD can give leather higher values of resistance to bacteria and antioxidant activities. This work provides a sustainable resource utilization approach for DD.

Abbreviations

DD	Deodorizer distillate
FA	Fatty acids
FFA	Free fatty acids
T	Tocopherols
FS	Free sterols
AS	Acylated sterols
FSG	Free sterylglycosides
ASG	Acylated sterylglycosides
9-AN	9-Anthroylnitrile
1-AN	1-Anthroylnitrile
NA	Nutrient agar medium
NB	Nutrient broth medium
ZI	Zones of inhibition
SFA	Saturated fatty acids
USFA	Unsaturated fatty acids
TAGs	Triacyglycerols
P	Palmitic acid
S	Stearic acid
O	Oleic acid
L	Linoleic acid
Ln	Linolenic acid
ECN	Equivalent carbon number
SEM	Scanning electron microscopy

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s42825-023-00124-8.

Additional file 1: S1. EDS spectroscopy peaks. **S2**. SEM image of (a) 8 % phosphorylated fatliquored leather and EDS mapping of the corresponding area for (b) carbon, (c) oxygen, (d) phosphorus and (e) chromium.

Availability of data and materials
All data generated or analysed during this study are included in this published article.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare that they have no competing interests.

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