Moisture Desorption Characteristics of Raw Sheep and Goat Skins: A Tool for Eco-friendly Method of Preservation

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Abstract

Preservation of animal skins by conventional salt or brine curing methods leads to environmental pollution. Controlled drying up to acceptable moisture levels could be an effective, cleaner and environmentally friendly alternative for skin preservation. The selection of optimum storage and drying conditions requires the knowledge of moisture desorption isotherms. Hence this work focuses on the experimental determination of desorption isotherms for south Indian sheep and goat skins at three different temperatures 30, 40 and 45°C. The goodness of fit of four sorption models to experimental results was determined. Of the models tested, the modified Oswin gave the best fit followed by modified Halsey. Modified Henderson and modified Chung Pfost models showed relatively larger deviations from the experimental values. The deviation was larger in sheep skins compared to goat skins. The net isosteric heat of sorption was determined for both sheep and goat skins using the Clausius - Clapeyron equation and is expressed mathematically as an empirical polynomial function of equilibrium moisture content. The net isosteric heat of sorption for sheep skin was higher than the goat skin.

Resumen

La preservación de las pieles por métodos convencionales por medio de sal o salmuera conducen a la contaminación ambiental. Secamiento bajo control hasta niveles aceptables podría ser un efectivo, más limpio y ambientalmente amigable alternativa para la preservación de las pieles. La selección de las condiciones óptimas para almacenar y secar requiere el conocimiento de las isotermas relacionadas con la desorción de humedad. Consecuentemente este trabajo se enfoca en determinar experimentalmente las isotermas de desorción asociadas con pieles de ovejas y cabras a tres temperaturas diferentes, 30, 40 y 45 °C. La cercanía al buen ajuste descriptivo de cuatro modelos de absorción a los datos experimentales fue determinada. De los modelos probados, el de Oswin modificado dio el mejor ajuste seguido por el de Halsey modificado. Los modelos modificados de Henderson como así el Chung Pfost mostraron mayores desviaciones de resultados de los experimentales. La desviación fue relativamente más extensa en pieles ovinas en comparación con caprinas. La absorción neta isoestérica de calor fue determinada tanto para los ovinos cómo los caprinos por medio de la ecuación de Clausius-Clapeyron y matemáticamente expresada cómo una función polinómica empírica del contenido de humedad en equilibrio. El contenido neto isoestérico de calor absorbido por las pieles de oveja fue mayor que en las caprinas.

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Manuscript received June 15, 2012, accepted for publication September 26, 2012.

Introduction

Many moisture bearing materials such as animal skins, fruits, leaves and grains need to be better preserved for further processing and extended use. Animal skins, especially after separation from carcass are more susceptible to deterioration, owing to their high moisture (60-70%) and protein contents (25-30%).[1] Because of such favourable moisture conditions, autolytic degradation of skin starts within 5 - 6 hours after the death of the animal. The rate of deterioration depends on several factors such as temperature, humidity, skin contamination etc.[2]

There are several skin preservation techniques such as conventional salt curing, chemical treatment methods, biocidal treatment methods, chilling, drying etc. Preservation of skins and hides by salt is based on application of sodium chloride at a concentration of 40 - 50%.[1] The dual functions of common salt viz., dehydrating ability and bacteriostatic effects are used advantageously in this method.Other chemical treatment methods use boric acid,[3] soda ash,[4] sodium sulphide and sodium borate [5] for skin preservation.Biocidal methods use benzalkonium chloride,[6] antibiotics viz., Aureomycin, Terramycin and tetracycline.[7] Chilling the skins at about 5 - 10°C has been reported as a preservation technique.[8] However, many of the above mentioned methods are either inefficient or energy intensive or environmentally polluting.[5] Controlled drying of animal skins up to acceptable moisture levels has been proved to be an effective, environmentally friendly and energy efficient skin preservation technique. [9-11] Simultaneous heat and moisture transfer take place during the drying of skins. Many of the changes occurring during drying are functions of temperature, moisture content and time.[12] Therefore, undesirable effects could be better controlled, if temperature and moisture distributions in materials as a function of drying time could be accurately predicted.

Mathematical models are very useful in the design and analysis of simultaneous heat and moisture transfer processes. For a moisture bearing material such as skin, water activity is function of moisture content and the temperature. Knowledge of this relationship (the moisture sorption isotherm, MSI) is essential for the prediction of evaporative losses and potential for microbial growth.[13] These moisture sorption isotherms are useful thermodynamic tools for the selection of appropriate storage and drying conditions of animal skins. These isotherms are developed through the relationship between equilibrium moisture content and equilibrium relative humidity or water activity.Most bacterial growth causing deterioration ceases at a water activity below 0.9. Most yeast stop to grow below a water activity of 0.8 and moulds cease at a value of 0.7. Materials below a water activity of 0.6 are stable to microbial growth and are classified as dehydrated.[14] The interaction between water vapour and the adsorbent material should be determined to define the temperature effect, characterised by isosteric heat of sorption (Q_{st}) values. The adsorption and desorption equilibrium in these systems is most often described by the sorption isotherms. Based on these isotherms we can define the heat of sorption released when water is bound to the material.

There are several models available in the literature[15-19] which relates equilibrium moisture content and water activity of a material with temperature. The focus of this work is to experimentally determine the moisture desorption isotherms for sheep and goat skins of south Indian origin at different temperatures and to fit the experimental data with different desorption models. The south Indian sheep skins do not contain wool but has hairs like goat skins. In general the percentage of water, fat, proteins etc. in animal skins varies from one region to the other and also depends upon age, species, breed and health of animals.[20]

Therefore the objectives of this work are to:

- Experimentally obtain moisture desorption isotherms for south Indian sheep and goat skins at three temperatures 30, 40 and 45°C;
- Analyse four desorption isotherm models available in the literature;
- Find the most suitable model describing the isotherms of sheep and goat skins under consideration;
- Calculate the net isosteric heat of water sorption from the experimental data.

Experimental

Materials

Freshly flayed skins of goat and sheep were purchased from a local abattoir (Chennai, India) and used for this work. Identical pieces of skin from the neck and butt portions were considered for analysis due to the following reasons: The fibre structure in the butt region is tight and relatively consistent. Hence the physical properties of the butt skin are also consistent. Moreover, the butt skin is relatively firm, stiff and thick compared to the belly. The skin from the neck region is the thickest compared to all other portions, however with an open structure.[21] Hair removed skins were refrigerated in order to prevent deterioration. The skins were then cut into small pieces of size 5 × 5 cm.Five pieces of skin each from the neck and the butt regions were used for each analysis and the measurements were averaged. Free and total moisture contents were determined using differential scanning calorimetry and thermo gravimetric analysis respectively.Analytical equipments, 2910 DSC V4.4E and 2950 TGA V5.4A (both supplied by TA Instruments, USA) were used for the above mentioned analysis. A vacuum oven (supplied by M.C. Dalal & Co, India) was used for the drying purpose. Analytical grade sulphuric acid procured from S.D. Fine Chemicals Limited, Mumbai was used for varying the relative humidity and hence the water activity of the skin.

Methods

Estimation of Free and Bound Moisture

To estimate the amount of free moisture present in the skin, 10 - 15 mg of skin sample from the neck portions was scanned in a DSC at the heating rate of 5°C/min from – 40°C to 40°C. The experimental results were then compared with enthalpy of melting of ice made using de-ionized water, under identical conditions. In order to find out the total moisture content of skins, thermo gravimetric analysis (TGA) was used.

Pre-drying

Initial drying was carried out in a vacuum oven at a temperature of 40 - 45°C for 4 days until the free moisture is removed. This was verified through the DSC experiments. The skin pieces were hanged using pointed clips so that both the faces are exposed to the same drying conditions.

Drying Studies at Thermodynamic Equilibrium

The pre-dried skins were subjected to thermodynamic equilibrium studies under various relative humidity atmospheres at constant temperature. The relative humidity was varied by varying the concentration of sulphuric acid placed in the oven.[22, 23] Experiment was carried out at temperatures of 30, 40 and 45°C. Drying was limited to 45°C as temperature beyond that can lead to significant reduction in the properties of the processed leather.[5] The schematic of the experimental setup is shown in Fig. 1. After equilibrium is reached, the samples were re-weighed and the moisture content was determined. Thus the desorption isotherms for goat and sheepskins were obtained.

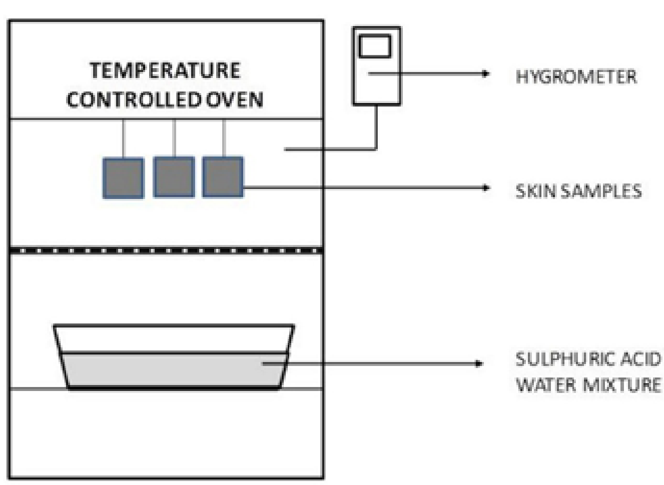

Figure 1. Schematic of the experimental setup.

Analysis of Sorption Data

A large number of models have been proposed in the literature for the sorption isotherms. In the present study, the description of the relationship between equilibrium moisture, equilibrium relative humidity or water activity, and temperature for sheep and goat skins was verified according to the following models. These models are widely used for predicting the desorption characteristics of food products.[17, 19]

1. Modified Chung Pfost [24]

$$x = \frac{-1}{A} ln\left(-ln(a_w)\frac{t+B}{C}\right) \quad (1)$$

2. Modified Halsey [25]

$$x = \left(\frac{-\exp(A+Bt)}{ln(a_w)}\right)^{\frac{1}{c}} \quad (2)$$

3. Modified Oswin [26]

$$x = (A+Bt)\left(\frac{a_w}{1-a_w}\right)^{c} \quad (3)$$

4. Modified Henderson [27]

$$x = \left[\frac{-ln(1-a_w)}{A(t+B)}\right]^{\frac{1}{c}} \quad (4)$$

Where X is the Equilibrium Moisture Content (EMC) as ratio, a_w is the water activity, t is the temperature in °C, A, B and C are model parameters. The model parameters vary from one material to the other.

To find the model that fits the experimental data with less error the Mean Relative Error (MRE) was found and this is calculated by using eqn. (5)

$$MRE = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{(X_{i,\exp} - X_{i,pred})}{X_{i,\exp}}\right| \quad (5)$$

Where N is the number of experimental data, and $X_{i,exp}$ and $X_{i,pred}$ are the experimental and predicted moisture content (ratio) respectively.

Determination of Heat of Sorption

The differential heat of sorption can be determined from the moisture sorption isotherm data by applying the Clausius - Clayperon equation on the isosteric equilibrium pressures at different temperatures.[16, 25] Like foodstuffs, the complexity of the physical and chemical structure of animal skins makes the theoretical prediction of heat of sorption impossible. However, the isosteric heat of sorption is a very useful quantity, especially in drying operations. Isosteric heat of sorption is defined as the total heat of sorption of water from the material minus the heat of vaporization of water. The definition of isosteric heat of sorption as a differential molar quantity is as follows.

$$Q_{st} = \frac{-[R\ d(ln a_w)]}{d\left(\frac{1}{T}\right)} \quad (6)$$

Where Q_{st} is the isosteric heat of sorption, (KJ/mol) and R is the universal gas constant (KJ/mol K). The net isosteric heat of sorption can be calculated by plotting the sorption isotherm as - $ln(a_w)$ vs (l/T) for certain values of the material moisture content and then determining the slope which is equal to Q_{st}/R. This net isosteric heat is assumed to be invariant with temperature. However, the application of this method requires the measurement of sorption isotherms at two or more temperatures.

RESULTS AND DISCUSSIONS

Free and Total Moisture

Analysis revealed that the moisture content of sheep skin was relatively higher than that of goat skin. The free moisture content of sheep and goat skins as determined by DSC was 60.18 and 52% respectively. The total moisture content of sheep and goat skins as determined by TGA was 76.18 and 68.51% respectively. Sheep skin is said to possess fat content higher than goat skin. However, it is relatively porous and less fibrous than goat skin. This porous nature could be the reason for relatively higher free moisture content of sheep skins.

Moisture Sorption Isotherms

The sorption isotherms of sheep and goat skins obtained at three different temperatures 30, 40 and 45°C are shown in Fig. 2. From these isotherms, it can be noted that the equilibrium moisture content increases with decreasing temperature at constant water activity.

This may be due to the higher excitation state of water molecules at higher temperatures, thus increasing their distances apart and decreasing the attractive forces between them. This could have led to decrease in the degree of water sorption at a given water activity (or equilibrium relative humidity) with increasing temperature. Furthermore, at constant temperature, the equilibrium moisture content increases with increasing water activity. Results similar to this have been reported for food stuffs.[13,16,17,19] Skins or any moisture bearing materials have higher moisture levels at higher relative humidity than at lower relative humidities. Hence the sigmoid shape of the moisture sorption isotherms can be attributed to the changes in the vapour pressure of water in the skins.

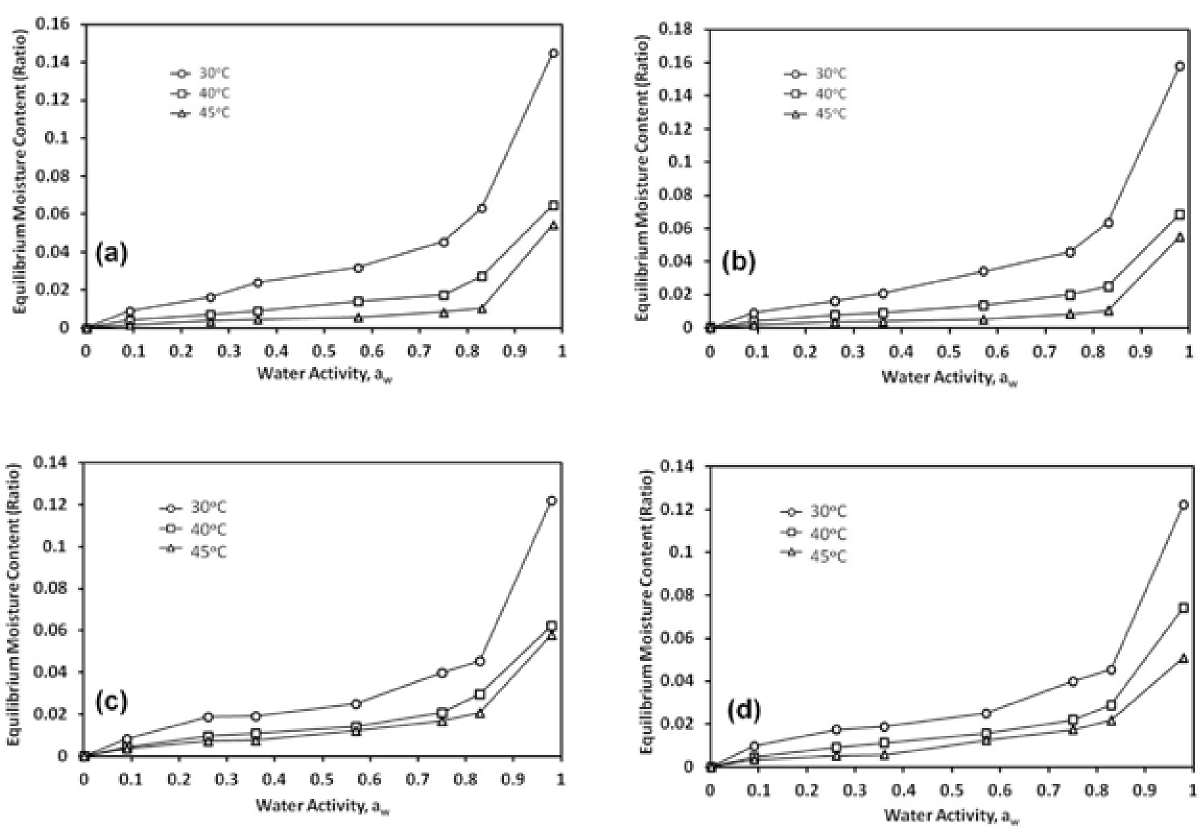

Figure 2. Influence of temperature on the desorption isotherm of (a) Sheep neck skin; (b) Sheep butt skin; (c) Goat neck skin; (d) Goat butt skin.

Fitting Sorption Models to Experimental Isotherms
The four models mentioned in equations (1) to (4) were fitted to the sorption isotherm data presented on Fig. 2. Graphical representation of the goodness of fit of theoretically determined isotherms at 30, 40 and 45°C are shown in Fig. 3 and Fig. 4 for sheep and goat skins respectively.

The model fit coefficients, error criterion and the standard deviation (S.D) for sheep and goat skins are presented in Table I. On comparing the four models, modified Oswin isotherm gave the best fit and also the least MRE value. This was followed by modified Halsey isotherm which gave the second best fit. Modified Henderson and modified Chung Pfost isotherms showed relatively larger deviations from the experimental values with marked differences at a_w values above 0.8. The deviation was more pronounced in the case of sheep skin than in goat skin. Consequently the modified Oswin model can be selected for better description of the desorption isotherm of sheep and goat skins.

Heat of Sorption
The values of isosteric heat of sorption for both sheep and goat skins were calculated from the slope of the plot between $-ln$ (a_w) versus $1/T$ at constant moisture content as shown in Fig. 5. The net isosteric heat of sorption for different moisture contents is shown in Fig. 6. It can be observed that the net isosteric heat decreases when the moisture content increases. Many similar trends have been reported in the literature for other materials.[16,19,28]This may be due to sorption occurring on more number of active sites available at low moisture contents.

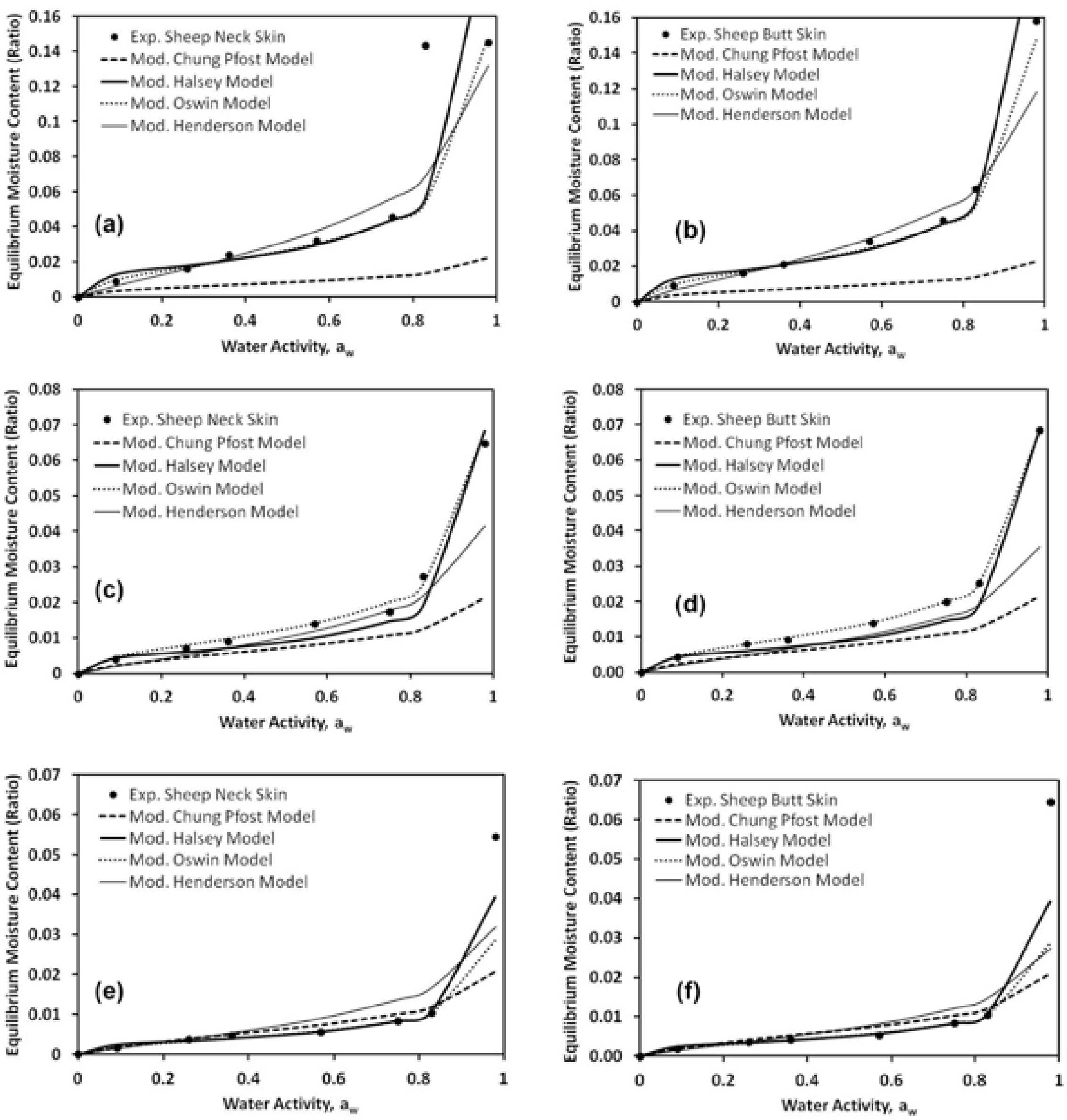

Figure 3. Desorption isotherms of (a) Sheep neck skin fitted by four models at 30°C; (b) Sheep butt skin fitted by four models at 30°C; (c) Sheep neck skin fitted by four models at 40°C; (d) Sheep butt skin fitted by four models at 40°C; (e) Sheep neck skin fitted by four models at 45°C; (f) Sheep butt skin fitted by four models at 45°C.

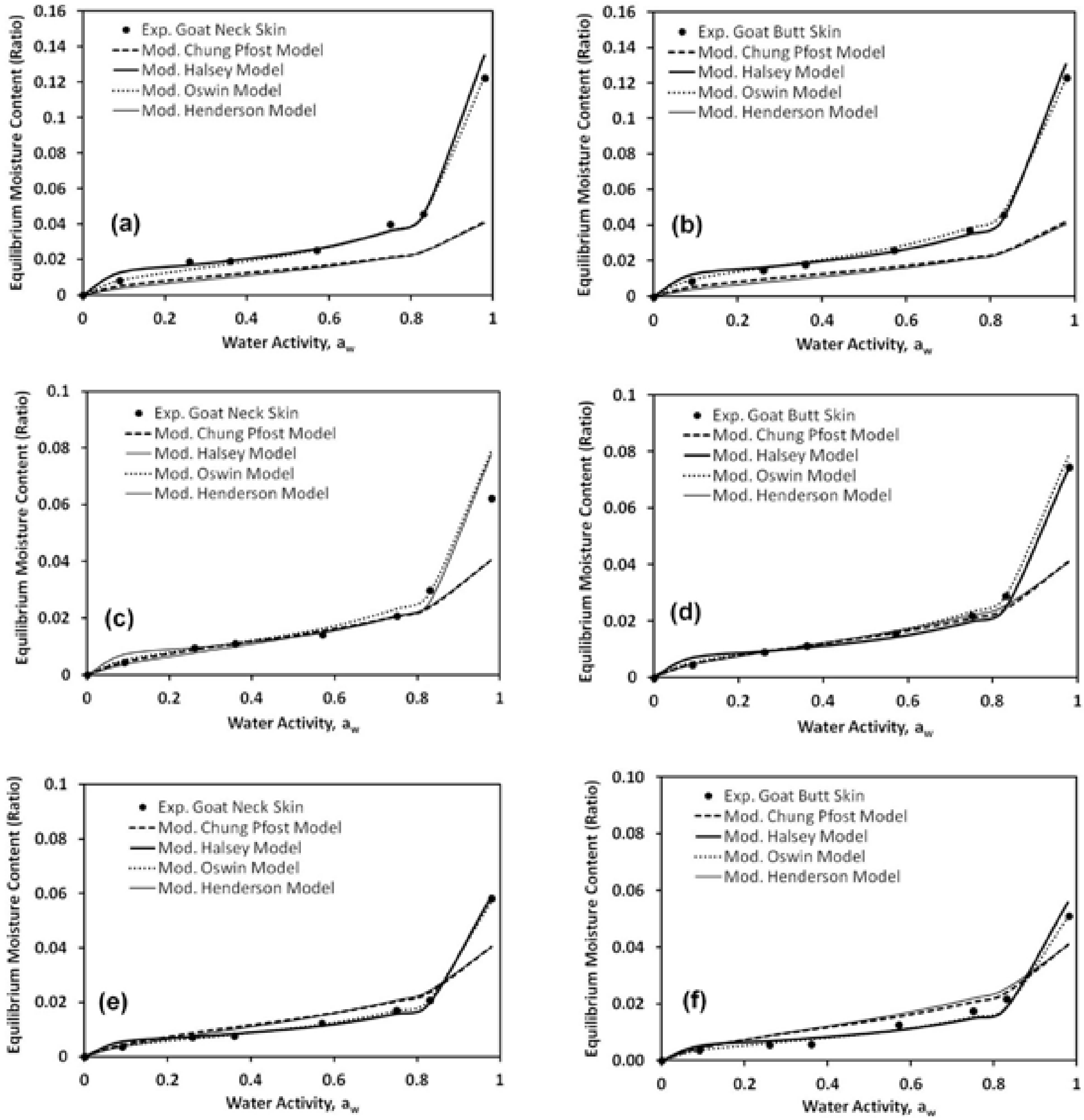

Figure 4. Desorption isotherms of (a) Goat neck skin fitted by four models at 30°C; (b) Goat butt skin fitted by four models at 30°C; (c) Goat neck skin fitted by four models at 40°C; (d) Goat butt skin fitted by four models at 40°C; (e) Goat neck skin fitted by four models at 45°C; (f) Goat butt skin fitted by four models at 45°C.

As moisture levels increase, only fewer active sites are available to the water molecules to bind. This leads to lower isosteric heats of sorption. On further increasing of moisture levels, heat of sorption tends to approach the value of pure water. This indicates that the existence of moisture in its free form.[25,28] For the skins under consideration, the magnitude of heat of sorption for the neck skin is close to the butt skin for both sheep and goat skins. However, the Q_{st} values for the sheep skin are roughly two times that of goat skin at given moisture content. This could be due to the resistance offered by the fat content to moisture removal in the sheep skin.

The magnitude of heat of sorption at given moisture content indicates the state of the sorbed water in a material. Hence this could be used to determine the physical, chemical and microbiological stability of the sheep and goat skins. The net isosteric heats of desorption of water in sheep and goat skins can be expressed mathematically as a function of% moisture content on dry basis (M) as follows:

Sheep neck skin:

$$Q_{st} = 4.5166\,M^2 - 46.495\,M + 132.39 \; (r = 0.9987) \quad (7)$$

Sheep butt skin:

$$Q_{st} = 2.799\,M^2 - 32.913\,M + 106.64 \; (r = 0.9961) \quad (8)$$

Goat neck skin:

$$Q_{st} = 1.4115\,M^2 - 17.156\,M + 56.248\ (r = 0.9965) \quad (9)$$

Goat butt skin:

$$Q_{st} = 1.0215\,M^2 - 14.325\,M + 51.729\ (r = 0.9977) \quad (10)$$

Here r is the product moment correlation coefficient. These mathematical relationships may be used to calculate the heat of sorption of sheep and goat skins for various moisture contents.

CONCLUSIONS

Desorption equilibrium moisture data have been collected for a range of temperatures and relative humidities commonly used in drying and storage of sheep and goat skins. The sorption isotherms of sheep and goat skins obtained at three temperatures (30, 40, and 45°C) showed a trend similar to other moisture bearing materials reported in the previous studies. The experimental data were fitted to four isotherm models. The modified Oswin equation gave the best fit followed by modified Halsey equation, for desorption isotherms of sheep and goat skins. The equilibrium moisture

TABLE I
Model parameters estimation and MRE of the four models fitted to sorption isotherms of the skins studied.

Skin Type	Model	Model Parameters			MRE (%)	S.D
		A	B	C		
Sheep neck skin	Modified Chung Pfost	250.2653	-2.5756	154.3057	46.70	0.0339
	Modified Halsey	-0.9455	-0.1891	1.7198	16.75	0.0144
	Modified Oswin	0.0703	-0.0015	0.4383	9.42	0.0064
	Modified Henderson	14.5080	-26.7782	1.2232	25.33	0.0088
Sheep butt skin	Modified Chung Pfost	250.2199	-4.4870	154.5940	47.74	0.0364
	Modified Halsey	-0.9455	-0.1892	1.7199	15.18	0.0116
	Modified Oswin	0.0703	-0.0015	0.4383	6.87	0.0067
	Modified Henderson	22.2001	-27.2830	1.2801	25.82	0.0135
Goat neck skin	Modified Chung Pfost	132.0549	114.2541	672.9171	26.64	0.0205
	Modified Halsey	-4.5816	-0.1109	2.0044	12.85	0.0050
	Modified Oswin	0.0464	-0.0008	0.4374	7.30	0.0041
	Modified Henderson	0.0272	20979.9700	1.5537	28.45	0.0208
Goat butt skin	Modified Chung Pfost	130.4573	113.7688	672.9820	30.40	0.0209
	Modified Halsey	-4.5816	-0.1132	2.0041	15.00	0.0032
	Modified Oswin	0.0505	-0.0009	0.4292	7.25	0.0014
	Modified Henderson	0.0395	20979.7700	1.6757	32.36	0.0211

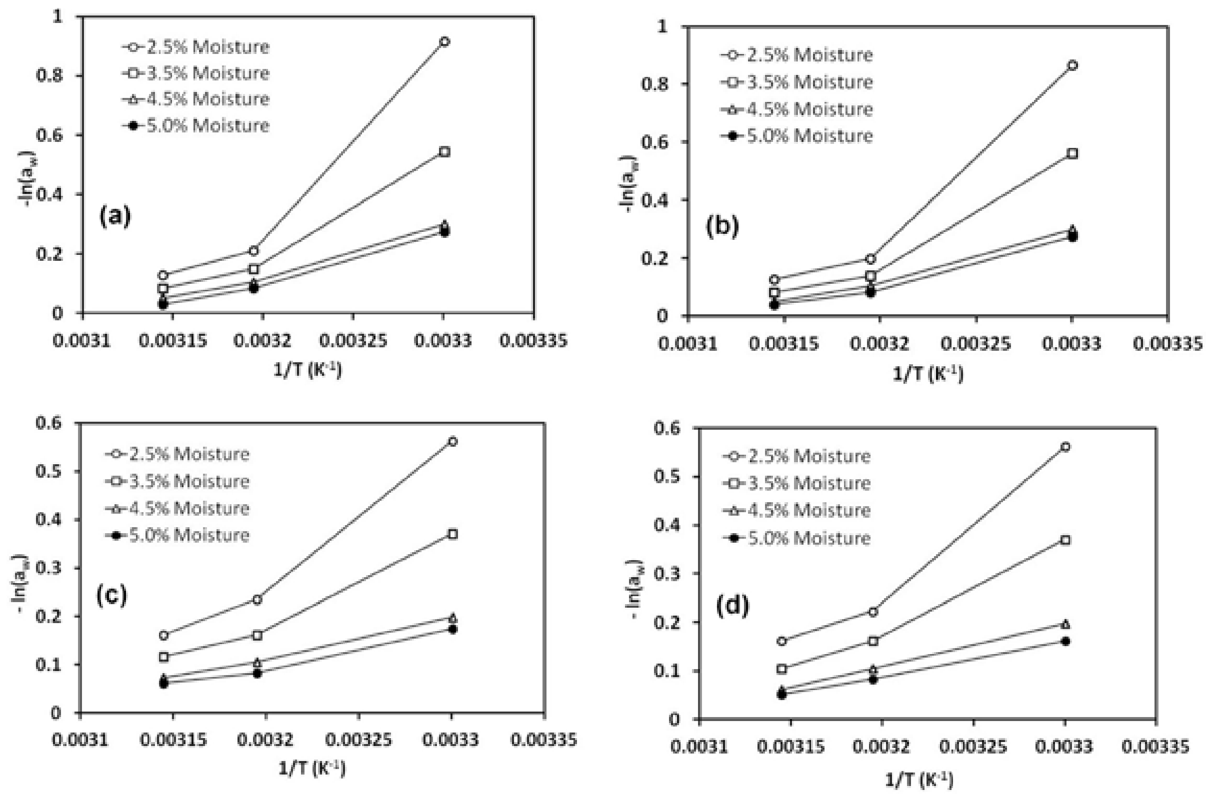

Figure 5. - ln (a_w) vs 1/T graph for calculating the heat of sorption of (a) Sheep neck skin;(b) Sheep butt skin; (c) Goat neck skin; (d) Goat butt skin.

content decreased with increasing temperature. By applying the Clausius – Clapeyron concept, the net isosteric heats for desorption were evaluated and it is expressed as an empirical polynomial function of moisture content. Sheep skins showed higher heat of desorption of moisture than goat skins. The moisture desorption isotherms and the heat of sorption values would be highly useful for the determination of optimum storage and drying conditions for sheep and goat skins.

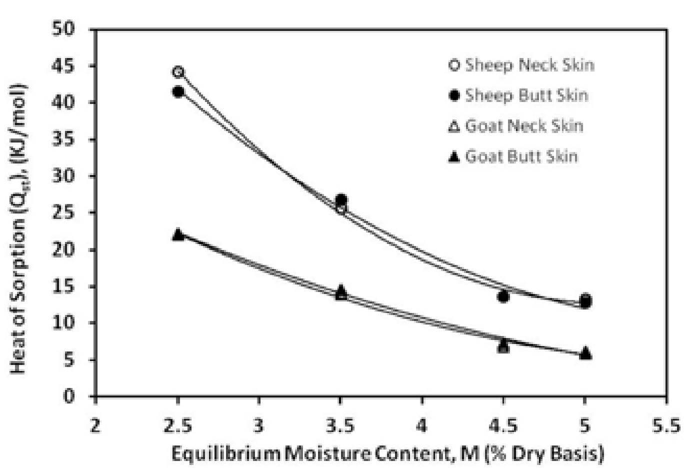

Figure 6. Net isosteric heat of sorption for Sheep and Goat skins of different moisture contents.

Nomenclature

EMC	Equilibrium Moisture Content
X	Equilibrium moisture content (kg of water/kg of dry sample)
$X_{i, exp}$	ith experimental moisture content (kg of water/kg of dry sample)
$X_{i, pred}$	ith predicted moisture content (kg of water/kg of dry sample)
M	Equilibrium moisture content (% dry basis)
t	Temperature in (°C)
T	Temperature in (K)
a_w	Water Activity (decimal)
A, B, C	Model coefficients
MRE	Mean Relative Error (%)
N	Number of data points
Q_{st}	Net isosteric heat of sorption (kJ/mol)
R	Universal gas constant (8.314 J/mol K)
S.D	Standard Deviation

REFERENCES

1. Kanagaraj, J., Sundar, V. J., Muralidharan, C., and Sadulla, S.; Alternatives to sodium chloride in prevention of skin protein degradation - a case study. *J. Clean Prod.* **13**, 825 – 831, 2005.
2. Bienkiewicz, K.J.; Physical Chemistry of Leather Making, Robert E. Krieger Publishing Company, Florida, USA, 1983
3. Hughes, I. R.; Temporary preservation of hides using boric acid. *J. Soc. Leather Tech. Chem.* **58**, 100 – 103, 1974.
4. Rao, B. R., and Henrickson, R. L.; Preservation of hides with soda ash. *JALCA* **78**, 48–53, 1983.
5. Rai, C. L., Surianarayanan, M., Sivasamy, A., and Chandrasekaran, F.; Pollution prevention by salt free preservation of raw goatskins through stepwise drying. *Int. J. Environ Eng.* **1**, 295-305, 2009.
6. Cordon, T. C., Jones, H. W., Naghski, J., and Jiffee, J. W.; Benzalkonium chloride as a preservative for hide and skin. *J. Soc. Leather Tech. Chem.* **59**, 317–326, 1964.
7. Berwick, P. G., Berbi, S. A., and Russel, A. E.; Use of antibiotics for short term preservation. *J. Soc. Leather Tech. Chem.* **74**, 142-150, 1996.
8. Marsal, A., Dratacos, E., and Portavella, M.; Drying of raw goatskins by heat pump: an alternative to salting. *J. Soc. Leather Tech. Chem.* **81**, 156-159, 1997.
9. Yates, J. R.; Investigations into the controlled drying of sheepskins. *J. Soc. Leather Tech. Chem.***61**, 235–255, 1966.
10. Waters, P. J., Stephen, L. J., and Sunridge, S.; Controlled drying. J. *Soc. Leather Tech. Chem.* **65**, 32, 1997.
11. Bailey, D. G.; Evergreen hide market ready, *The Leather Manufacturer***115**, 22–26, 1997.
12. Wang, N., and Brennan, J. G.; A mathematical model of simultaneous heat and moisture transfer during drying of potato. *J. Food Eng.* **24**, 47-60, 1995.
13. Trujillo, F. J., Yeow, P. C., and Pham, Q. T.; Moisture sorption isotherm of fresh lean beef and external beef fat. *J. Food Eng.* **60**, 357-366, 2003.
14. Labuza, T. P.; The effect of water activity on reaction kinetics of food deterioration. *J. Food Technol.* **34**, 36-41, 1980.
15. Van den Berg, C., and Bruin, S.; Water activity and its estimation in food systems: theoretical aspects. In Rockland LB and Stewart GF (Eds.). Water activity: influences on food quality, New York: Academic Press, 1981
16. McLaughlin, C. P., and Magee, T. R. A.; The Determination of sorption isotherm and the isosteric heats of sorption for potatoes. *J. Food Eng.* **35**, 261-280, 1998.
17. Chen, C.; Moisture sorption isotherms of pea seeds. *J. Food Eng.* **58**, 45-51, 2003
18. Al-Muhtaseb, A. H., McMinn, W. A. M., and Magee, T. R. A.; Moisture sorption isotherm characteristics of food products: a review. *Trans IchemE, Part C.* **80**, 118 -128, 2002.
19. Mohamed, L. A., Kouhila, M., Jamali, A., Lahsasni, S., and Mahrouz, M.; Moisture sorption isotherms and heat of sorption of bitter orange leaves (Citrus aurantium). *J. Food Eng.* **67**, 491 – 498, 2005.
20. Dutta, S. S.; An Introduction to the Principles of Leather Manufacture, fourth ed. Indian Leather Technologists Association, Calcutta, 1999.
21. Covington, A. D., Covington, T.; Tanning Chemistry: The Science of Leather. Royal Society of Chemistry, Cambridge, UK, 2009.
22. Vaxelaire, J.; Moisture sorption characteristics of waste activated sludge, *J. Chem. Technol. Biotechnol.* **76**, 377-382, 2001.
23. Collins, E. M.; The partial pressures of water in equilibrium with aqueous solutions of sulphuric acid. *J Phys Chem.* **37**, 1191-1203, 1933.
24. Pfost, H. B., Maurer, S.G., Chung, D. S., and Milliken, G. A.; Summarizing and reporting equilibrium moisture data for grains, American Society of Agricultural Engineers, Paper No. 76-3520, St. Joseph, MI, USA, 1976.
25. Iglesias, H.; Chirife, J. Prediction of effect of temperature on water sorption isotherms of food materials. *J. Food Technol.* **11**, 109–116, 1976.
26. Oswin, C. R.; The kinetics of package life. III. Isotherm. *J. Soc. Chem. Ind.* **65**, 419 – 421, 1946.
27. Thompson, T. L., Peart, R. M., and Foster, G. H.; Mathematical simulation of corn drying - a new model. *Trans. Am. Soc. Agr. Eng.* **11**, 582–586, 1968.
28. Correa, P. C., Goneli, A. L. D., Junior, P. C. A., de Oliveira1, G. H. H., and Valente,D. S. M.; Moisture sorption isotherms and isosteric heat of sorption of coffee in different processing levels. *Int. J Food Sci Technol.* **45**, 2016 – 2022, 2010.