Development of Improved Liming Process based on Automated pH Monitoring and Control System

by

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Abstract

The control of pH of a process plays an important role in many chemical or biological reactions. The monitoring and control of pH of processes like wastewater treatment, manufacturing food and leather making facilitate to reduce pollution and improve the quality of the final product. The focus of this study is to optimize the usage of lime and recycling of spent liquor through continuous monitoring system of pH to achieve near zero residue from liming operation. But the challenges are nonlinear behaviour of the system and frequent fouling of pH sensors. The system developed monitors the pH values and controls the cycling time and the addition of lime as per the user set profile. The real time data of pH values in the process is logged on to the PC for further analysis. The efficacy of the system developed was validated at lab level and can be easily scaled up for implementation in industries. The results showed that the effluent from leather making can be minimized by adopting automated pH monitoring and control systems.

Introduction

Typically, treatment of animal skin or hides with Calcium hydroxide –($Ca(OH)_2$) is called liming. Liming is an important process in leather processing where soaked hides/skins are treated with a Calcium Hydroxide ($Ca(OH)_2$) solution along with Sodium Sulfide (Na_2S) or other unhairing agents in pit/drum/paddle methods. It is a slow process and depending upon the type of leather, the processing time varies from a few hours to a few days. During this process,alkali soluble proteins - interfibrillary proteins and keratinous matter are removed in addition to opening up the fiber bundles of skin. After unhairing the hides/skins are treated with $Ca(OH)_2$ solution again in the reliming process to achieve the required degree of fiber opening and taken for flesh removal. This process is also time consuming and requires large quantities of alkalis.

A detailed literature survey on liming showed different chemicals and different methods to speed up liming process have been attempted by many researchers. A very rapid liming and subsequent tanning process without effluent by dipping in sodium sulfide solution and followed by treatment with 10% sodium peroxide solution for 1 hour has been attempted earlier.[1,2] A lime free unhairing system has been reported by using 3% caustic soda, 1% salt, ,1-2% sodium sulfhydrate.[3]A continuous automatic beamhouse processing was reported by rapid soaking of brine cured hides and unhairing using 4-6% sodium sulfide solution for 10 minutes.[4] Other reports include rapid oxidative unhairing using calcium peroxide to avoid using sodium sulfide in the unhairing process.[5] Attempts were made to apply the beam-house chemicals with optimal requirement to minimize pollution.[6,7] A modified method where the unhairing-liming liquids were reused several times after being recharged by reduced quantities of chemicals.[8] Some reported other methods such as oxidative unhairing of skin using hydrogen peroxide, amine,[9] oxidative unhairing,[10] sulfide free unhairing using ozone,[11] ionic liquids,[12] and phase transfer catalyst[13]as alternative improved liming methods.

The monitoring and control of the pH in the liming process is needed because the degree of swelling of skin or hide is high at higher concentrations of lime solution. The hair is also loosened at higher concentrations, making it suitable for further processing.

Automation of processes in different industries such as food processing are pursued in order to ensure product safety and quality.[14] In garment manufacturing automation has been reported to reduce the labor cost and improve the quality of the finished products.[15] In fertilizer industry the soil nutrient sensor detects and quantifies the amount of nitrogen, potassium and phosphorous in the soil and the automation system helps in recommending the right amount of fertilizers to be added to the soil.[16] Programmable logic controller (PLC) based dosing systems in leather making reduces wastage of chemicals and help in reducing pollution load.[17]

The main objective of this research work is to develop a process technology to minimize the usage of lime and the reduction of lime sludge and effluents from the liming process through suitable instrumentation technology.

This research work describes an automated liming process. It also includes development of an instrumentation system along with

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its application software for measurement, data logging, analysis, control and generation of reports. Testing of developed automated pH monitoring and control system in the liming process under various conditions in real time have been carried out and presented in this paper.

Experimental

Materials and Methods

The automated pH monitoring and control system for liming operation was installed and studied at Central Leather Research Institute, India. A model of automated pH monitoring and control system is provided in Figure 1. This consists of lime saturation tank, magnetic stirrer, liming tank, liquid transfer pump and pH electrodes for continuous monitoring of pH of the solution. Lime, sodium sulfide used were of industrial grade supplied by commercial manufacturers, India. The experiments were carried out with goat skins weighing approximately 1 kg per piece. The requirements of lime and water have been optimized through preliminary experiments. The process details are given in Table I. Studies have been carried for 6 batches using 3 skins per batch.

Lime at 0.375% and 2.0% sodium sulfide added and stirred to 250% water in the lime saturation tank to attain pH 12. Subsequently, computer monitoring and control was initiated. Then through the solenoid valve the transfer of fluid took place from the saturation tank to the reaction tank where soaked goat skin was processed for the removal of hair for 4 hours duration. After 4 hours duration, the spent liquor was transferred to the saturation tank and the next instalment of lime 0.375% was added. The stirrer starts through application software and the lime dissolves and pH raises close to 12 within 10 minutes. Then the transfer of liquid to reaction tank

Figure 1. Automated pH Monitoring and Control System

and comes in contact with the skin for liming. Then, the cycle was repeated for six times(six instalments of lime addition) and monitored for quality parameters of the skins. Then the skin was unhaired, weighed and reliming was done for the duration of 24 hours. The experimental and conventionally limed skins were taken for further processing into crust leather as per the process details given in Annexure.

Description of Instrumentation System

Based on the requirements of the automated liming process, the prototype system has been developed with two tanks - one for holding saturated lime solution with a stirrer and one reaction tank for liming and reliming of the skin. The instrumentation system consists of acrylic tanks, pump, pH sensors, stirrer which operates on the power supply of 230 V AC 50Hz. Two pH measurement systems with industrial grade sensors and transmitters were installed in

Table I
Chemical usage of Liming Process

Chemicals	Automated Liming (based on skin wt)		Conventional Liming (based on skin wt)	
	Liming Process	Reliming Process	Liming Process	Reliming Process
Quantity of Water (%)	250	250	250	250
Quantity of Lime (%) (per installment)	0.375	0.375	10	5
Quantity of sodium sulfide (%)	2.0	Nil	2	Nil
Total amount of lime used for 6 batches (%)	2.25	2.25	Nil	Nil
Total amount of lime used (%)	2.25	2.25	10	5

both the tanks. Since this process deals with high caustic pH values (10-12 pH), the transmitters should work in the desired range with an accuracy of 0.01% full scale display and communication output either 4-20 mA or digital output like RS485 based MODBUS communication. The pH measurement is dependent on the temperature of the process; hence, auto temperature compensating pH transmitters were used.

Sensing pH Electrodes (Industrial grade pH electrode, SIMS instrumentation, India) were selected with suitable construction for continuous operation in caustic pH values and to facilitate accurate measurement. Pumps were selected with variable speed to control the transfer of lime saturated liquor with high level of particulate matter.

The control system was developed with desk top PC and Data Acquisition Cards to acquire the pH inputs and generate control signals to the solenoid valves and pumps through Solid State Relays. The system was an open-source integrated development that supports the functions and utilities to develop all types of real-time automation and control applications with appropriate drivers for the data acquisition boards/cards.

Figure 2 shows the functional block diagram of the automated liming process. The instrumentation system consists of two pH meters, PC with data acquisition (DAQ) module, with an output signal through solid state relay (SSR) for actuating stirrer, solenoid valve and peristaltic pump. The pH meter records pH values in real time from both the tanks to obtain pH of the solution. The DAQ is programmed to log inputs from the two pH meters and analyzes the status and time. Based on the decision-making algorithm digital outputs generated through the DAQ card is applied to the SSR to the actuators.

The specification of the DAQ board is given below:

USB-4711A is a multifunctional module, which has 16-ch Analog Input, 2-ch Analog Output, 16-ch Digital I/O and counter channel which is able to output a constant frequency square wave.

Device Features

a) Analog Input

- 16-channel Single-Ended A/D Input for USB4711/A, 8-channel Differential-Ended A/D Input for USB4711A
- 12-bit A/D conversion
- Sampling rate for USB4711 from 1 Hz to 100 kHz
- Input Range: +/-0.625V, +/-1.25V, +/-2.5V, +/-5V and +/-10 V
- Automatic Channel/Gain Scanning

b) Analog Output

- 2-channel D/A Output
- Output Range with internal reference: +/-10V, +/-5V, 0~10V, 0~5V

c) Digital Input and Output

- ˜8-channel Digital Input

d) Counter

- USB4711: one 32 bit counter with max to 1k input rate

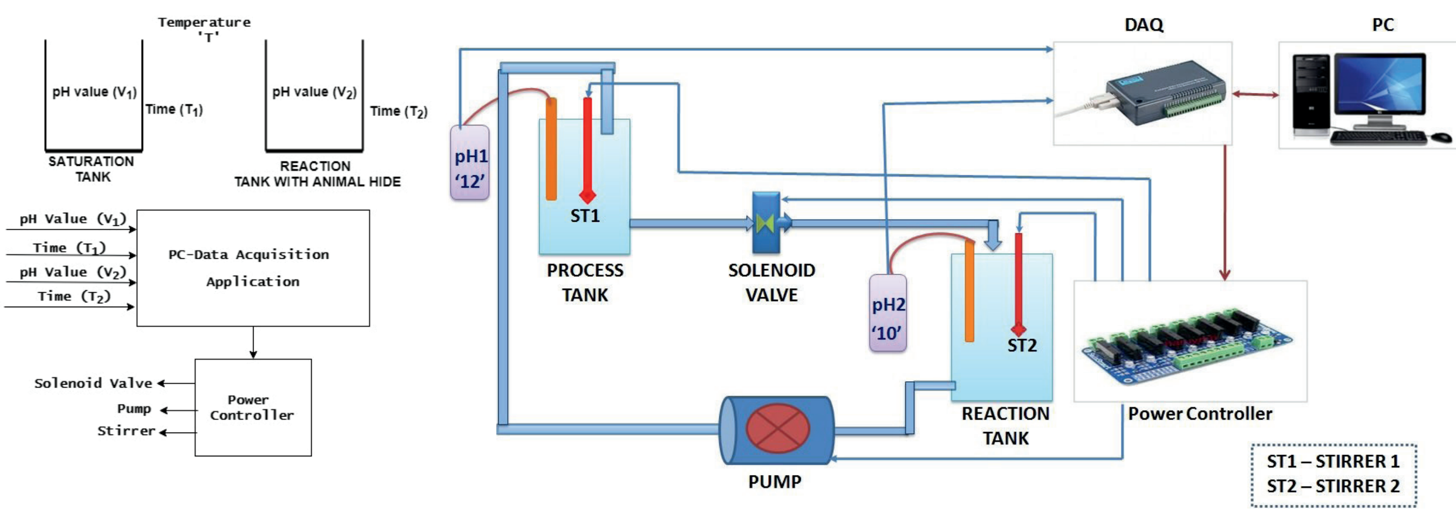

Figure 2. Functional Block Diagram of Automated Liming Process

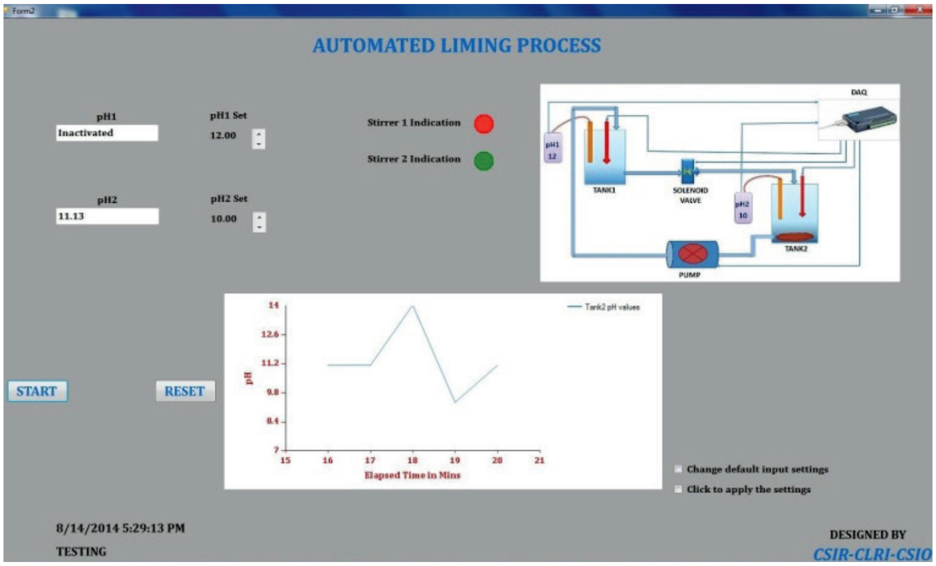

Figure 3. Window of Application Software

Application Software Description

Automated liming process application software was developed using Visual Studio IDE and compatible DAQ drivers. The application comprises of two windows, Form 1 deals with security and process details. Form 2 window comprises the automated liming process as shown in Figure 3. As per the storage interval entered, the data will be logged once for the specified interval in an Excel file.

The Form 2 window displays the real-time analog pH values against the programmable pH set-points, the status of the stirrers, solenoid valve and a peristaltic pump. The real time pH values of the elapsed time in the process are plotted and displayed continuously. This plot along with the current date and time and the project name, as indicated in the Form 2 Window, will be stored in an Excel file for future analysis. Moreover, an indication will appear in the window during the instant the data is logged along with the location of the file regularly.

Application Software

The various functions in the application software are explained in Figure 4. *Load and Initialize Process (Form 2 Window):* Form 2 is the process algorithm to control the pump, solenoid valve and stirrer based on the real time values of pH monitored in the two tanks and time.

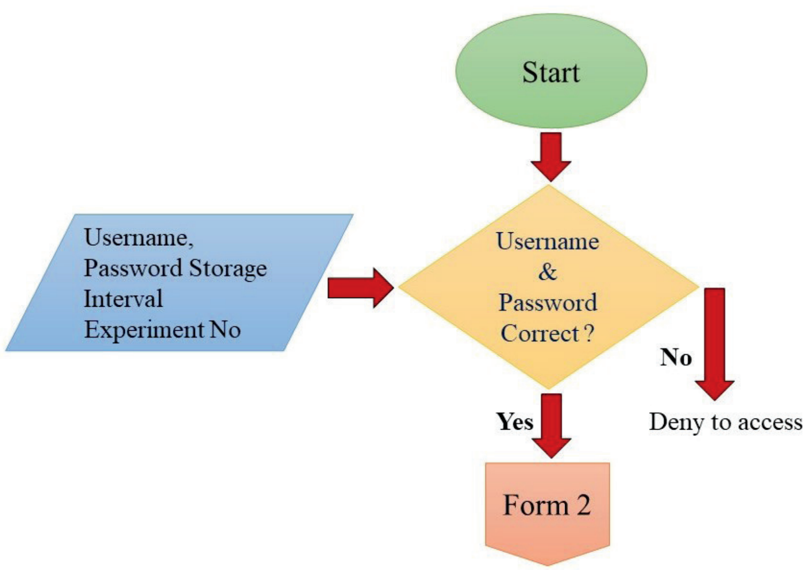

Figure 4. Functions of application software

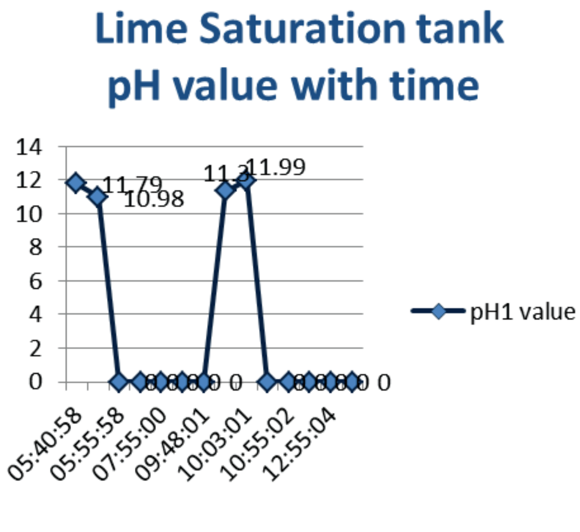

Figure 5. pH profile of saturation tank

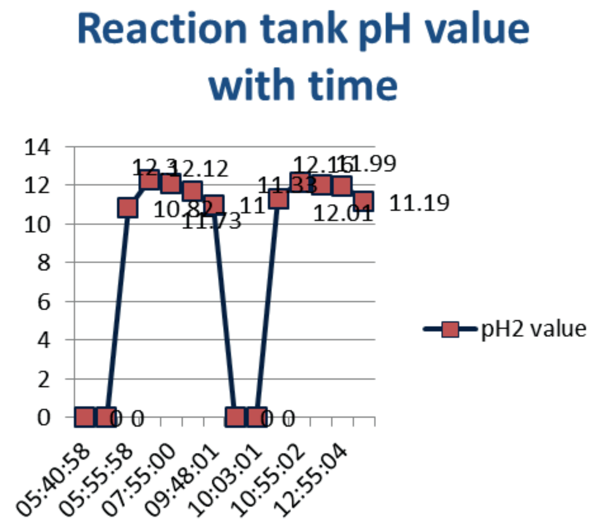

Figure 6. pH profile of reaction tank

Analyses of chemical, mechanical and organoleptic properties

The limed pelts were converted into crust leathers and conditioned at 20° ±2°C and 65 ± 2 % of relative humidity over a period of 48 hours before analysis. The chrome content and fat content and physical properties (shrinkage temperature, tear and tensile strength) were examined as per standard procedures (BIS 1971,[18] ASTM D6076,[19] IUP 2000a[20] and IUP 2000b[21]). The organoleptic properties were evaluated by a group of experienced leather technologists.

Results and Discussion

Addition of lime and sodium sulfide in case of liming or lime alone in case of reliming the pH raises close to 12 in saturation tank after 10 minutes stirring. Then the liquid is transferred to reaction tank through solenoid valve where the skins are placed and the reaction starts. The pH of the solution comes down close to 10 in 4 hours duration. Since the pH change is marginal after that, the liquid is transferred to saturation tank and the 0.375% lime is added, redissolved and sent again to reaction tank. This cycle continues for 6 times with fresh installment of 0.375% lime addition and liming / reliming process takes place. The pH profiles of saturation tank and reaction tank are given in Figures 5 & 6.

In conventional liming process 10% lime along with 2% sodium sulfide is used and during reliming 5% lime is used whereas in the case of experiment 2.25% lime is used for in unhairing and 2.25% lime is used during reliming process was used as shown in Fig 7. This enables to save up to 70% lime compared to conventional

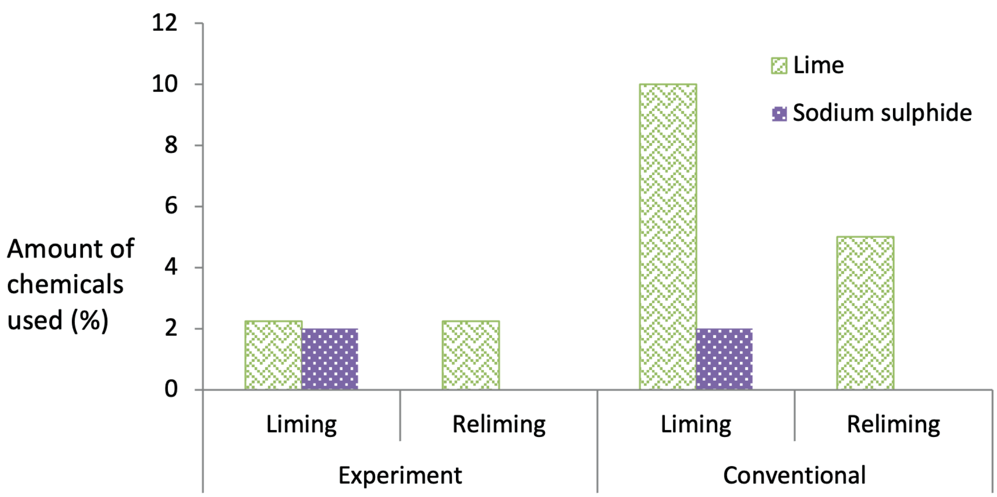

Figure 7. The amount of lime and sodium sulfide used in the process

Table II

Physical and chemical analysis of chrome tanned and crust leather

Process	Shrinkage Temperature °C	Chrome content % Cr_2O_3	Fat content %	Tensile Strength N/mm²	Tear Strength N
Conventional	103±0.5	3.2±0.1	6.2±0.2	23.1±1	86±2
Automated Liming	102±0.5	3.1±0.1	6.1±0.2	23.0±1	85±2

(Average value of three experiments)

Table III

Organoleptic properties of chrome tanned crust leather

	Softness	Smoothness	Grain characteristics	Overall appearance
Conventional	7±1	6±0.5	7±0.5	7±1
Automated Liming	6±1	7±0.5	7±0.5	7±1

0- poor, 10-Excelleant (Average value of three experiments)

process and 90% reduction in sludge generation. The study also proved theoretical alkali binding capacity of skin which is 2.15% lime.

The solubility of lime is 0.15% at room temperature and due to mutual solubilizing effect because of other constituents extricated from skin some quantity of lime will dissolve and get into effluent streams. Table II and Table III show chemical analysis, strength properties and organoleptic properties of leathers produced by both conventional and automated liming process.

The above results show properties of crust leathers produced from both conventional and automated liming processes have comparable characteristics.

Conclusion

This instrumentation system provides an efficient and automated pH monitoring and control system in the liming process. Several experiments have been carried out to ensure that the continuous monitoring and control of pH of liming process. Substantial reduction in lime input and consequent pollution reduction was observed in the experimental process. The technology is suitable for tanneries where pH monitoring and control will impact the material quality while providing significant environmental benefits.

Acknowledgment

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Annexure

Conventional process of goat skins

Process	Quantity	Product	Duration	Remarks
Soaking I	300 %	Water	30min	
Soaking II	300 %	Water	Left overnight	
	0.1 %	Preservative		
	0.5 %	Wetting agent		
Next day washing	200 %	Water		
Liming	250%	Water	Left overnight	This quantity is only for conventional liming process.
	10%	Lime		
	2%	Sodium sulfide		
Unhairing				Unhairing was done mechanically.
Reliming	250%	Water	Left overnight	This quantity is only for conventional liming process.
	5%	Lime		
Fleshing				The limed pelts were fleshed and taken for washing
Washing	200 %	Water	10 min	Conventional and experimental skins were processed together.
Deliming	150 %	Water	Run for 1 h Run for 45 Min.	Washed and drained pH 8-8.5
	1 %	Ammonium chloride		
	0.75 %	Bating agent		
Washing	100 %	Water	10 min	
Pickling	80 %	Water		pH 2.8-3
	8 %	Sodium chloride	Run for 15 min	
	1 %	Formic acid	3 x 10 min, Run for 10 min	
	0.75 %	Sulphuric acid	4 x 15 min, Run for 1 h	
Next day the pelts drummed for 30 min pH at cross section adjusted to 2.8- 3.0. Then 50% of pickle bath drained.				
Chrome tanning	8 %	Basic chromium sulfate (BCS)	2 x 30 min	Check for penetration in cross section
	1.0 %	Sodium formate	10 min	
	1 %	Sodium bicarbonate	3 x 20 min, run for 1 h	Check the pH to be 3.8 to 4. Drain the bath and pile overnight.
Next day sammyed and shaved in 1.0 mm. The shaved weight noted.				
Washing	200 %	Water		Drain
Neutralization	150 %	Water		pH 5-5.5
	0.5 %	Sodium formate	10 min	
	1.0 %	Sodium bicarbonate	3 x 15 min + 1 h	
Washing	100 %	Water	10 min	
Retanning and Fatliquoring	100 %	Water		Drain, rinse, pile over night
	10 %	Fatliquors (Semisynthetic fatliquor FB20 Balmer Lawrie, India; synthetic fatliquor SXE Balmer Lawrie, India)	1 h	
	6 %	Syntans (Phenolic based FBDI (BASF India), Renakotan FBN Melamine resin based syntan (Stahl,India),	45 min	
	1 %	Formic acid	3 x 5 min + 40 min	

Finally, leathers were dried and then conditioned for testing and evaluation.

Lifelines

Cigdem Kilicarislan Ozkan graduated from Ege University Department of Leather Engineering in 2008. The same year she started to M.Sc. She studied on extraction of vegetable tanning materials. She joined the staff of Leather Engineering Department as research assistant in 2010 and completed her PhD in 2018. Her research activities and fields of interests are tanning materials, extraction techniques, modification of biopolymers and leather technologies.

Hasan Ozgunay studied Leather Technology at the University of Ege (Turkey). After working in Leather Industry for one year, he joined the staff of Leather Engineering Department as research assistant in 1996. He obtained his M.Sc. in the same department. He studied on vegetable tanning materials and obtained his PhD in Leather Engineering. He is currently working as researcher / lecturer in the Leather Engineering Department. His research activities and fields of interests are tanning materials, leather processing technologies and cleaner leather processing methodologies.

Tesfay Gebryergs is student pursuing Master's degree in Leather Technology at Addis Ababa University, Ethiopia. He carried out this work in CSIR-CLRI as part of his Master's project under the Twinning program.

C. Sivaranjani is MSc Chemistry graduate working in CSIR-CLRI as Project assistant.

N. Nishad Fathima, see *JALCA* **98**, 263, 2003.

Vimudha Muralidharan received her master's degree in Leather technology from same university in 2016. She is currently pursuing her doctoral program in Leather technology under the supervision of Dr. Balaraman Madhan in Central Leather Research Institute, Chennai, India. Her research interests include leather processing, microbiology of leather, waste management and material science.

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Balaraman Madhan is a Senior Principal Scientist in Central Leather Research Institute, India. He has been a visiting faculty to Anna University, Chennai, India. His research interests include cleaner leather processing, enzyme technology, value added products from solid wastes, and waste management.

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Kota Srinivas completed his M.S (Electronics & Control) from BITS, Pilani and has 36 years of R&D experience in projects as Project member, Project leader and Principal investigator - Process control, Energy Management Systems, Bio Sensor based instrumentation for health. He is been teaching advanced instrumentation course for M.Tech Students of AcSIR from 2009 at SERC, Chennai. Has presented/ published more than 60 papers and 5 reports.

D. Krishnamoorthy completed his Diploma in Electrical & Communication from S.V. Polytechnic, Tirupati, A.P. India. He has obtained his bachelor degree in Engineering & Masters degree in software systems from BITS, Pilani, India under DLPD program. Started his carrier in CSIR-CSIO, Chennai Centre in the year 1983.In his 39 years of experience, He has actively participated in Repairing & Servicing (AMC) of Instruments at his early age of career, Research & Development of Embedded and PC based systems and installation of systems for various industries in mid years. Finally, served the industry in calibration & testing of instruments. CSIR-CSIO acquired NABL accreditation for the calibration activity for Electro –technical & mechanical sections as he was the Quality Manager.

V. Aparna received her undergraduate and postgraduate degrees in Electronics & Instrumentation Engineering. She has over 3 years of experience from reputed research organizations and has extensively published and presented research articles on Process Control & Instrumentation, Artificial Intelligence, Machine Learning, DCS & PLC Engineering, and Embedded Systems.

V. P. Anand holds Masters in Renewable Energy & Bachelors in Electrical and Electronics Engineering & is currently a scientist with CSIR CSIO. He has been actively engaged in instrumentation related to health monitoring of energy infrastructures for process and discrete industries for more than 5 years.

A. Saravana Raj, a post graduate chemical engineer with 10 years academic experience in engineering institution, is about to complete his doctoral research in the area of bioprocess and metabolic engineering from Anna University, Chennai. He has guided many student research projects in some key research areas such as process optimization, bioremediation and food nanoemulsions. He has 7 publications to his credit.

Mohammed Abu Javid. H. obtained his B.Tech degree in Leather technology from Anna University, Chennai. He has been actively engaged in different process control and development. He has actively working on environmental impact oriented leather process and technology. He has 7 research papers to his credit.

K. Iyappan obtained his Ph.D. Degree in Engineering from Anna University, Chennai, India. He has been actively engaged in Renewable energy generation & storage, environmental & eco-friendly process development, value added products, waste to energy and scale-up studies of green chemical for leather sectors for more than 30 years. He has developed number of leather process methodologies using renewable energy, by-product utilization and waste minimization. He has to his credit about 32 research papers and 5 patents.

N. Vedaraman, see JALCA 107, 435, 2012

V. John Sundar, see JALCA 107, 435, 2012

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