Use of Ternary Solvent (Water – Ethanol – Ethyl Acetate) Medium for Leather Processing: A Possible Paradigm Change

by

Bhargavi Narayana Reddy Gari,[1] Solomon Fessehaye,[2] Rathinam Aravindhan,[1] Kalarical Janardhanan Sreeram,[1]*
Jonnalagadda Raghava Rao[1] and Balachandran Unni Nair[1]

[1]*Chemical laboratory, CSIR-Central Leather Research Institute,*
Adyar, Chennai, India

[2]*Leather Industry Development Institute,*
Addis Ababa, Ethiopia

Abstract

An attempt to replace water (7-10 m^3/ton) in leather processing with a ternary mixture of solvents that would have a lower boiling point than water (for easy recovery through evaporation) and also bring about maximum solubility of conventional dyes, syntans and fatliquors is reported. The ternary mixture (Water – ethanol – ethyl acetate) reported in this study provided for good solubility/dispersion of leather chemicals. Average particle size of the syntan/dye in solvent / water remaining the same, particle size distribution of dyes and syntans was advantageous in the solvent medium, leading to better diffusion. Amongst various trials, neutralization of the leathers after tanning in solvent medium followed by use of neutralization syntans was found to be more advantageous to obtain leather properties comparable to conventional controls. The adsorption studies of dye used in the present study followed Freundlich model in both solvent and water medium indicates multilayer adsorption. Physical properties of the leathers were similar to that of control, indicating clearly that the solvent had no adversary effect on collagen and also provided for good diffusion and fixation of chemicals. The method thus reported in this study could provide for a minimum change approach to leather processing with ample contribution to water saving.

Introduction

During the last two decades, the leather industry is emerging out of its traditional practices to one adopting best clean practices. A review of the literature would suggest that there is a basket of technologies for each processing step, adoption of which could be more environmentally benign and economically sustainable than the dependence on end-of-pipe treatment system alone. A look into the historical setting of leather clusters would reveal that their locations were predominantly in water rich zones. Many of these zones had no inherent raw material but had to be transported in. Today, some of these zones have gone barren or are highly polluted, leading to either close down or shifting of the industry from such locations.[1,2]

The growth of material science has enabled human kind to understand the benefits of using leather in some of our routines. Typical example is the case of footwear. It is slowly emerging that this industry may not be in a position to meet all the requirements of its customers, unless some out-of-box thinking and methodologies are developed to ensure independence from water in processing. Values such as 30-35 L/kg of hide/skin processed, effluent discharge of 50,000 m^3/day from Indian leather sector alone etc.[3,4] need to be those of the past to ensure sustainable leather production.[5]

During the last two years, an approach towards use of solvents for diffusion of leather chemicals into the skin matrix has been reported. This includes use of eutectic solvents, extraction of vegetable tanning materials and subsequent leather tanning in solvent media, ionic liquids as the fibre opening agents etc.[6-8] While most of these research works have pertained to the emission intensive processes in pre-tanning and tanning stage, adoption of such methodologies in post-tanning is considered challenging. This is predominantly because of a large number of specialized auxiliaries – trademark products of industrial houses, which are in use to obtain customer desired properties. The common feature of these products is that they have been subjected to reactions such as sulfonation that would make them water soluble. In spite of this challenge, water consumption in post-tanning cannot be ignored as the contributes to about 23% of the water consumed in leather processing.[9]

Based on this background, in the initial survey leading to this publication, a set of solvents selected from the GSK Solvent Selection Guide were evaluated for their ability to dissolve or disperse a significant number of commercial auxiliaries drawn from various classes of compounds.[10] Such of those selected

*Corresponding author e-mail: kjsreeram@clri.res.in
Manuscript reveived September 1, 2015, accepted for publication March 7, 2016

solvents were then tested for any adverse effect on collagen. Based on these initial studies, two solvents, viz., ethanol (EtOH) and ethyl acetate (EtOAc) were shortlisted based on the following considerations: a) good biodegradability and recyclability of these solvents and current use to replace water in processes such as dry cleaning, textiles and paints[11] and b) have no adverse effect on collagen.[12] Solvents chosen in this study are not marked in the red category with respect to VOC.[13] One of the major considerations, during our initial studies was the manner in which the identified solvents would interact with free water present in hides/skins or leather.

A further relook into these considerations led us to investigate various binary and ternary solvent mixtures involving water for dispersing/solubilizing commercial auxiliaries. This work reports in detail the results observed with one of the successful combinations, involving a set of auxiliaries employed for the manufacture of leather.

Experimental

Materials and Methods

A ternary mixture of water, ethyl acetate and ethanol (1:1:2) was employed in this study. The study reported here was carried out using analytical grade solvents to avoid interference from impurities. Auxiliaries selected for investigation were of commercial grade and those which were easily dispersed or had good solubility in the solvent mixture investigated were chosen for the leather trials. Wet blue goat skins were employed for the trials.

Dynamic Light Scattering Measurements

The changes in the particle size distribution of the syntans and dyes on dispersion into the solvent mixture was evaluated by dynamic light scattering technique using a Zetasizer Nano ZS (M/s. Malvern UK). The measurements were carried out at 25°C using a 4 mW He-Ne laser operating at 633 nm. Data was collected at a scattering angle of 173°.

Post Tanning Experiments

The experiments were carried out in tight fitting stainless steel drums without any acrylic transparent windows for observation. The speed of the drum was maintained at 15 RPM throughout the studies. Two wet blue goat shins were used for the study. The experiments were carried out employing the butt portion of the wet blue goat skins. Left sides were used for experiments trial, where ternary mixture was used for post tanning and the right sides were used for control trial, where water was used as medium. The post tanning process recipe is presented in Table I.

In order to have an understanding of the effect of neutralization on the processed leathers, neutralization was carried out in water as well as in solvent and employing mild alkali/neutralization syntans. Scheme of work carried out is presented in Figure. 1 for better understanding. In all 3 trials (marked as **1** – **3**) was carried out with corresponding water based control (marked as **1a** – **3a**). Conventional mechanical operations were carried out on the crust leathers.

Characterization of the Leathers

Employing IUP methods for sampling and analysis, the strength parameters were determined for both control and experimental leathers.[14-16] Color fastness properties to and fro rubbing of the dyed crust leathers was tested according to ISO 11640:1993(E) test method. Dry rub fastness was measured using Giuliani Rub Fastness tester. Quantification of color was carried out by reflectance measurements using Techkon SpectroDrive (TKSDEB) in order to know intensity of dye on grain side of the leather surface. The CIELAB 1976 color coordinates were determined using in built software.

Scanning Electron Microscopic (SEM) Analysis

A sample from experimental (**1**) and control crust leathers (**1a**) were cut from official sampling position. All specimens were then coated with Gold using Edwards E306m sputter coater. A Leica Cambridge Stereoscan 440 Scanning electron microscope was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 20kVat different magnification levels.

Visual Assessment

The experimental and control leathers were visually evaluated for various properties by experts drawn from the industry. The ratings have been provided in a scale of 1-10, with 10 being the best.

Adsorption Equilibrium and Diffusion Coefficient Studies of the Dye

Adsorption studies of the dye on the leather in the ternary solvent medium were carried out by contacting the leather with various initial concentrations of the dye solution. The samples for the experiments were obtained from the official sampling position

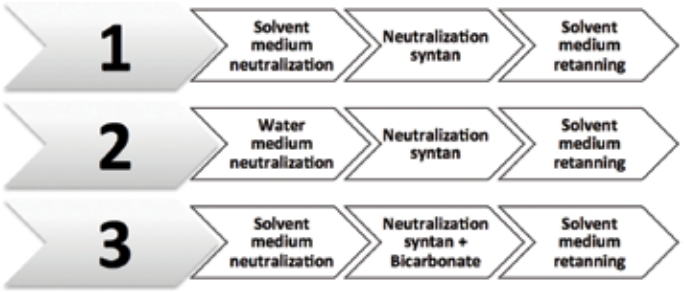

Figure 1. Scheme of trials employed to test the efficiency of ternary solvent mixture (Water-Ethanol-Ethyl acetate) to replace water in post-tanning processes.

Table I

Post tanning recipe (Product – Shoe Upper) employed to evaluate the efficacy of ternary solvent medium in leather processing.

Raw material: Wet blue goat skins. Ternary solvent: Water:EtOAc:EtOH (1:1:2).
All percentages calculated on shaved weight of wet blue goat skins.

Process	Chemicals	%	Time (minutes)	Remarks
Washing	Water	100	10	Drained
Neutralization	Ternary Solvent (Trial 1, 3) or Water (Trial 2) or water (all controls)	100		pH adjusted to 5.2 – 5.4 and bath drained and washed with solvent
	Neutralization syntan (Trial 1 and 2) or Neutralization syntan: sodium bicarbonate 1:1 for Trial 3	0.7	20	
Post-tanning	Ternary solvent (for all trials) or water (for control)	150		Dispersed the products in ternary solvents (1:10 ratio) for addition
	Acrylic syntan	2	20	
	Dye (anionic metal complex red)	2	20	
	Lecithin based fatliquor	3	30	
	Phenol-formaldehyde condensate based syntan	5	40	
	Melamine-formaldehyde condensate based syntan	5		
	Vegetable oil based fatliquor	3	60	
	Semi-synthetic fatliquor	3		
	Synthetic fatliquor	3		
	Formic acid	3	30x10+ 60	Addition in equal feeds of three, 10 min interval followed by 60 min
	Piled over night, toggle dry, staked			

(IUP 2) from a wet blue goat skin. In a shaker bottle, 6 g (dry weight) of the wet blue leather was weighed and 30 mL of dye solution containing various initial dye concentrations ranging from 167 to 1000 mg/L was added. The bottles were placed on a mechanical shaker for 2h at room temperature. The aliquots were drawn at every 15 min interval for 2h. The amount of the dye present in the samples was quantified using UV-Visible spectrophotometer (M/s. Shimadzu UV-1800) at 540nm. The absorbance was then converted into dye concentration value using a calibration graph. The amount of dye uptake was calculated by using the following formula

Where C_0 and C_e are the initial and equilibrium concentration of dye solution (mg/L) respectively, q_e is the equilibrium dye concentration on the leather (mg/g), V *is* the volume of the dye solution (L) and W is the weight of the leather (g).

Results and Discussion

The selected solvents, water, ethyl acetate and ethanol were employed in the ratio of 1:1:2 and found to be able to provide maximum solubility of leather auxiliaries selected for this study. The properties of this ternary system is well documented in the literature.[17-18] Interaction of these solvents with commercial leather auxiliaries, their performance on the leather was investigated.

Compatibility of Leather Auxiliaries with Ternary Solvent Mixture

The conventional leather auxiliaries are synthesized in such way to be completely soluble in water, so as to achieve better penetration. Accordingly, as expected, these auxiliaries were found to be insoluble in neat solvents (EtOAc and EtOH). When the solvents were in combination with water, i.e. ternary system, good solubility of the auxiliaries was observed. This has been attributed to the appropriate matching of dielectric constant of solvent mixture to the leather auxiliaries and/or reorientation of hydrogen bonding between the auxiliary and the solvents in the ternary mixture. Water acts as co-solvent to make auxiliaries soluble in ternary mixture. Recently the possibility of solubilisation of oils in binary mixtures of solvents has been attributed to matching of dielectric constants of binary mixtures with that of water.[7]

Particle Size Distribution

Penetration of the dyes and syntans into the skin matrix depends on the particle size of the dispersion in solution. Lesser the particle size of syntans and dyes in solution, better will be the penetration down to the hierarchy.[19] It can be seen from Figure. 2 that a mono dispersed system is observed for the dye dispersed in solvent mixture, indicating a homogeneous dispersion and thus a uniform hue can be expected. In tune with the size distribution observed, visual assessment by experts indicated good penetration, color uniformity, depth of shade and dry rub fastness for leathers post-tanned using solvent as the dispersion medium.

The average particle size of the syntan in water as well as in solvent mixture was found to be around 260nm (Figure 3). The pores between fibre bundles in collagen is known to be 50-500 nm so the syntan can gently penetrate into the leather in solvent medium same as in conventional water processing.

Characteristic Features of the Leather

The Strength properties of the leather are presented in Table II. The physical strength values are a measure of efficiency of tanning and fatliquoring. The leathers processed both in solvent and in water medium are satisfying standard values. This indicates that the process developed using the ternary solvent medium does not deteriorating the quality of the leathers. A characteristic observation made in this study is that the neutralization in the solvent medium followed by retanning and fatliquoring in the solvent medium resulted (Trial **1**) in leathers whose strength properties matched well with control rather than those where neutralization was carried out in water (Trial **2**). This is possibly because in Trial **1**, the free water in leather was completely replaced with the solvent medium during neutralization process. Our earlier studies (data not shown) indicated that the solubility of alkalis such as sodium bicarbonate was minimal in the binary system of EtOH- EtOAc and hence the ability of the same to raise the pH during neutralization was poor. However, in Trial 3, the presence of water in the ternary system enabled the dissolution of the alkali and thus a combination of this system could uniformly raise the pH to desired values. A complete and thorough neutralization resulted in leathers with properties similar to that of control (Trial **3**).

Proper distribution of the dye through matrix, followed by its fixation is critical to achieve the desired levels of rub fastness. From Table II, it could be seen that the experimental leathers had excellent dry rub fastness, indicating that the fixation of the retanning and fatliquoring agents were good even in the presence of the ternary solvent medium.

Color Coordinates

Color difference, calculated as $\Delta E = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2}$, where L_1, a_1 and b_1 are the color coordinates of trial and L_2, a_2 and b_2 are the

Table II

Physical properties and color difference of the leathers (trial vis-à-vis respective controls).

Product	Tensile strength (N/mm^2)	Percentage elongation at break (%)	Tear strength (N/mm)	Dry rub fastness (scale of 0 – 5)	ΔE
1	22.4	84.0	47.6	4	9.1
1a	24.9	83.9	51.0	4	
2	23.1	66.7	49.7	4/5	3.8
2a	29.0	97.1	58.1	4/5	
3	18.0	47.7	33.1	4	2.9
3a	18.2	51.4	34.6	4	

color coordinates of control respectively, is presented in Table II. It can be seen that other than in the case of Trial **1**, the ΔE values are below 5, indicating that the color difference between control and trial leathers will not be perceptible to an untrained eye. A closer look at the color coordinates for **1** and **1a** (54.02, 20.29, 20.73 and 45.09, 21.01, 19.13, respectively for L, a* and b* of 1 and 1a) indicates that the perceptible change was only in the L (lightness value). The leathers from Trial **1** were lighter than the control leathers, where water has been used as dispersing medium. The color coordinates have been obtained from the grain side of the leather. It is likely that for a given concentration of dye, the predominant part of dye penetrated well into the matrix for **1**. A likely offshoot to this observation could be that the solvent based dispersion medium could be advantageous for making suede leathers. As a whole, color measurement values depict that no major difference exists between solvent processed and water control leathers.

Visual Assessment

Three tanners have evaluated the crust leather from both control and experimental processes. Their evaluation in a scale of 0-10, with 10 being the highest is presented in Table III. Comparison between 1 and 1a reveals that the fullness for control trial is lesser by 1 unit. Deeper look at the Figure 3 would indicate that the maximum observed particle size when syntan in dispersed in solvent is 400 nm, while the same is slightly more aggregated in water (600 nm). Further the number of particles in the range of 1 – 10 nm, is significant in the case of syntan dispersed in solvent, indicating a better filling of the smaller pores leading to an increased grain smoothness (I unit more than control). Shade

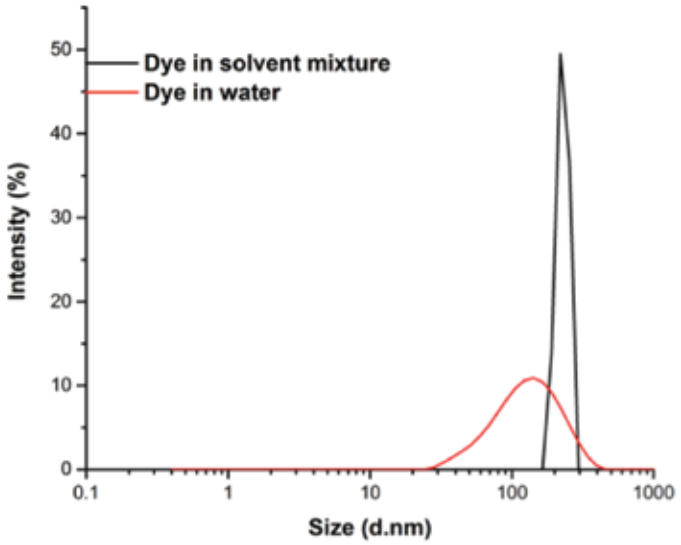

Figure 2. A comparison of the particle size distribution of dye dispersions in water and ternary solvent mixture.

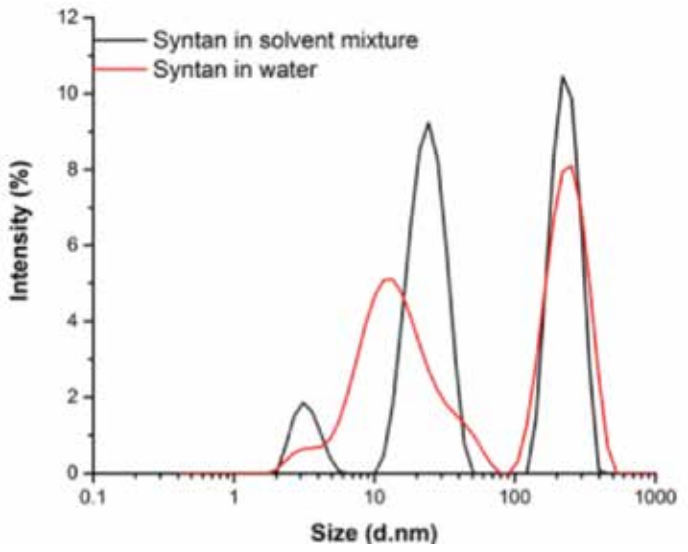

Figure 3. A comparison of the particle size distribution of a commercial aromatic syntan in water and ternary solvent mixture.

Table III

Visual assessment rating (scale of 1 – 10) provided for leathers prepared using conventional (water as diffusion medium) vis-à-vis experimental (solvent as diffusion medium).

Product	Full ness	Softness	Grain tightness	Grain smoothness	Dye penetration	Dye uniformity	Shade
1	7	8	8	8	8	8	7
1a	8	8	8	7	8	8	8
2	5	7	7	6	7	7	8
2a	7	8	8	9	9	9	8
3	7	6	7	7	5	7	6
3a	7	7	7	7	7	7	7

for experimental Trial 1 was lesser by 1 unit and this commensurate with observation on color coordinates. A further look into Figure 2, indicates that the particle size distribution of the dye employed in this study (indicated by black line in the figure) in solvent being homogenous and mono dispersed, a deeper penetration is expected compared to the same in water (indicated by red line in figure).

When neutralization was carried out in water medium, penetration was probably hampered due to aggregation of syntans at the interface of leather and solvent. This leads to a 2 unit decrease in fullness for Trial **2**. Aggregated particles create inhomogeneity leading to decreased rating when compared to control.

Except for dye penetration, softness and shade all parameters were similar between **3** and **3a.** This can be attributed to presence of neutral salts in the leather, arising from a bicarbonate neutralization, which was not completely removed by solvent washing after neutralization.

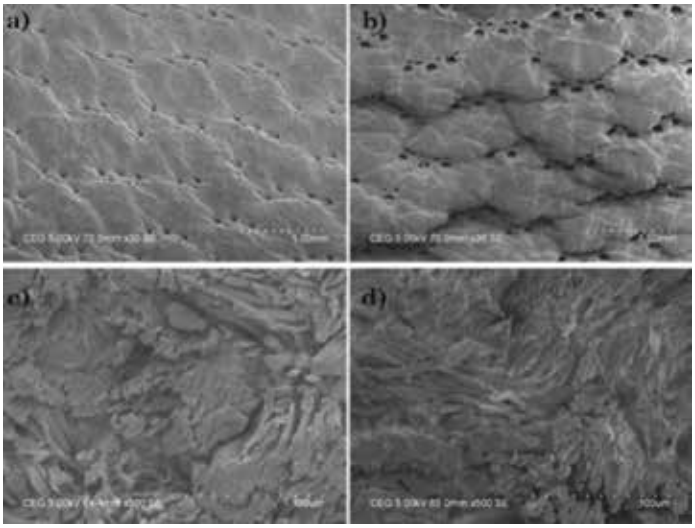

Figure 4. Scanning electron microscopic images a. grain **1**, b. grain **1a,** c. cross section of **1**, d. cross section of **1a**.

An inter comparison between the three trials clearly indicates that a solvent neutralization followed by neutralization using syntans was the best way forward.

Morphological Evaluation of Leather

Morphological study of **1** and **1a** was carried out using scanning electron micrograph. The grain surface and cross-section of the control and experimental leathers at magnification of 30X and 500X respectively, are depicted in Fiure 4. It has been observed that the grain surface is clean without any foreign particles for both water and solvent processed leathers. This could be due to the optimal solubilization and dispersion of post tanning auxiliaries especially syntans and fatliquors. Pores are well opened and showed uniformity in grain pattern for both control and experimental leather. Cross section shows compact fibres, indicating solvents were not involved in damage of fibres of collagen.

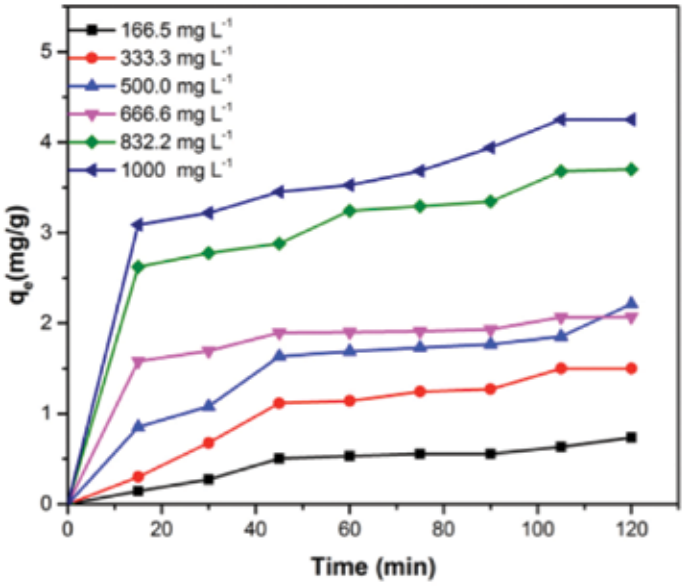

Figure 5. Trend in equilibrium dye uptake as against time in the solvent medium.

Table IV
Freundlich and Langmuir constants for water and solvent medium.

	Freundlich			Langmuir		
	K	**n**	**R^2**	**q_0**	**b**	**R^2**
Water	0.325	1.677	0.889	9.398	0.012	0.6141
Solvent	0.0121	1.1287	0.8939	6.25	0.0015	0.737

Adsorption Isotherms

Adsorption studies have been carried out in order to find out the maximum uptake capacity of the wet blue leather for the dye used in the study. The studies have been carried out both in water and in solvent medium in order to establish the effect of solvent on the dye uptake behaviour of the wet blue leather. Adsorption of dye to the surface of the leather is limited by the number of active sites (-NH_3^+) available. The equilibrium dye uptake capacity of the wet blue leather in both water and solvent medium at various concentration of the dye are shown in Figure 5 and 6, respectively, It could be observed that the equilibrium dye uptake capacity of the wet blue (mg/g of leather) increased with increase in initial dye concentration, in both the medium. However, it is inferred from the data, trend in dye removal and equilibrium dye uptake has been similar in both solvent and water. Hence, it could be inferred that the solvent does not affect the dye uptake behaviour of the wet blue leather.

The experimental data obtained has been analysed by two models namely Langmuir and Freundlich isotherm models in order to know the adsorption phenomena on the leather surface in the water and solvent medium. Langmuir isotherm assumes that the adsorbent surface is homogenous and the adsorbate forms a monolayer on the adsorbent surface. The Langmuir

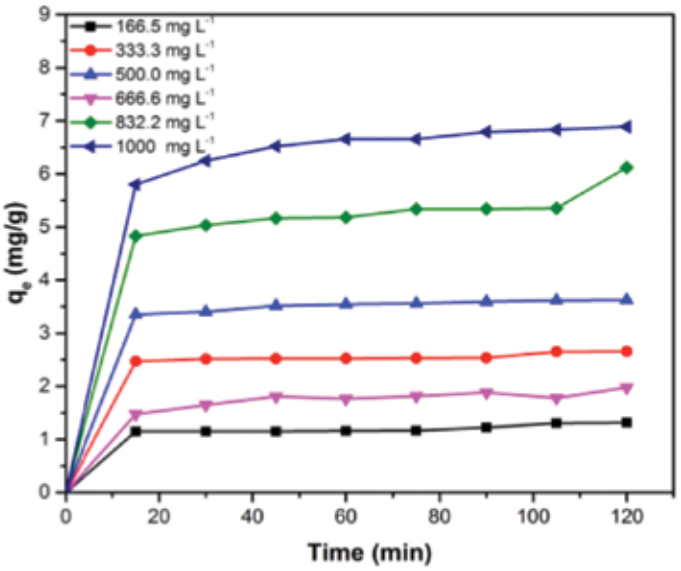

Figure 6. Trend in equilibrium dye uptake as against time in the water medium.

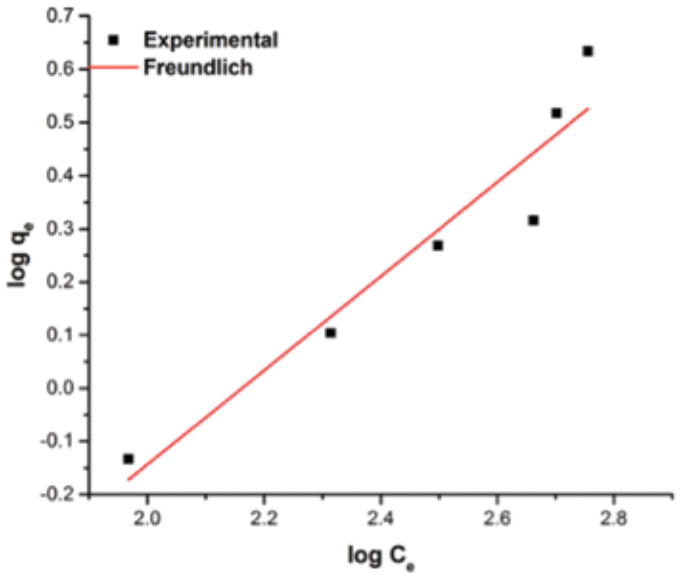

Figure 7. Comparison of solvent medium (experimental) data by using Freundlich isotherms model fit.

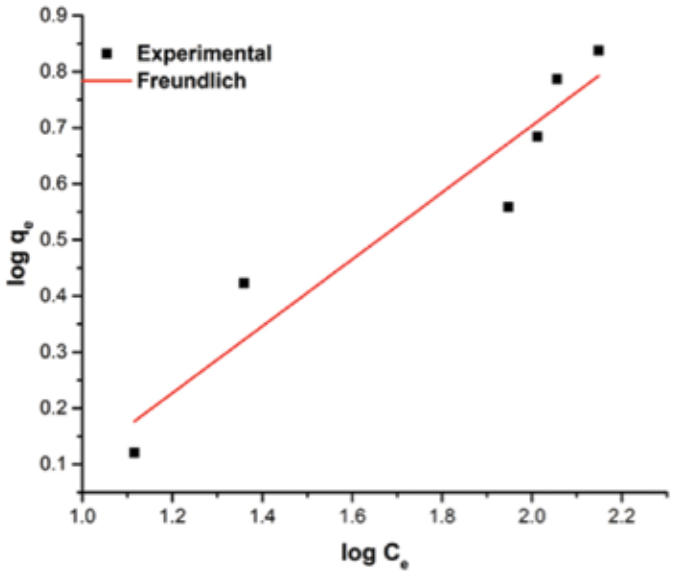

Figure 8. Comparison of water medium (control) data by using Freundlich isotherms model fit.

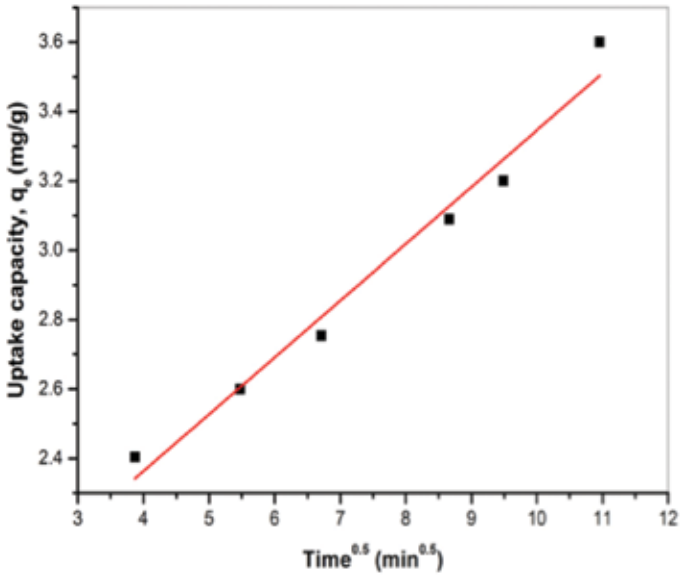

Figure 9. Plot to determine the diffusion coefficient of dye (red metal complex dye dispersed in ternary solvent medium) on leather.

constants q_0 and b has been obtained from the linear plot of C_e/q_e versus C_e, which has a slope of $1/q_0$ and an intercept of $1/q_0b$. The linear form of Langmuir expression is given in the following equation.

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0}$$

The adsorption of dye by the wet blue leather has also been analysed by Freundlich isotherm model. This model express that the surface is heterogeneous and consists different adsorption sites. The Freundlich constants *n* and *k* were obtained from the following linear regression equation.

$$\log q_e = \log K + \frac{1}{n}\log C_e$$

Where n and K are Freundlich constants and can be obtained by liner plot of log *q*e versus log *C*e contains log K intercept and 1/n as the slope.

Figure 7 and 8 shows Freundlich isotherm for the solvent and water medium, respectively. The obtained Freundlich and Langmuir constants for the solvent and water medium are presented in Table IV. From the table, correlation coefficient (R^2) value for water and solvent as per Freundlich model is higher compared to Langmuir model. This observation reveals that the adsorption of dye on to the wet blue leathers in both water and solvent medium are heterogeneous in nature and follows Freundlich model.

Calculation of Diffusion Coefficient of the Dye in Solvent Medium

The process of transfer of solute from the solvent medium is studies by calculating diffusion coefficients for the initial concentration of 0.833×10^{-3} g.cm^{-3}. From the Figure 9, plot of dye uptake versus $t^{0.5}$, the slope of the linear plot was found to be 0.16386 mg/g.min. In order to predict the actual slow step involved, the kinetic data are further analyzed using Boyd kinetic expression, which is given by[20-21]

$$F = 1 - \frac{6}{\pi^2}\exp(-B_t)$$

and

$$F = \frac{q_t}{q_e}$$

Where q_e is the amount of dye adsorbed at infinite time (mg/g) and q_t represents the amount of dye adsorbed at any time t (min), F represents the fraction of solute adsorbed at any time t and B_t is a mathematical function of F, given by:

$$B_t = -0.4977 - \ln(1 - F)$$

The linearity of the plot of Bt vs time is used to distinguish whether external and intraparticle transport controls the adsorption rate. It is observed that the relation between B_t and t is linear (Average R^2=0.991) and does not pass through origin, confirming that surface diffusion is the rate-limiting step.[20, 22] The calculated B values are used to calculate the effective diffusion coefficient, D_i (cm^{2}s^{-1}) using the relation:

$$B = \pi^2 \frac{D_i}{r^2}$$

Where r represents the radius of the particle (assuming as spherical particles). The average D_i value was found to be 3.48 x10^{-4} cm^{2}s^{-1}.

Conclusions

The feasibility of use of green solvents in post tanning operations as alternative to water for leather processing was explored in this paper. The judicial choice of the solvents from GSK solvent selection guide for the present study is of particular importance. The green solvents chosen to be used as an alternative medium for leather processing should give the same or enhanced leather properties and at the same time should not give rise to any pollution load. The physic-chemical properties of the post tanning chemicals in the solvent medium present uniform size distribution, leading to good penetration into the matrix. Metal complex dyes in solvent mixture were found to have a homogenous and narrow particle size distribution compared to water medium which was also confirmed with respect to penetration, depth of dye and dry rub fastness on processed leather. When it comes to the neutralising medium solvent neutralised and solvent processed samples were having good appearance and properties. Adsorption isotherms of the dye in water and solvent medium follows same trend and fits to the Freundlich model, with multilayer adsorption being observed. The average diffusion coefficients of the dye in solvent medium was found to be 3.48 x 10^{-4} cm^2.s^{-1} and found to be comparable with water mediated diffusion. Microscopic images of the leather treated with solvent mixture showed uniform grain pattern and compact cross section. The physical strength measurements of solvents processed leather portrays that solvents are not deteriorating the functional properties of collagen fibres.

This report thus opens up an opportunity to explore ternary solvent mixtures as a diffusion vehicle for current auxiliaries, leading to water reduction in leather processing with minimum change. Though not investigated as a part of the study, the boiling point of the ternary mixture being less than that of water, a complete recovery of the solvent through evaporative methods is feasible.

Acknowledgements

CLRI Communication Number 1165. The authors acknowledge the financial support of Supra Institutional project Research Initiatives in Waterless Tanning (RIWT) under the CSIR XII Plan programs. Authors thanks to Mr. G.C. Jayakumar for his support. Mr. Solomon Fessehaye thanks the Government of Ethiopia and the Twinning project between CLRI and LIDI for enabling him to carry out this research partly at CLRI and LIDI.

References

1. Tünay, O., Kabdaşli, I., Orhon, D., Cansever, G.; Use and minimization of water in leather tanning processes. *Water Sci. Technol.* ***40,*** 237-244, 1999.
2. Durai, G., Rajasimman, M.; Biological Treatment of Tannery Wastewater- A Review. *Environ. Sci. Technol.* ***4,*** 1-17, 2011.
3. Ozgunay, H., Colak, S., Mutlu, M., Akyuz, F.; Characterization of leather industry wastes. *Polish J. Env. Stud.* ***16,*** 867, 2007.
4. MIDHA, V., DEY, A.; Biological treatment of tannery wastewater for sulfide removal. *Int. J. Chem. Sc* ***6,*** 472-486, 2008.
5. Jessop, P. G.; Searching for green solvents. *Green Chem.* ***13,*** 1391-1398, 2011.
6. Abbott, A. P., Alaysuy, O., Antunes, P., Douglas, A. C., Guthrie-Strachan, J., Wise, W. R.; Processing of Leather Using Deep Eutectic Solvents. *ACS Sustain Chem Eng 3, 1241-1247, 2015*
7. Bhargavi, N., Jayakumar, G. C., Sreeram, K. J., Raghava Rao, J., Nair, B. U.; Towards Sustainable Leather Production: Vegetable Tanning in Non-aqueous Medium. *JALCA* ***110,*** 97-102, 2015.
8. Jayakumar, G. C., Ami, M., Raghava Rao, J., Nishad Fathima, N.; Ionic liquids: new age materials for eco-friendly leather processing. *RSC Adv* ***5,*** 31998-32005, 2015.
9. Raghava Rao, J., Chandrababu, N., Muralidharan, C., Balachandran, U. N., Rao, P., Ramasami, T.; Recouping the wastewater: a way forward for cleaner leather processing. *J. Cleaner Prodn.* ***11,*** 591-599, 2003.
10. Henderson, R. K., Jiménez-González, C., Constable, D. J., Alston, S. R., Inglis, G. G., Fisher, G., Sherwood, J., Binks, S. P., Curzons, A. D.; Expanding GSK's solvent selection guide–embedding sustainability into solvent selection starting at medicinal chemistry. *Green Chem.* ***13,*** 854-862, 2011.
11. Capello, C., Fischer, U., Hungerbühler, K.; What is a green solvent? A comprehensive framework for the environmental assessment of solvents. *Green Chem.* ***9,*** 927-934, 2007.
12. Ami, M., Raghava Rao, J., Nishad Fathima, N.; Can green solvents be alternatives for thermal stabilization of collagen? *Int. J. Biol. Macromol.* ***69,*** 361-368, 2014.
13. Henderson, R. K., Jiménez-González, C., Constable, D. J., Alston, S. R., Inglis, G. G., Fisher, G., Sherwood, J., Binks, S. P., Curzons, A. D.; Expanding GSK's solvent selection guide–embedding sustainability into solvent selection starting at medicinal chemistry. *Green Chem* ***13,*** 854-862, 2011.
14. IUP2. Sampling. *J. Soc. Leather Technol. Chem* ***84,*** 303-309, 2000.
15. IUP6. Measurement of tensile strength and percentage elongation. *J. Soc. Leather Technol. Chem* ***84,*** 317-321, 2000.
16. IUP8. Measurement of tear load - Double edge tear. *J. Soc. Leather Technol. Chem* 327-329, 2000.
17. Resa, J. M., Goenaga, J. M., Iglesias, M., Gonzalez-Olmos, R., Pozuelo, D.; Liquid-liquid equilibrium diagrams of ethanol+ water+(ethyl acetate or 1-pentanol) at several temperatures. *J Chem Eng Data* ***51,*** 1300-1305, 2006.
18. Trofimova, M., Toikka, M., Toikka, A.; Solubility, liquid–liquid equilibrium and critical states for the quaternary system acetic acid–ethanol–ethyl acetate–water at 293.15 K. *Fluid Phase Equilibria* ***313,*** 46-51, 2012.
19. Burgess, D.; General aspects of fatliquoring: an introduction to the application and chemistry of fat liquoring. *J. Soc. Leather Technol. Chem.* ***78,*** 39-43, 1993.
20. Boyd, G., Adamson, A., Myers Jr, L.; The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics1. *J. Am. Chem. Soc.* ***69,*** 2836-2848, 1947.
21. Aravindhan, R., Rao, J. R., Nair, B. U.; Removal of basic yellow dye from aqueous solution by sorption on green alga Caulerpa scalpelliformis. *J Hazard Mater* ***142,*** 68-76, 2007.
22. Gupta, V. K., Ali, I.; Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste. *Water Res.* ***35,*** 33-40, 2001.