(REFEREED RESEARCH)

EVALUATION OF DEGREASING PROCESS WITH PLANT DERIVED BIOSURFACTANT FOR LEATHER MAKING: AN ECOLOGICAL APPROACH

DERİ ÜRETİMİNDE BİTKİSEL KAYNAKLI BİYOSÜRFEKTANLA YAĞ GİDERME İŞLEMİNİN DEĞERLENDİRİLMESİ: EKOLOJİK BİR YAKLAŞIM

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ABSTRACT

This paper describes the application of extracts of Quillaja bark saponin, a plant derived biosurfactant, as alternative low cost natural surfactants for the degreasing of sheep skins. Pickled sheep skins were treated using three commercial products of *Quillaja saponaria* saponins with different degrees of sapogenin content: Q1 (Sigma, 26%), Q2 (AppliChem, 12%) and Q3 (Carl Roth, 10%). The effect of saponin based biodegreasing was investigated in terms of chemical oxygen demand (COD) of residual floats, quantification of colour and scanning electron microscopic visualization of the biodegreased leathers. Degreasing efficiency levels up to 82%, 79% and 78% was attained with 3.75% sapogenin content of Q1, Q2 and Q3 respectively. COD values for degreasing effluents were reduced by 70%, with 3.125% offer of Q1 saponin. The results indicate that the properties of biodegreased leathers are comparable with those of conventionally processed leathers with respect to dye levelness and physical texture. This novel saponin based degreasing process can be a viable and promising ecological degreasing option for leather industry.

Key Words: Saponin, Plant derived biosurfactant, *Quillaja saponaria*, Ecological degreasing, Leather.

ÖZET

Bu makalede bitkisel kaynaklı bir biyosürfektan olan Quillaja saponini ekstraktlarının alternatif, düşük maliyetli ve doğal sürfektan olarak koyun derilerinin yağ giderme işleminde kullanımı incelenmiştir. Pikle koyun derileri farklı oranlarda sapogenin içeren üç ticari *Quillaja saponaria* ürünüyle Q1 (Sigma, 26%), Q2 (AppliChem, 12%) ve Q3 (Carl Roth, 10%) işlenmiştir. Saponin kullanımına dayalı biyo-yağ giderme işleminin etkisi atık banyoların kimyasal oksijen ihtiyacı (KOİ), derilerin rengi ve taramalı elektron mikroskobuyla derilerin kesiti incelenerek belirlenmiştir. Q1, Q2 ve Q3'ün %3.75 sapogenin konsantrasyonuyla gerçekleştirilen yağ giderme işlemlerinde sırasıyla %82, %79 ve %78'e varan oranlarda yağ giderme etkinlikleri elde edilmiştir. Q1 saponini % 3.125 oranında kullanıldığında yağ giderme atık sularının KOİ değerleri %70 oranında azaltılmıştır. Sonuçlar biyosürfektanlar ile yağ gidermesi yapılmış derilerin düzgün boya dağılımı ve fiziksel yapı açısından geleneksel yöntemle işlenen derilere benzer özelliklere sahip olduğunu ve bu çalışmada geliştirilen, saponin kullanımına dayalı yağ giderme işleminin deri endüstrisi için uygulanabilir, gelecek vaat eden ve ekolojik bir alternatif olabileceğini göstermektedir.

Anahtar Kelimeler: Saponin, Bitkisel kaynaklı biyosürfektan, *Quillaja saponaria*, Ekolojik yağ giderme, Deri.

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1. INTRODUCTION

The degreasing of animal skins in leather production is an important processing step where the excess of natural fat substances is removed from skin. The raw skins from sheep can contain significant amounts of natural fat to the extent that 30-40% based on raw weight (1). This fat is generally unevenly distributed across the skin and if the skin is insufficiently degreased, the existence of high amount of fat can cause uneven tanning, dyeing imperfections and crystallization of the high molecular fatty acids that can also produce fatty spues on leather surface (2). The degreasing methods commonly used for degreasing of skins usually involve the inconvenience of using highly polluting products such as organic solvents and/or synthetic surfactants, or their mixture in the form of aqueous emulsions (3, 1, 4).

The industrial use of these methods has been questioned and raises the question of sustainability because of non-biodegradable structure of surfactants, which is shown to be toxic

to aquatic organisms, and readily inflammable and toxic nature of solvents. The presence of surfactants and solvents in process effluents generate severe environmental burdens due to use of large amounts of water and cause significant problems in the conventional wastewater treatment process (4).

Global environmental concerns and government regulations has driven increased emphasis on the concept of cleaner production and use of improved product and process alternatives become one of the key research activities (5, 6). Different systems have been proposed and various approaches such as use of ultrasound (7) supercritical carbon dioxide (8) ultrafiltration (9) and enzymes (10) were adopted in order to minimize the environmental impact of degreasing operation. The employment of enzymes is a more environmentally acceptable degreasing method, however does not yield a remedy, in fact, the presence of non-ionic surfactants accompanies their use, moreover their commercial production and application in degreasing is limited due to lack of sufficient enzyme specificity for process requirements and high production cost (11). On the other hand the main drawbacks of ultrasound, ultrafiltration and supercritical CO_2 degreasing methods are high production costs and operational difficulties, therefore the proposed systems have not gained commercial significance. In the last decade there has been an increasing interest in using environmentally sustainable natural products that could substitute for synthetic ones, considering the environmental issues caused by nonrenewable and highly polluting synthetic chemicals. To this respect microbial biosurfactants produced by bacteria, and plant derived biosurfactants have gained particular interest as promising non-toxic washing agents due to their low toxicity and biodegradability. The feasibility of using biosurfactants in environmental bioremediation applications as well as in several leather production processes (12, 13) was demonstrated. Furthermore they do not cause secondary pollution even if they are leaked and discharged to the ecosystem (14).

A review of the current literature indicates that there is a limited number of studies concerning the use of microbial biosurfactants for cleaning and degreasing applications in leather making process, and they were focused on their use as soaking agent and brine curing additive (15, 16). Up to date no scientific research has been reported applying naturally occurring plant-derived saponins for extraction of fat from sheep skins.

The objective of this study is to investigate the applicability of plant derived biosurfactants, in degreasing process of sheep skins to develop an eco-friendly degreasing system. Among their desirable properties such as biodegradability, nontoxicity, they are low-foaming as well. The environmental benefits make the investigation of the potential for their use in the leather industry as a degreasing agent interesting and worthy of consideration, when compared with the aforementioned methods described in the literature.

2. MATERIAL AND METHOD

2.1. Material

Six English Domestic pickled sheep skins were used in order to perform the degreasing experiments. The chemicals used in the leather production processes were those conventionally used in the leather production. A fatty alcohol polyglycol ether based commercial non-ionic surfactant was used as a control according to the recommended dosage level (5%) of the manufacturer. All chemicals used for the analysis were of analytical reagent grade and purchased from Merck (Darmstadt, Germany).

2.2. Saponin

Saponins are naturally occurring surface-active glycosides which are predominantly found in the plant kingdom (17). One of the most important sources of saponin is *Quillaja saponaria* tree that grows naturally in Chile and the bark of this tree is the preferred raw material for the production of triterpenoid saponin owing to its high content of saponin and ease of transportation. Saponins as biosurfactants are advantageous due to their easy production from renewable sources, availability on market, lower price and possibility of reuse. Therefore the use of saponins is considered to be cost-effective process as compared to other microbial and plant derived biosurfactants (18). In this study, three commercial products of *Quillaja saponaria* saponins with different degrees of sapogenin content: 26% saponin from Sigma Chemical, St Louis MO (Q1); 12% saponin from AppliChem GmbH (Q2); and 10% saponin from Carl Roth GmbH (Q3) were used. Quillaja saponin products are entirely soluble in distilled water and used without further purification.

2.3. Degreasing procedure

The pickled English Domestic sheep skins were cut along the backbones into halves with the left and right sides being used for experimental and control processes respectively. The left sides of the skins were treated with different types of saponins at various concentrations. In each case a control was also carried out on the corresponding side of the skins with an offer of 5% synthetic surfactant containing 95% active substance and all experiments were performed in triplicate. The saponin degreasing procedure is presented in Figure 1.

Pickled pelts were depickled by treating with 200% water and 8% NaCl (percentages based on pickled weight +30%) for 15 minutes, followed by addition of sodium formate and sodium bicarbonate for 30 minutes of each. Bating was carried out for 20 minutes using 1% commercial acidic bating enzyme. The bated pelts were washed with 200% water for 10 minutes.

Conventional depickling and bating processes were followed by degreasing of skins. Experiments were carried out using different concentrations of saponin solutions such as 1.25, 2.5, 3.125 and 3.75% based on the sapogenin content of each product. Saponin solutions were prepared by dissolving saponins in 1:4 water (based on saponin weight). For control trials 5% commercial degreasing agent was added in dry float. The drums were run for 1 hour. Subsequently, the degreased pelts were washed twice with water following the double brine solution washing for a period of 15 minutes each. Re-pickling process was initiated by treating the degreased pelts with 100% water and 8% sodium chloride for 10 minutes. This was followed by the addition of 1% formic acid (w/w) in 3 feeds with 10 minutes interval. Drumming was continued for 1 hour after the addition of 0.8% sulfuric acid till pH 2.8 was reached.

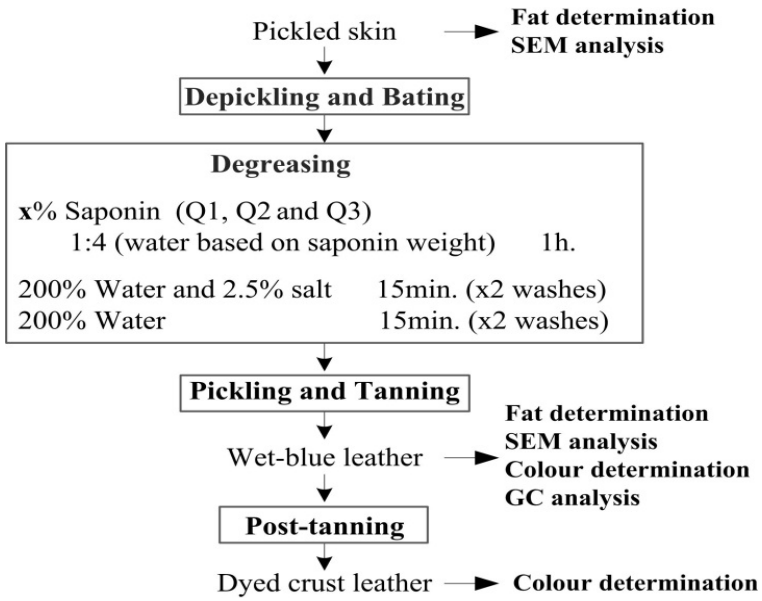

Figure 1. Flow diagram of the biodegreasing procedure (Sapogenin concentrations x:1.25, 2.5, 3.125 and 3.75%)

All trials were carried out in accordance with the same conventional formulation throughout the tanning and retanning processes. Following the determination of optimum saponin concentration for degreasing effect, wet blue leathers were converted into crust leathers employing standard post tanning procedures for garment leather. Since the effect of saponin degreasing on dyeing process will be evaluated, post-tanning of wet blue leather was carried out with reduced offer of chemicals in a conventional way using 3% dye; 6% retanning agent and 5% fatliquor. Finally the leathers were dried.

2.4. Determination of natural Fat Content and Degreasing Efficiency

The initial and the residual natural fat remained after degreasing operation in sheep skins were determined in accordance with the procedure described by Zengin et.al (2). The efficiency of the degreasing with saponin in each experiment was expressed as the ratio between the fat extracted with saponin and the total amount of natural fat extractable from each sample, which consists of fat extracted with saponin plus the residual natural fat.

2.5. Determination of chemical oxygen demand in degreasing floats

Effluent samples were taken from the main degreasing baths and subsequent washing steps for the purpose of assessing the pollution load. COD values of effluents were measured photometrically using test kits and Merck SQ300 device.

2.6. Determination of Colour Differences of Biodegreased Wet Blue And Dyed Crust Leathers

In order to assess the effect of biosurfactant degreasing on colour of chrome tanned leather and dyeing uniformity, colour differences between biodegreased and control samples were determined using Minolta CM 508D Spectrophotometer. Device was calibrated with a standard black and white plate before measurement and colour of biosurfactant degreased samples were read against control samples. Values representing the whole measuring area were recorded and the average colours on the CIE L, a, b scale as a comparison to the control samples were determined quantitatively. The total colour difference (ΔE) has been calculated using the following equation (19):

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

2.7. Scanning Electron Microscopic (SEM) Examination

In order to study the effect of saponin degreasing on the dispersion of fiber bundles, samples from pickled skins and wet-blue leather samples were cut into uniform sizes dehydrated gradually as per standard procedure previously described in the literature (2). The samples were viewed under 250x magnification using Table Top SEM (Hitachi TM 1000).

2.8. Gas Chromatography Analysis of Fatty Acids

Gas chromatography (GC) analyses were conducted prior to degreasing on pickled skin samples and wet-blue leathers after degreasing. GC experiments were carried out by transesterification of fatty acids to produce fatty acid methyl esters following the procedure previously described in the literature (2). Data were acquired by HP 6890 GC-FID device operated with a split/splitless injector.

3. RESULTS AND DISCUSSION

3.1. Effect of Saponin Concentrations on Biodegreasing Efficiency

In order to optimize the saponin offer, while achieving the highest level of degreasing, series of trials were performed. Figure 2 shows that degreasing efficiencies increase as Quillaja saponin concentrations increase. Mean degreasing efficiency values at the lowest saponin concentrations were 15%, 14% and 7%, for Q1, Q2 and Q3 respectively. In the same order improved degreasing efficiency values of 82%, 77% and 72%, was achieved with the highest saponin offer, which are higher than

the previously reported values (3, 9). Considering the offered amount, based on the active substance content of commercial degreasing agent (95%) and sapogenin content of saponin products (Q1, 26%; Q2, 12%; and Q3, 10%), it can be stated that comparable values to control samples can be acquired with 35% less offer in the proposed biodegreasing method.

Commercial degreasing agent used for control trials presented an approximate degreasing efficiency about 50% in overall applications. For all types of saponin offer of 2.5% yielded comparable results to control trials, whilst better degreasing efficiencies was achieved with higher concentrations. In previous studies performed by Marsal (8) and Palop (3) higher degreasing efficiencies such as 89% and 94% were obtained. Nevertheless, too strong degreasing effect is not advantageous in terms of quality of resulting leather and an over dosage of surfactant may also lead formation of a finer particle sized more stable emulsion that result in redistribution of fat through the cross-section of the hide (20), therefore %3.125 saponin offer is regarded as the optimum concentration.

3.2. Effect of Washing Cycles on Biodegreasing Efficiency

Q1 saponin solution at 2.5% concentration was selected to determine the effect of number of washings on fat removal efficiency. The results are presented in Figure 3. It is noticeable from this figure that both for control and saponin trials single wash with water or brine solution resulted in lower degreasing efficiencies, when the washing stages were repeated for a second time fat removal rates increased and water washings showed better degreasing efficiency than double brine washings. The results reveal that reduced washing cycles in saponin degreasing yielded lower degreasing efficiencies than control on the contrary to comparative values obtained for double water and brine washings. Nevertheless performing more than double washes improves the overall degreasing efficiency less than 15% for saponin samples.

With the aim of reducing water consumption and salinity in effluents, washing steps with brine solutions were eliminated and further experiments were carried out using optimum saponin offer of 3.125% by only application of double water washings cycles following the degreasing operation. Elimination of brine washings yielded approximately 10, 45 and 18% lower degreasing efficiencies than the values previously obtained for Q1, Q2 and Q3 respectively at 3.125%, despite this it is accepted as reasonable washing option, due to providing comparable values to control, reducing water consumption and enabling a decrease in the amount of waste water discharged. SEMs of leather samples, GC analysis of extracted fat, COD determination of effluents and colour measurement of both wet blue and dyed crust leather were performed with data obtained from this trial.

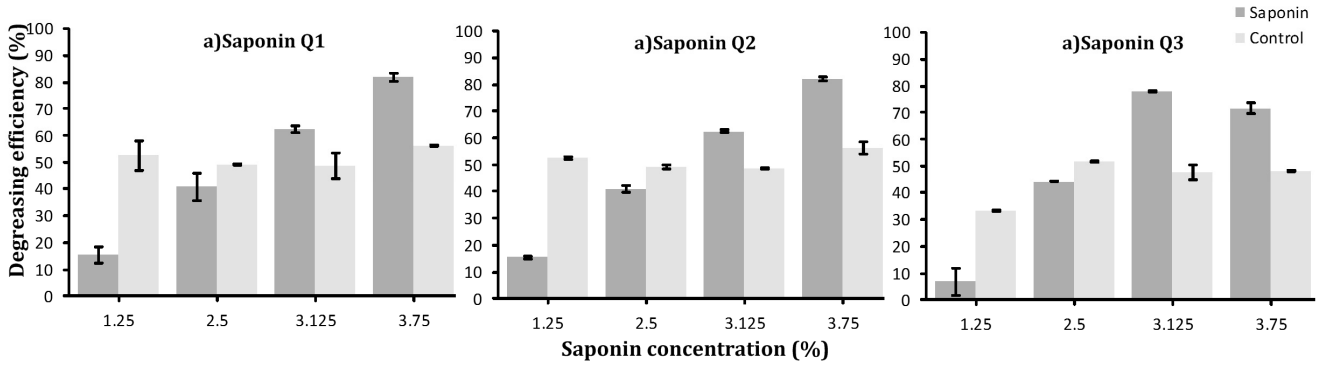

Figure 2. Effect of increasing saponin concentrations of a) Q1; b) Q2; c) Q3 on degreasing efficiency (Data are mean ± standard error)

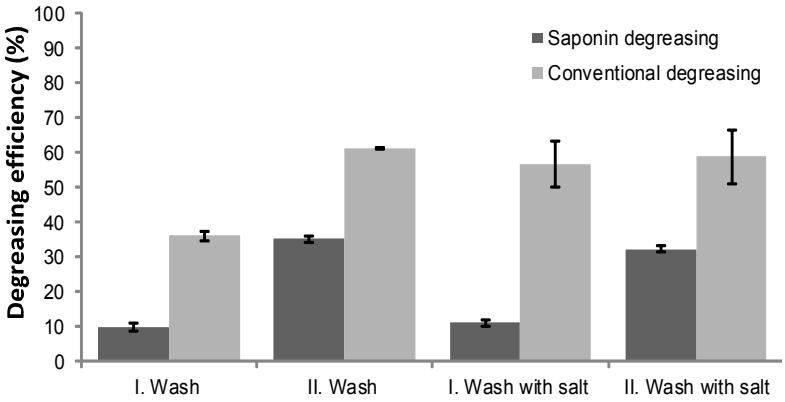

Figure 3. The effect of washing cycles on degreasing efficiency of 2.5% saponin (Q1) (Data are presented as mean ± standard error of the mean)

3.3. Effect of Biodegreasing on Effluent

The effect of biosurfactants degreasing on pollution load of process effluents was determined using 3.125% of saponin concentration. The floats resulted from degreasing and washing processes were analyzed for COD values. In order to compare the results obtained from different volumes of residual bath, emission loads were calculated by multiplying COD values (mg/L) with effluent volume. The values are presented in Figure 4. The COD values of main degreasing float for both conventional and saponin processes are comparatively higher than the previously reported values however washing effluents achieved significantly lower COD loads (3). All saponin products gave higher COD values than conventional process for main degreasing residual bath. The use of biosurfactants performed better in washing effluents and reduced the COD of washing effluents between 76 and 94%. COD values were decreased with increasing sapogenin content and purification degrees of saponin products. Q1 saponin provided the lowest COD values both for the first and second washing effluents and reduced the total COD emission load of the degreasing process by 70%.

3.4. Effect of Biodegreasing on Colour of Wet Blue and Crust Leathers

The variation in colour observed between corresponding control and experimental matched pair of wet-blue and dyed crust leather is presented in Figure 5. All saponin products exhibited very slight differences in luminosity (L) as indicated by ΔL values, while Q1 and Q3 has the darkest shade in wet blue and dyed crust leathers respectively. For redness (a) wet blue samples yielded higher, whereas crust leathers showed lower values than control.

All saponin biodegreased samples showed a slight increase in yellow colour both for wet blue and dyed crust leathers. Biodegreasing with Q1 gave leathers with a slightly yellower than the control, this is mainly related to the colour of saponin products, as Q1 has the highest yellow colour among saponin products used in the study, whereas Q2 appears the whitest in colour. The overall colour differences show that Q1 has the maximum ΔE values of 7.4 and 4.06 for crust and wet blue leather respectively. On the other hand Q2 yielded the minimum overall colour difference of 1.3 for wet blue and 4.8 for crust leathers. The results indicate that there has not been much of overall colour (ΔE) differences in wet blue and dyed crust leathers as compared to control samples (18, 3). The results are based on the experiments performed on different areas of sheep skins and the variance in the results can be assigned to some extent to the variability always found in biological material.

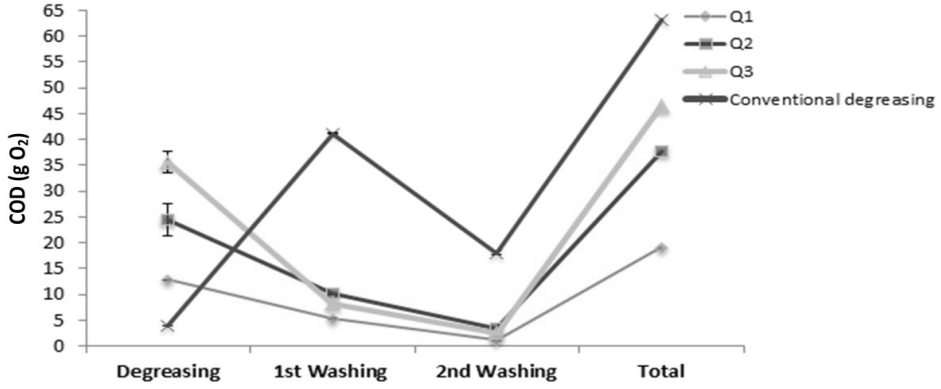

Figure 4. Chemical oxygen demand in degreasing effluents (Data are mean ± standard error)

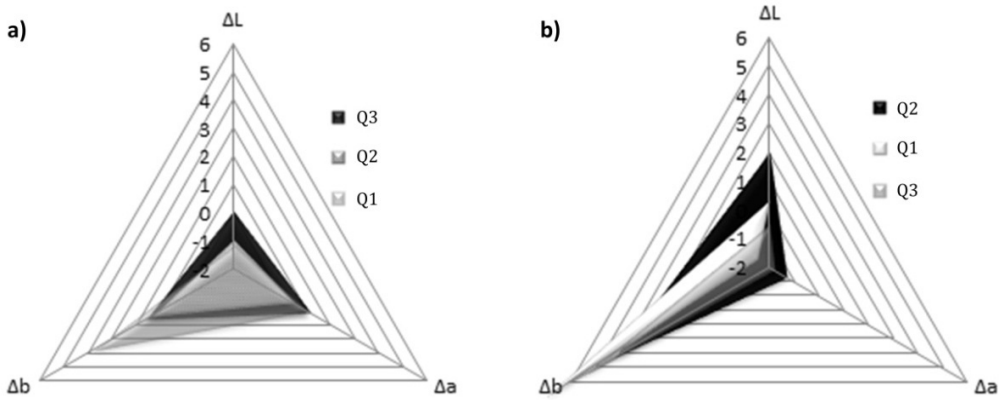

Figure 5. Colour differences between control and (a) wet blue leathers and (b) dyed crust leathers

3.5. SEM Analysis of Skins Before and After Biodegreasing

Scanning electron micrographs showing the cross section of papillary and reticular layers of pickled skins before degreasing and wet blue leathers degreased with both conventional degreasing agent and different saponin solutions at a magnification of x250 are depicted in Figure 7.

Sample degreased with Q1 saponin exhibit a slightly dispersed fiber structure, which is similar to the conventionally degreased control. The fiber bundles seem to be less isolated in Q2 and Q3 samples compared to control sample. It's thought to be due to different sampling areas of the skin and the variability always found in natural material. The overall physical texture and dispersion of fiber bundles after tanning process in saponin degreased leathers have been found similar and comparable to that of conventionally processed control leathers.

3.6. Gas Chromatography Analysis

The results obtained from GC analysis of extracted fat from pickled skins, experimental and control leathers are presented in Figure 6.

When the fatty acid composition of extracted fat was examined at least eleven fatty acid methyl esters were observed. The free saturated fatty acids especially palmitic and stearic acids and/or their esters of glycerol or phospholigidic esters are mainly responsible for the fatty spews (2, 21).

The ratio of the palmitic and stearic acid in pickled skin was found clearly higher than the biodegreased and control samples, which is consistent with reports from other researchers (2, 22) The results revealed that, leathers degreased with Q1 and Q3 has 6.7 and 9.8% lower, whereas Q2 has 6.4% higher palmitic acid (C16:0) content when compared with control samples. All saponin degreased samples have lower stearic acid content as compared to control. Higher reduction in stearic acid (C18:0) content was achieved by Q1 (33.2%) that is followed by Q3 (16.6%) and Q2 (2.5%).

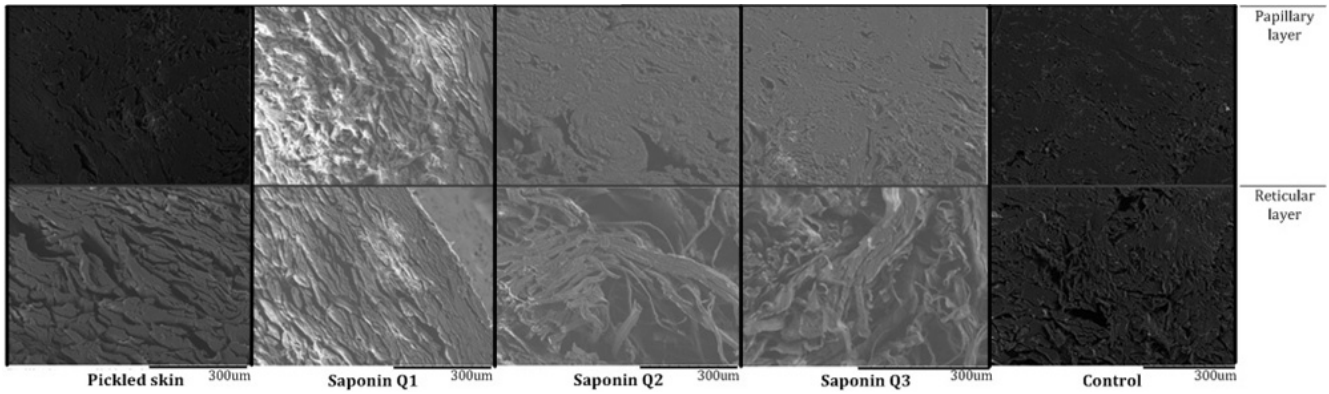

Figure 6. SEM microscopic images (250x magnification) of leather cross sections before and after biodegreasing with different saponin products comparable to control

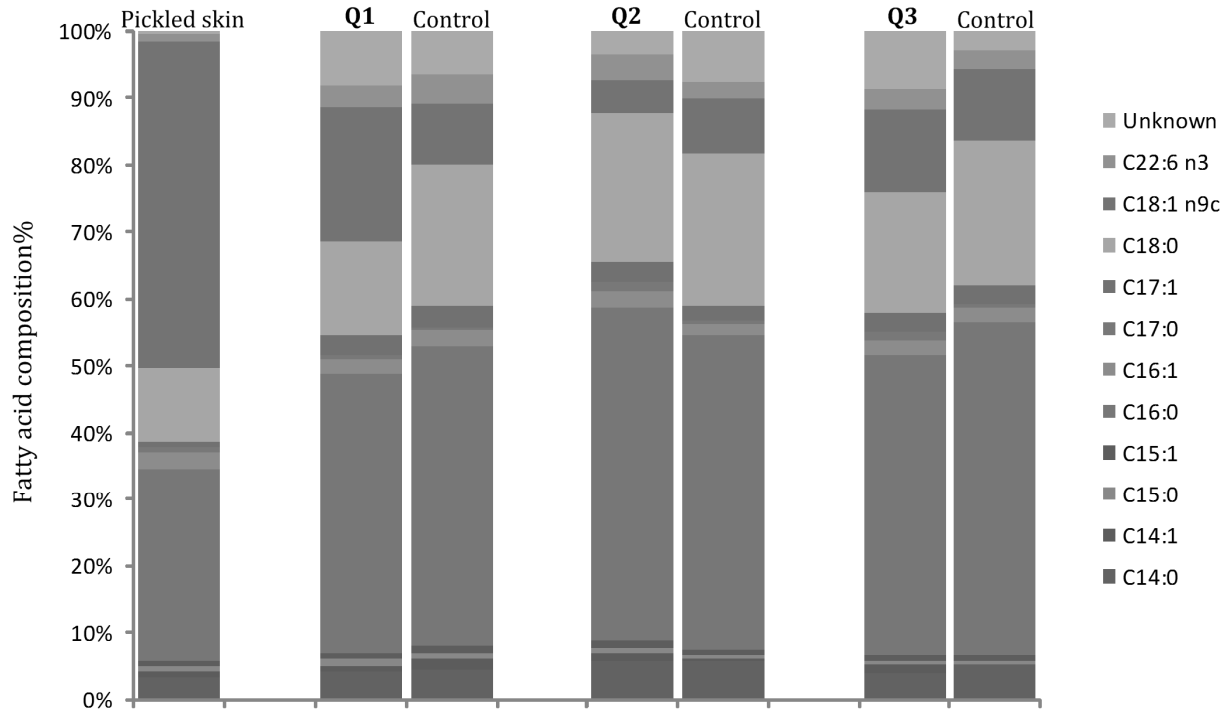

Figure 7. Comparison of fatty acid compositions (as percent fatty acid methyl esters) in pickled skin, control and biodegreased leathers

4. CONCLUSION

This research focused on the investigation of potential application of plant derived biosurfactant as an alternative biodegreasing agent for sheepskin degreasing. For this aim, applicability of three commercial Quillaja bark saponin products, with different degrees of sapogenin content were evaluated and the following conclusions have been drawn.

The saponin based biodegreasing method was more effective for concentrations above 2.5% when compared to control trials. The maximum fat removal rate 82% was obtained with 3.75% Q1 saponin. The degreasing efficiency, COD reduction in effluents and reduction of stearic acid content increased with increasing sapogenin concentration. The overall colour differences of samples also increased, mainly due to specific yellow colour of saponin product with higher levels of sapogenin.

Saponin based biodegreasing method allowed to obtain, comparable properties of biodegreased leathers to conventionally processed leathers in terms of dye levelness and physical texture corroborated by the micrographs taken with a scanning electron microscope. Moreover it will provide environmental protection and economical benefit as it enables high percentage of degreasing efficiency and reduction of wastewater discharged to the environment by eliminating subsequent brine washing cycles, both enabling salt and water saving. The results showed that plant derived saponin can be a viable and promising biodegreasing agent for leather industry.

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