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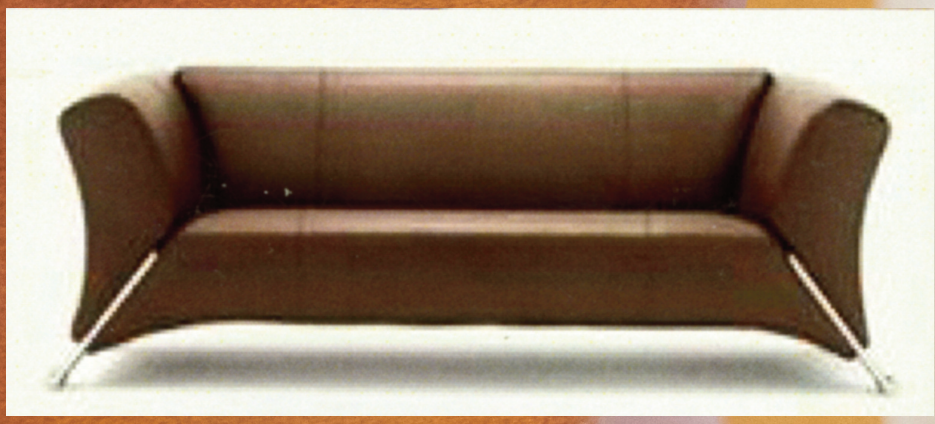

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Treatment of Slaughterhouse Wastewater by Integrated Anaerobic/Aerobic Bioreactors Loaded with Immobilized Nanoporous Activated Carbon

by

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Abstract

Slaughterhouse wastewater consists of moderate to high strength complex wastewater comprising about 45% soluble and 55% coarse suspended organics exhibiting high COD and BOD levels. Conventional wastewater treatment methods cannot effectively treat slaughterhouse wastewater. Thus, a four-stage sequential anaerobic/aerobic immobilized bio reactor system comprising a two stage Fluidized Anaerobic immobilized Reactor (FAIR – I and FAIR – II), a Fluidized Immobilized Cell Carbon Oxidation (FICCO) reactor and a Chemo Autotrophic Activated Carbon Oxidation (CAACO) reactor was tested in a slaughterhouse treating wastewater between 3 m^3 /day to 17 m^3 /day. Nanoporous activated carbon (NPAC) was used for the immobilization of microorganisms in all of the reactors. The NPAC BET surface area was found to be 291 m^2/g with the average pore diameter of 28 Å. Spin density (free electrons) in the NPAC, was calculated to be 16×10^{18} spins/g using ESR spectroscopy. The overall NH_3-N, TKN, COD and BOD removal efficiency was 64%, 71%, 82% and 85% respectively. Multivariate analysis (PCA and cluster analysis) found that the COD removal by the FICCO and CAACO reactors is more efficient than the FAIR reactors. The treatment was confirmed through UV-visible and UV-fluorescence spectroscopic analysis.

Introduction

India has the largest population of livestock in the world (509 million), with 191 million cattle, 135 million goats, 109 million buffaloes, 64 million sheep, and 10 million pigs and over 729 million poultry referenced in the Department of Animal Husbandry, Dairying & Fisheries report, 2012. There are more than 3600 authorized slaughterhouses in the country. About 32.5% of sheep, 36.5% of goats, 1.9% of buffaloes, 28% of pigs, and 0.9% of cattle are slaughtered every year.[1,2] Slaughterhouse produces wastewater containing about 45% soluble and 55% coarse suspended organics exhibiting high Chemical oxygen demand (COD) and Biochemical oxygen demand (BOD) levels.[3] Moreover, the slaughterhouse wastewater is highly proteinaceous in nature and thus it has a high putrefaction rate which leads to environmental pollution problems.[4,5] Further, it also contains blood, undigested food, suspended solids due to rumen contents, flesh pieces, feathers, and pieces of bone.[6] Thus, it may cause many diseases such as tuberculosis, Salmonellosis and Helminthosis if not properly treated before disposal. Improperly treated slaughterhouse wastewater results in de-oxygenation of the water bodies and leads to ground water contamination.[1,7]

Conventionally, anaerobic treatment systems were found to be suitable for the slaughterhouse wastewater treatment.[8-10] Later the Dissolved Air Flotation (DAF) process,[11,12] the Up-flow Sludge Blanket Reactor (USAB) process,[1,13-14] and an anaerobic up-flow contact process[15,16] were used for the treatment. Due to the inefficiency of a single process alone for the treatment of complex slaughterhouse wastewater, many hybrid systems were subsequently explored. Manjunath et. al. (2000) studied the slaughterhouse wastewater treatment by DAF-UASB hybrid reactors.[17] Chen and Lo (2003) studied the slaughterhouse wastewater in treatment plant using two-phase biological system of activated sludge/contact aeration process.[18] Rajkumar et. al. (2012) used Anaerobic Hybrid Reactor System packed with pleated polyvinylchloride rings to treat poultry slaughterhouse waste water.[19] Later Sunder and Satyanarayanan (2013) investigated an Anaerobic Hybrid Reactor System packed with special floating media to treat poultry slaughterhouse wastewater.[1] Though many lab scale hybrid reactors system were successful, only a few processes were proven in the field scale studies. Hence, there has been a constant search for the optimal hybrid reactor system for effective oxidation with minimal sludge production. Thus, this present research was designed to study the efficacy of a four-stage sequential hybrid anaerobic and aerobic bioreactor system containing NPAC, as a catalyst to immobilize and enhance microorganism participation, at field scale.

Specifically, this research evaluates the efficiency of sequential bio reactors comprising of a two stage Fluidized Anaerobic Immobilized

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Reactor (FAIR – I and FAIR – II) followed by a FICCO (Fluidized Immobilized Cell Carbon Oxidation) reactor and a CAACO (Chemo Autotrophic Activated Carbon Oxidation) reactor installed in a slaughterhouse.

Materials and methods

Materials

All the chemicals used in the study were purchased from Merck, India. The mixed consortia used for the degradation of the organics present in the slaughterhouse waste water was cultivated from the acclimatized slaughterhouse wastewater.

Source and collection of slaughterhouse wastewater

The common facility center in Chennai used to slaughter goat and sheep was selected to validate the treatment scheme. The slaughterhouse was to slaughter 100 to 600 animals per day with the maximum number of 600 animals on Sundays. The facility center has a provision to collect blood, animal organs and skin in a scientific way. The water consumption of the facility center varied from 2 m^3 /day to 19 m^3 /day at an average of 30 L per animal. The large and small intestines of the animals are washed to remove the ruminal contents. The wastewater along with ruminal fluids and cattle dung is collected in a collection tank.

NPAC preparation

Rice husk was pre-carbonized at 400°C, then activated at 800°C using phosphoric acid, washed several times with hot water, dried in a hot air oven and stored in desiccators. The NPAC prepared in this manner was used as the base catalyst in the four stage reactors.

NPAC characterization

N_2 adsorption–desorption isotherms were used to determine the surface area and pore size distribution. The NPAC N_2 adsorption–desorption isotherm was measured using an automatic adsorption instrument (Quantachrome Corp. Nova-1000 gas sorption analyzer). Electron spin resonance (ESR) spectra and spin density was obtained using a Bruker-IFS spectrometer. TEMPOL was used as the reference spin probe compound to carry out preliminary experiments. The detailed ESR methodology was referenced from Swarnalatha et al. (2009).[20] The C, H, and N content for NPAC produced at varying heat treatments was determined using a CHNS 1108 model Carlo Erba analyzer. The NPAC surface morphology was determined, using a Leo-Jeol scanning electron microscope (SEM). The NPAC sample was coated with gold by a gold sputtering device to enhance surface morphology visibility.

Treatment scheme for slaughterhouse wastewater

The wastewater from the slaughterhouse was screened two times, first through a coarse 25 mm screen followed by a fine 10mm screen. The screened slaughterhouse wastewater was treated through four-unit operation in series comprising of a two stage FAIR– I and FAIR – II reactor set followed by a FICCO and CAACO reactor (Figure 1). The slaughterhouse wastewater was tested through the above treatment sequence continuously for 30 days.

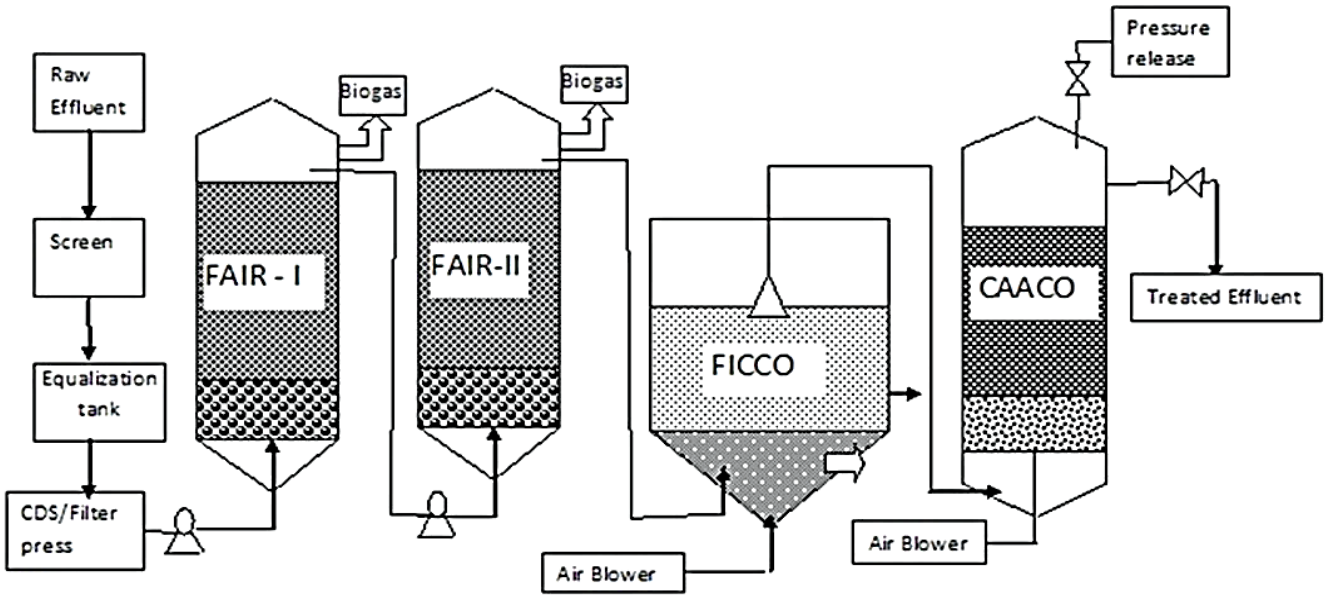

Figure 1. Schematic diagram of the four stage integrated treatment processes for the slaughterhouse wastewater

Description of the reactors

FAIR reactor details

The FAIR reactor is operated in an up-flow direction. The reactor was filled with NPAC to immobilize the microbes in the pores of the carbon matrix. The reactor has a provision to collect biogas generated during soluble and insoluble anaerobic mineralization. The settling zone in the reactor is filled with polypropylene contact medium to separate out suspended solids from the treated wastewater.

FICCO reactor details

The FICCO reactor comprises of three zones. The first zone is recognized as the "react zone" and is comprised of the immobilized carbon which is fluidized by air and wastewater at an up-flow velocity of 5 m/min. The quantity of air needed for the oxidation of organic compounds in wastewater is decided by the organic oxidation kinetics. The air required for the fluidization and oxidation of organics is supplied through the perforated pipe lines provided at the bottom of the reactor. The pressure of air required is a function of up-flow velocity, viscosity of medium, total solids content of the medium, temperature and height of the reactor. The second zone is the fluid separation zone. The unspent oxygen and nitrogen in air are separated using a triangular septum provided at the optimum height of the reactor. The separated air is collected through the perforated chamber. The third zone is the settling zone. The treated wastewater enters through the aperture and is allowed to settle on the inclined baffle plate. The angle of the plate is determined by the suspended solids settling velocity. The settling tendency was enhanced by extending the surface area to capture the particles by including a polypropylene plastic media of defined geometry. The screened suspended solids are sloughed off from the media upon exceeding a critical thickness. The sloughed suspended solids slide back into the reactor through the aperture. The sludge accumulated in the reactor is withdrawn daily through a sludge withdrawal pipe line provided in the reactor.

CAACO reactor details

The CAACO reactor contains a bacterial cell (chemo autotroph) immobilized packed bed filled with NPAC immobilized with *Bacillus sp.,* which is isolated from a facultative lagoon.[21] The air required for the oxidation is provided through a packed bed at two levels passing through perforated pipelines. The wastewater to be treated is transferred to the bottom of the reactor and in an upward flow direction. The treated wastewater is collected from the top of the reactor. The air required for the oxidation of organics is determined by the COD load in the wastewater. The pressure of air is determined by the head loss encountered during the oxidation of the organics in wastewater.

Chemical analysis and instrumental methods

In accordance with standard methods,[22] parameters such as pH, Total Kjeldahl nitrogen (TKN), chemical oxygen demand (COD), biological oxygen demand (BOD), ammoniacal nitrogen (NH_4–N), and volatile fatty acids (VFA) were characterized in triplicate and average of the results were calculated. The attachment of microbes in NPAC used in FAIR-I, FAIR-II, FICCO and CAACO reactors was examined by JEOL JM 5600 Scanning Electron Microscope at 20 kV (JEOL, Japan) accelerating voltage with an electron beam of 5-6 nm.

Statistical analysis

SPSS software (version 18) was used to evaluate the descriptive statistics and correlation analysis. Principal component analysis (PCA) was executed with Varimax rotation (Kaiser Normalization). By applying Ward's method, Square Euclidian distances of standardized median values (Z scores) were used for cluster analysis (CA).

Results and Discussion

Characteristics of NPAC

The complete details of the characterization of the NPAC were elaborated in our previous studies[20, 22-25] and it was used for the effective immobilization of bio catalysts for the treatment of wastewater.[26-28] The carbon, hydrogen and nitrogen percentages were 48.45, 0.70 and 0.10, respectively. Spin density, which is equal to the free electrons, was calculated as 16×10^{18} spins/g by using ESR spectroscopy. The specific surface area of NPAC was calculated using the BET model. The mesoporous surface area was calculated by the *t*-plot method. The results are presented in Table I.

Table I

Surface areas, pore volume and pore dimension of ECS

Parameters	Values
S_{BET} (m^2/g)	291
S_{mes} (m^2/g)	83
S_{mic} (m^2/g)	208
Mesopore volume, V_{meso} (cm^3/g)	0.08801
Micropore volume, V_{micro} (cm^3/g)	0.10035
Total pore volume, V_{tot} (cm^3/g)	0.18836
V_{meso}/V_{total} (%)	46.72
Average pore diameter (Å)	28

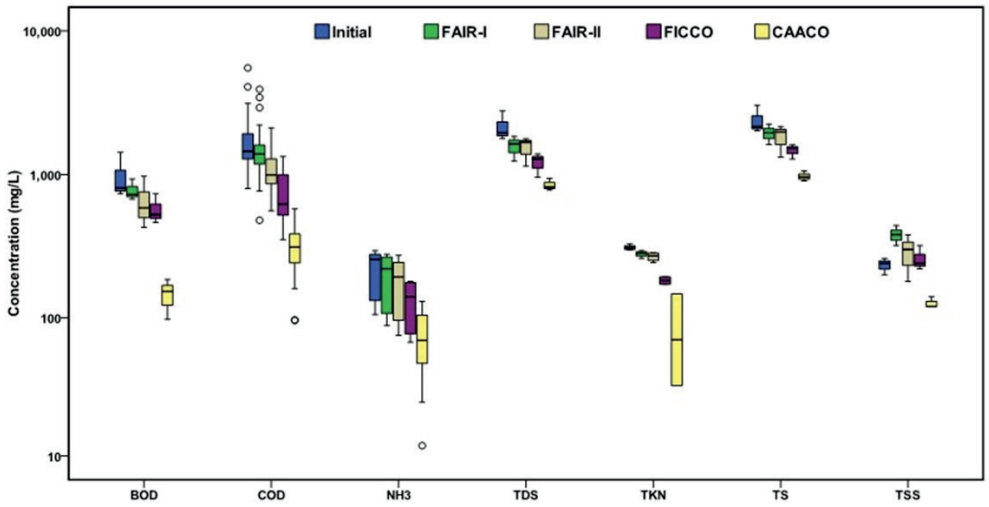

Figure 2. Four stage integrated treatment Box-and-whisker plots

Table II

Slaughterhouse wastewater treatment efficacy at the various stages

Parameters	Values	Initial	FAIR-I	FAIR-II	FICCO	CACCO
BOD, mg/L	Mean	855.00	777.33	662.33	575.00	145.17
	Median	735.00	727.00	585.00	525.00	153.00
	Std. Deviation	520.48	134.75	282.07	141.77	44.27
COD, mg/L	Mean	1832.24	1552.36	1084.40	741.92	314.88
	Median	1452.00	1392.00	992.00	621.50	312.00
	Std. Deviation	1061.35	803.52	413.84	302.27	125.70
NH_3-N, mg/L	Mean	216.17	198.17	181.75	130.67	72.50
	Median	256.00	220.00	193.00	140.50	69.50
	Std. Deviation	76.26	76.11	76.32	46.46	38.57
TDS, mg/L	Mean	2166.67	1570.00	1530.00	1210.00	846.67
	Median	1950.00	1630.00	1680.00	1280.00	820.00
	Std. Deviation	529.37	304.47	340.73	223.38	83.27
TKN, mg/L	Mean	309.25	280.00	267.25	182.50	90.00
	Median	306.00	283.00	270.50	182.50	90.00
	Std. Deviation	12.84	14.40	19.53	12.12	65.82
TS, mg/L	Mean	2400.00	1936.67	1816.67	1470.00	973.33
	Median	2150.00	1950.00	1980.00	1520.00	960.00
	Std. Deviation	549.45	310.21	438.44	170.59	80.83
TSS, mg/L	Mean	233.33	380.00	286.67	260.00	126.67
	Median	240.00	380.00	300.00	240.00	120.00
	Std. Deviation	30.55	60.00	100.66	52.92	11.55
Total Bacterial Count, cfu/mL	Mean	16×10^6	12×10^7	18×10^6	13×10^5	6.9×10^4
	Median	14×10^6	11×10^7	17×10^6	16×10^5	2.5×10^4
	Std. Deviation	9.9×10^6	7.1×10^6	7×10^6	7.7×10^5	11×10^4
Total Coliforms, cfu/mL	Mean	13×10^5	11×10^6	17×10^5	3.5×10^5	2.6×10^4
	Median	12×10^5	10×10^6	13×10^5	2.1×10^4	2×10^3
	Std. Deviation	8.6×10^5	7.8×10^5	8×10^5	7.8×10^5	9.1×10^4

Performance evaluation of the four stage reactors

The multiple box and whisker plots for parameters such as BOD, COD, NH_3-N, TDS, TKN, TS and TSS for the initial wastewater, outlet of FAIR-I, FAIR-II, FICCO and CAACO are given in Figure 2. The normality of the data for each parameter in each reactor was elucidated through skewness and kurtosis along with Shapiro-Wilk test which is more appropriate for the sample size of less than 50.[29] The mean, median and Std. Dev. of initial wastewater, outlet of FAIR-I, FAIR-II, FICCO and CAACO for parameters such as BOD, COD, NH_3-N, TDS, TKN, TS and TSS is presented in Table II.

The COD and BOD median values present in the initial slaughterhouse wastewater were 1452 mg/L and 735 mg/L respectively with a biodegradable index of 0.50 indicating that the wastewater has significant biodegradable organics. The organic nitrogen content was only 50 mg/L derived from animal protein. The remaining part of biodegradable organics is contributed by polysaccharides and fatty substances. The wastewater characteristics suggest that it is a good candidate for anaerobic treatment by the FAIR reactor pairing.

The median COD and BOD values after treatment by the FAIR reactor pairing were 992 mg/L and 585 mg/L respectively. The median COD values after FICCO and CAACO was 622 mg/L and 312 mg/L respectively. The median BOD values after FICCO and CAACO was 525 mg/L and 153 mg/L. The organic nitrogen content was reduced to 20 mg/L whereas NH_3-N was finally reduced to 69.5 mg/L. ORP of wastewater was -47 mV indicating that the FICCO treated wastewater contained oxidized or stabilized products. In FICCO, the dissolved organics adsorb onto the carbon matrix and diffuse into the immobilized microbes and metabolized. The metabolized products are diffused back to the bulk medium. The oxidation of organics is facilitated by hydroxyl radicals generated from molecular oxygen (in the form of air).

Though the overall NH_3-N, TKN, COD and BOD removal efficiency was 64%, 71%, 82% and 85% respectively, a major removal of these parameters takes place at the CAACO reactor (COD, 63%; BOD, 77%; NH_3-N, 43% and TKN, 51%). The overall removal efficiency of TS and TDS is 61% and 62% respectively. Though the overall removal efficiency of TSS was 43%, increases in the TSS is observed in the anaerobic processes and FICCO when compared to the initial wastewater. This may be due to the suspended growth of anaerobic organism in the FAIR process which is also evident by the Total viable count.

Multivariate statistical analysis (PCA and cluster analysis)

Multivariate analysis was performed to find out the relation between several treatment systems[30,31] to study the trend of the COD and NH_3-N removal. Principal components (PC) with Eigen values higher than 1 were extracted by introducing a Varimax rotation along with Kaiser Normalization in the PCA analysis. Figure 3a signifies the relation between the treatment systems in COD removal while Figure 4a represents the relations of treatment systems in NH_3-N removal. PC1, PC2 and PC3 explained 48.8, 27.4 and 21.3 % (total of 97.5 %) of the variance in Figure 3a, whereas PC1 and PC2 in Figure 4b explained 73.7 and 24.7 % (total of 98.4 %) of variance in Figure 4a. To confirm the PCA associations, a comparison with cluster analysis can be made.[30] By applying Ward's method, Square Euclidean distances of standardized median values (Z scores) were used for clustering. Hierarchical clustering was performed and presented as a dendrogram by applying variables such as COD removal (Figure 3b) and NH_3-N removal (Figure 4b).

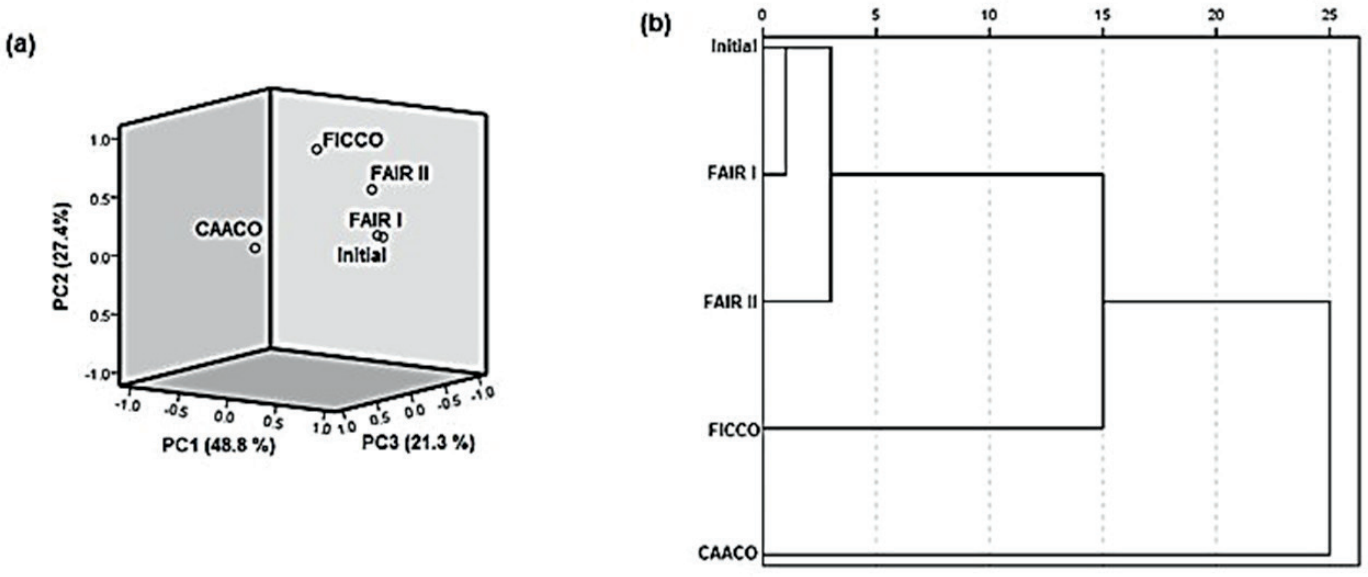

Figure 3. Trend comparison of various reactors in COD removal **(a)** Principal component analysis and **(b)** hierarchical cluster analysis

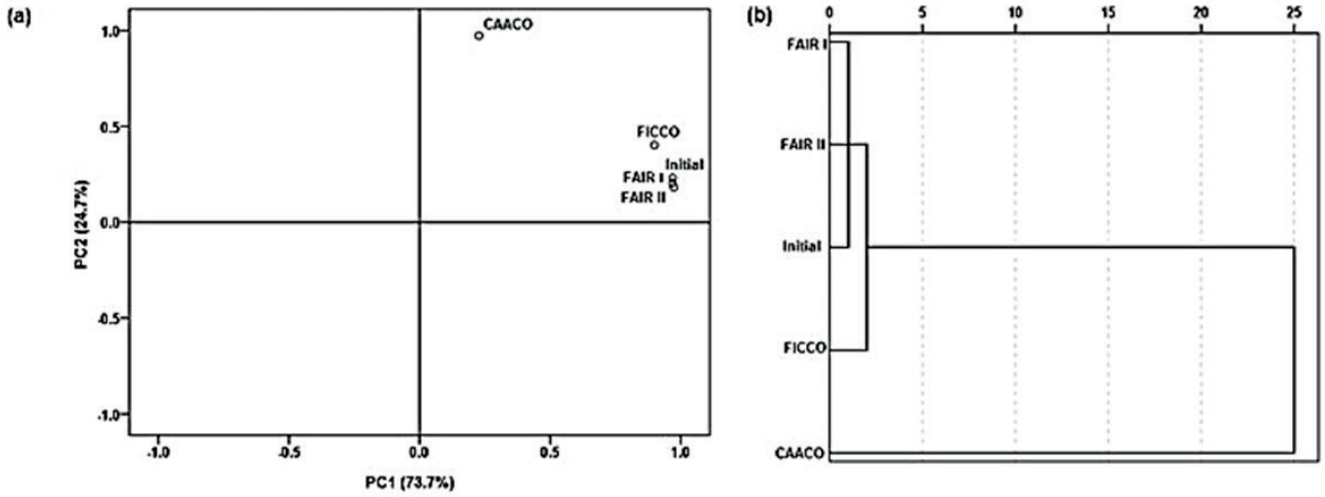

Figure 4. Trend comparison of various reactors in NH_3-N removal **(a)** Principal component analysis and **(b)** hierarchical cluster analysis for the integrated treatment processes for the slaughterhouse wastewater

The results indicated in Figure 3a and Figure 3b compared and can be elucidated as follows: PC3 in Figure 3a represented the treatment CAACO as a high positive score whereas FICCO represented in PC2 as high positive score. PC1 represented by Initial slaughterhouse water, FAIR I and FAIR II treatment process. In cluster analysis, the extreme distance among two clusters signifies the two most dissimilar groups.

The cluster analysis (Figure 3b) also showed the Initial, FAIR I and FAIR II as Group – I, whereas FICCO and CAACO as other individual groups. Thus, the trend of COD removal efficiency in FAIR reactors resembles each other and also to the initial slaughterhouse water whereas the trend in removal efficiency of CAACO and FICCO reactors are more efficient compared to the FAIR reactors. Figure 4b represents the CAACO as Group II which are all placed in a high positive score in PC1 of Figure 4a. Group I in Figure 4b is further sectioned into two groups in which group Ib represents FICCO which is placed in PC2 (Figure 4a) with a little lesser positive value when compared to Initial slaughterhouse water, FAIR I and FAIR II. Thus, it shows that the NH_3-N removal is more efficient in CAACO than other reactors.

Catalyst NPAC organic cleavage mechanistic view

NPAC use for organic compound degradation in slaughterhouse wastewater follows two pathways:

Can be used as the supporting matrix providing the space for the immobilization of microorganisms on its surface to increase the contact time between the organics and the organisms at aerobic/anaerobic conditions to enhance degradation.

NPAC itself serves as a better catalyst in presence of oxygen than anaerobic conditions. This may be due to the presence of free electrons in the conduction band and positive holes in the valence band. The electrons present in the conduction band initiate reaction (Equation 1) in the presence of oxygen to form reactive oxygen species.

$$-C\,(e^-_{cb}) + O_2 \rightarrow -C\,(O_2^{\bullet})_{ads} \quad (1)$$

The formation of hydroxyl radicals takes place through the formation of hydroperoxyl radicals (Equation 2),

$$-C\,(O_2^{\bullet})_{ads} + H^+_{(aq)} \rightarrow -C(HO_2^{\bullet})_{ads} \quad (2)$$

The adsorbed hydro peroxyl radicals are converted into hydroxyl radicals and remain adsorbed on the surface of NPAC (Eq. 3),

$$-C(HO_2^{\bullet})_{ads} + H^+_{aq} \rightarrow -C(2OH^{\bullet})_{ads} \quad (3)$$

The positive charged centers in NPAC serves to adsorb the organic substrate (OS) and degrades the organics (Equations 4 and 5),

$$-C(h^+_{vb}) + (OS) \rightarrow -C^*(OS^{\bullet})_{ads} \quad (4)$$

$$-C(2OH^{\bullet})_{ads} + -C^*(OS^{\bullet})_{ads} \rightarrow H_2O + CO_2 + -C(e^-_{cb}) + -C(h^+_{vb}) \quad (5)$$

The above-mentioned mechanisms are theorized to explain how organic pollutants can be degraded.

Instrumental evidence

The morphology and attachment of organisms to NPAC used in FAIR-I, FAIR-II, FICCO and CACCO reactors were studied by Scanning electron Microscopy (SEM). The Figure 5(a) indicated the presence of pores on the surface of NPAC with large surface area as mentioned in Table I. The occupancy of aerobic/anaerobic organisms onto NPAC clearly shown in Figure 5 (b) to 5 (d). The figures denoted that the presence of different kinds of organisms

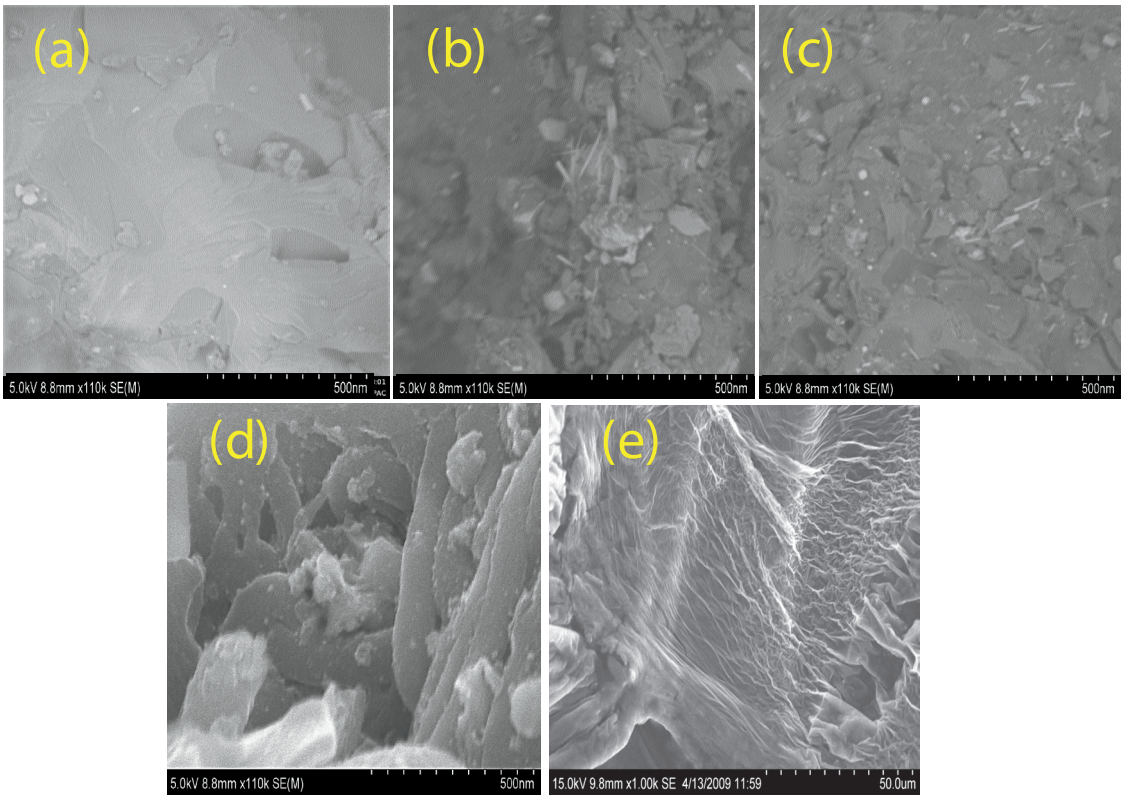

Figure 5. SEM images of **(a)** actual nanoporous activated carbon **(b)** nanoporous activated carbon used in FAIR-I **(c)** FAIR-II **(d)** FICCO and **(e)** CACCO reactors

on the surface of NPAC which were involved in the degradation of organic constituents from slaughterhouse wastewater discharged from tanneries.

UV-visible and fluorescence spectrum of initial and sequentially treated slaughterhouse wastewater was shown in Figure 6a and 6b. The results indicate that the peak around λ_{295} nm with high intensity due to the presence of π to π* transition and n to n* transition is responsible for unsaturated, reduced sulphur and nitrogen compounds present in slaughterhouse wastewater. After processing, a hypochromic shift was observed which indicates the removal of chemical population present in the wastewater and also a hypsochromic shift which indicates a breakdown of unsaturated compounds into simpler stable compounds which requires more energy to excite when compared with unsaturated compounds. UV-visible supports the data of Table II where the removal of both ammonia and TKN (n to n* transition) takes place with simultaneous removal of COD responsible of unsaturated compounds (π to π* transition). The UV-fluorescence spectrum supports the UV-visible results where both shifts reflect wastewater treatability.

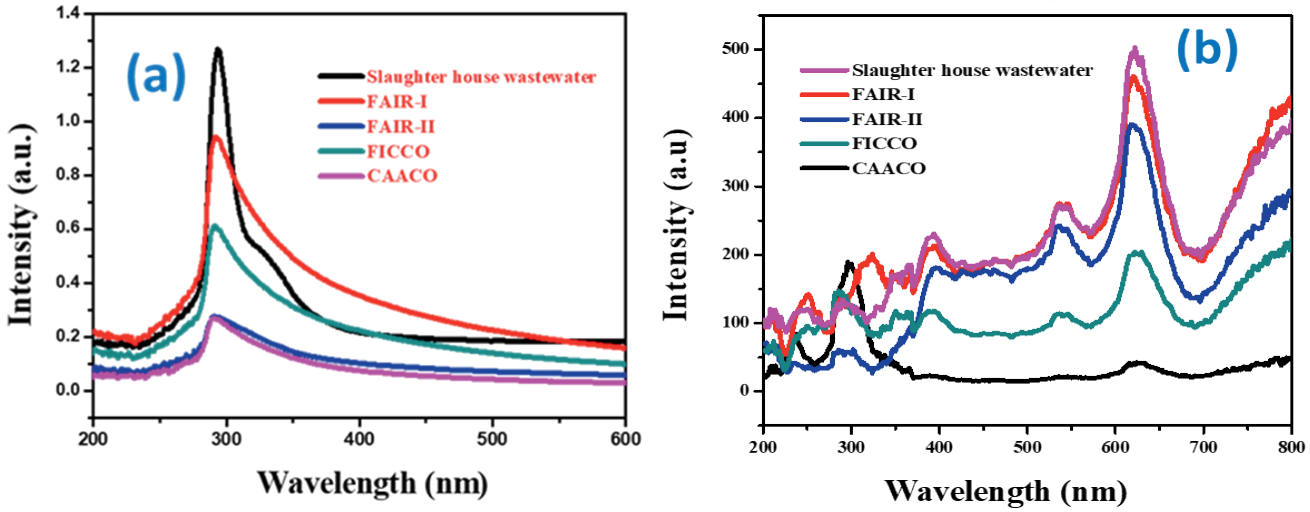

Figure 6. **(a)** UV-Visible and **(b)** UV-fluorescence spectrum for the treatment of slaughterhouse wastewater using integrated sequential anaerobic/aerobic reactor system

Conclusions

The wastewater generated from the slaughterhouse sector fluctuates extensively and thus the efficiency of conventional treatment systems is very much limited for the removal of organics. Hence, the treatment using sequential anaerobic/aerobic immobilized bioreactors comprised of FAIR, FICCO and CAACO was attempted in this study to meet the fluctuating organic load. The median values of the BOD and COD present in the initial slaughterhouse wastewater were 735 mg/L and 1452 mg/L respectively with a biodegradable index of 0.50 indicating the wastewater has biodegradable organics. The median COD values present in the FICCO and CAACO outlets was 622 mg/L and 312 mg/L respectively. The BOD present in the FICCO and CAACO outlets was 525 mg/L and 153 mg/L. The organic nitrogen content was reduced to 20 mg/L whereas NH_3-N was finally reduced to 69.5 mg/L. The efficiency of the reactors was statistically validated by way of a multivariate analysis (PCA and cluster analysis) for COD and NH_3-N removal which shows the trend observed in the FAIR reactors are almost equal, whereas the trend observed in CAACO is different from any other. The treatment was confirmed through UV-visible and UV-fluorescence spectroscopic analysis.

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Study on the Dry-Cleaning Process of Mink Fur Based on Subcritical Solvent

by

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Abstract

It is significant to apply environmentally benign technology to fur processing. In this paper, subcritical extraction with n-pentane was used to dry clean mink fur and the effect on the quality of mink fur was studied. The dispersion degree of the leather fibers and the morphology of the wool fiber were characterized with SEM, the mechanical properties, shrinkage temperature and oil content left in fur were determined and analyzed. The results showed that the fibers of mink fur were well separated and no excess lipids in the fibers or on the surface of mink fur and the hair of the mink fur is not damaged. The tensile strength and elongation of mink fur show slight increase respectively, and the shrinkage temperature of mink fur that was treated by subcritical solvent was significantly increased compared with that of the mink fur treated with tetrachloroethylene by conventional dry cleaning method.

Introduction

Mink skin is one of the most important fur industry resources in the world because of its beautiful appearance, soft and firm of leather, dense villus and glossy aciulum (guard hair), which it is the ideal fur product for fur clothing. It is estimated that the global quantity of mink skin will exceed 30 million pieces in 2021.

The current tanning process of mink mainly includes soaking, degreasing, softening, pickling, aluminum tanning, kicking (oil tanning), dry cleaning, etc.[1] In the kicking operation, it is to smear the kicking oil on the flesh side of alum-tanned mink fur, and then to put the skin into the kicking machine for processing. The oil penetrates into the leather and is well distributed among fibers but the excess grease is attached on the kicked mink fur. The following step, named dry cleaning, removes the excess grease and provides the softness and extensibility of mink fur.

Because of the large amount of grease in the kicked mink fur, the conventional chemical emulsification method could not remove the excess kick oil effectively. Solvent extraction with tetrachloroethylene or trichloroethylene is usually used to dry clean the kicked mink fur to remove excess kick oil. During the dry cleaning process, a common solvent (tetrachloroethylene) is used in closed-circuit machines, then centrifugating and drying (36-38°C), finally tetrachloroethylene is recovered as far as possible for reuse but some is left in mink fur. Because tetrachloroethylene is a harmful organic solvent which has the phenomenon of irritation and anesthetic effect, it must be removed from the cleaned fur after dry cleaning. However, due to the higher boiling point, tetrachloroethylene is hard to remove. Thus, harmful residues could cause air and water environment pollution.[2,3] According to the factory's statistics, each mink skin consumes about 15g, and the residual solvent in the skin will eventually evaporate into the air and cause air pollution. In order to solve this problem, Marsal et al.[4,5] studied the degreasing process of leather with supercritical CO_2, and the degreasing efficiency was as high as 94%. However, this is of no practical significance for fur degreasing due to equipment input and cumbersome operation. Bufalo et al.[6] studied the ultrasonic-assisted degreasing of mink skin in water system, which can effectively avoid the use of harmful substances and the discharge of degreasing waste liquid. Zhang et al.[7] put forward a concept of green controllable solvent for fur degreasing.

Subcritical extraction is a new technology developed within the past 20 years. It is a subcritical solvent extraction of lipids from biological materials.[8] When the temperature of a substance is above its boiling point but below its critical temperature, and the pressure of a substance is below its critical pressure, the state of a substance in the form of a fluid is said to be subcritical.[9,10] When a solvent is in a subcritical state, we call it a subcritical solvent. For a solvent in a subcritical state, its density is similar to that of a liquid, the viscosity and surface tension of the molecule may change, its viscosity is similar to that of a gas, the mass transfer speed becomes faster, the diffusion ability becomes stronger, and it will have more significant dissolution ability and dispersibility for some substances.[11,12]

According to the comparison and evaluation of the properties and environmental effects of various solvents, n-pentane has a low boiling point and small required subcritical pressure, making it favorable for transportation and use at room temperature. In addition, n-pentane

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has the characteristics of easy to recover, no physiological toxicity and stable chemical properties.[13]

In this paper, n-pentane was selected as the solvent to dry clean minks under a subcritical system. Compared with tetrachloroethylene, n-pentane has a low boiling point and small required subcritical pressure. It is easy to recover the solvent after dry cleaning and has low toxicity. The mechanical properties and moisture and heat resistance of mink skin after being treated with subcritical n-pentane dry cleaning were tested and determined, fiber dispersion and wool scale were observed and analyzed, which provided inspiration and scientific basis for the application of subcritical technology in fur production and processing, so as to promote cleaner production of fine fur.

Experiment

Device and instruments

Reaction kettle: Subcritical dry cleaning was performed in a high pressure reaction kettle (GSH-1/10-SJFZ magnetic coupling reaction kettle) to facilitate the control of temperature and pressure in the subcritical system, as schematically illustrated in Figure 1.

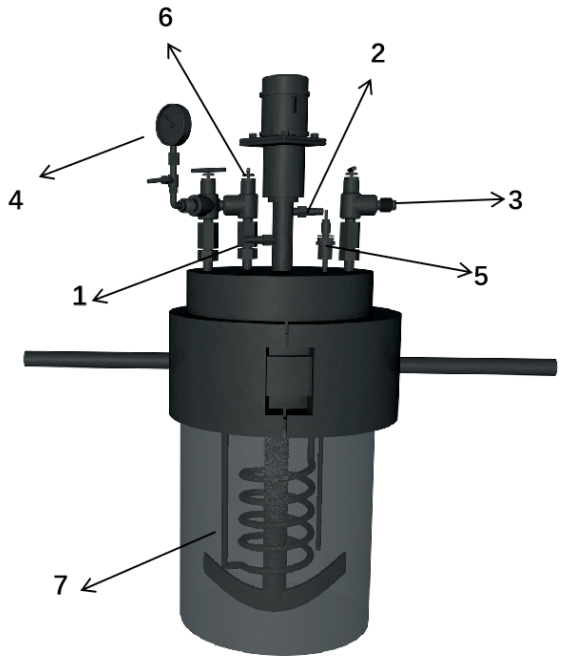


Figure 1. Reaction kettle for subcritical dry cleaning experiment.
(1) Circulation water inlet valve; **(2)** Circulating water outlet valve; **(3)** Inlet valve; **(4)** Piezometer; **(5)** Temperature probe; **(6)** Pressure valve; **(7)** Constant temperature circulating water

Scanning Electron Microscope (JSM-7500F) is used to observe mink fur samples to characterize the separation of fibers and the quality of the hair. Electronic tension machine (AI-7000) and leather shrinkage temperature test machine (HY-852) were used to determine the mechanical properties of the leather and hydrothermal stability, Moisture (YLS16A) meter to determine the moisture content, and automatic grease tester (SZC-101) to measure the grease content.

Materials and reagent

N-pentane: analytical reagent, purchased from Chengdu Jingsan Reagent Co. The critical temperature of n-pentane is 196.6°C. The critical pressure is 3.37 MPa and the boiling point of n-pentane is 36.1°C. The saturated vapor pressure is 121.48 kPa (38.5°C).

The raw material of mink fur was pastel mink imported from Denmark.

Methodology

Aluminum-oil tanning of mink fur

The aluminum-oil tanned mink fur was prepared by Sichuan Dehua Leather Co., Ltd. according to the existing mink fur processing. The processing process was as follows: soaking - softening - soaking - pickling - alum tanning - drying - smearing - kicking.

Control: The controlled sample was the mink skin tanned and kicked by process above, which was carried out in the dry cleaning machine with tetrachloroethylene for 5 minutes.

Subcritical n-pentane dry cleaning experiment

Two pieces of kicked mink furs (10×10cm each) were sampled. A quantity of n-pentane 30 times the mass of the sample was added to the kettle and preheated to 30°C, then the sample was put into the kettle. The closed reaction kettle was heated to the temperature of 40°C and pressure was increased to 0.5 MPa through compressed air at once. The dry cleaning duration is 3min and 1.5min respectively, as S1 and S2.

Shrinkage temperature

The Shrinkage temperature of mink fur was measured according to IULTCS/IUP 16, 2015. Each sample was measured three times and the average value taken.

Determination of fat content

First, the samples were dried with a moisture tester and the moisture content was measured. Then, according to the instructions of automatic fat tester (SZC-101), the fat content was measured with dichloromethane as the solvent. Each sample was measured twice and the average value taken.

Physical-mechanical tests

The tensile strength and percentage elongation of mink fur samples were determined according to the standard IULTCS (International Union of Leather and Chemists Association) methods. Tensile strength and percentage extension were measured according to IULTCS/IUP 6, 2011.

Morphological analyses

The longitudinal section of leather, over hair and wool of the samples were sprayed with gold respectively. Scanning Electron Microscope (SEM) was employed for the morphological characterization of fiber tissue dispersion and aciulum and villi.

Results and discussion

In a subcritical system, dry cleaning was carried out in a confined space with organic solvents using the principle of organic similarity and compatibility. The dry cleaning agent was separated from the mink fur by vacuum evaporation to obtain the mink fur after eluting oil. The gaseous dry cleaning agent was reused after condensation.

Influence on hydrothermal stability

Shrinkage temperature (T_s) of the fur is used to characterize the effectiveness of tanning, and it is closely related to the hydrothermal stability of the fur. The results of the furs are seen in Table I.

As can be seen from Table I, T_s of the kicked mink fur is 58.1°C, but T_s of mink fur treated with subcritical n-pentane and conventional dry cleaning were significantly decreased due to detanning in dry cleaning process. T_s of S1 is about 20°C higher than that of control which shows the better hydrothermal stability. This means that the mink fur dry-cleaned by subcritical n-pentane has better hydrothermal stability and durability.

Moisture and fat content

It can be seen from Table II that the fat content of S1 and S2 by subcritical n-pentane or conventional dry cleaning were low, indicating that the kick oil absorbed during oil tanning and the nature oil in raw skin were mostly washed out. Degreasing rate are 92.72%, 88.93% and 88.12% compared with the kicked fur. Although the fat content of the samples was higher than that of the control, this may be related to the type of solvent and degreasing time.

Influence on mechanical strength of leather

As can be seen from Table III, compared with the traditional dry cleaning process, the tensile strength and elongation of the mink fur treated by the subcritical n-pentane were both improved by 17.08% and 13.09% in S1, while the difference was not significant in S2. It is shown that the tensile strength and elongation would decrease along with extension of dry cleaning time.

Table I

Shrinkage temperature

Sample	Kicked fur	Control	S1	S2
Shrinkage temperature/°C	58.1±0.2	30.8±1.0	51.2±0.4	49.1±0.3

Table II

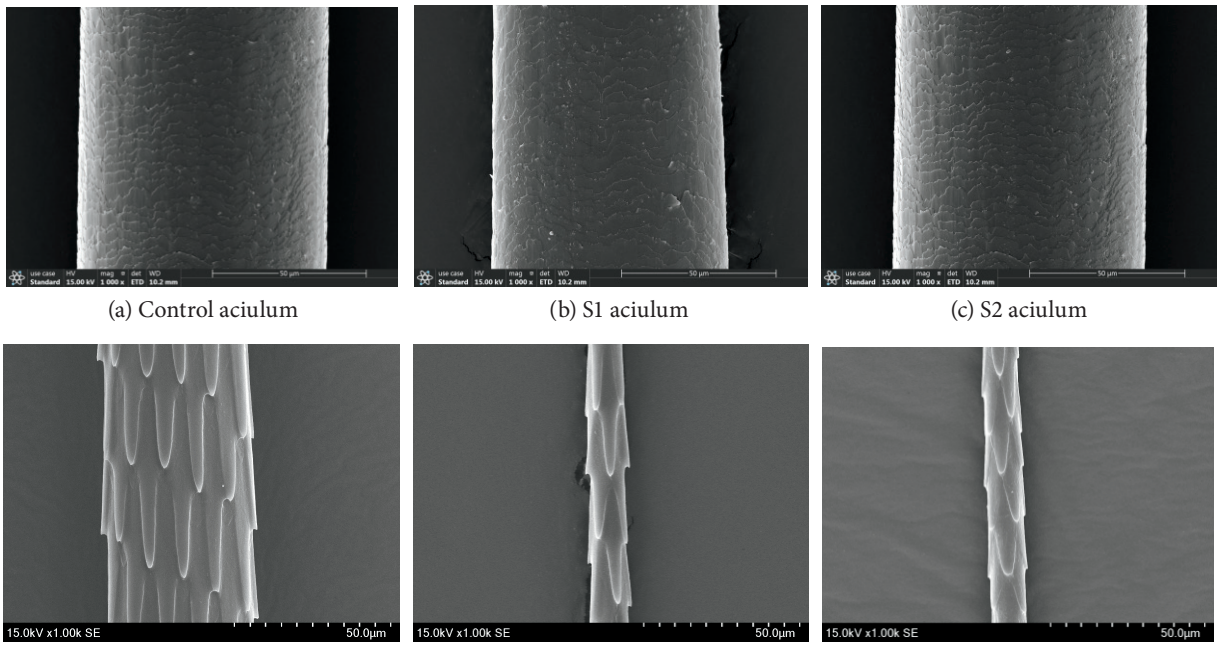
Moisture and fat content

Sample	Kicked fur	Control	S1	S2
Moisture content (%)	5.23	10.82	9.90	11.07
Fat content (%)	46.98±0.35	3.42±0.24	5.20±0.68	5.58±0.44

Table III

Mechanical properties

Sample	Thickness (mm)	Tensile strength (MPa)	Elongation (%)	Specify the load Elongation (5N/mm²)
Control	0.45±0.01	16.80±0.09	51.2±0.7	31.3±0.7
S1	0.44±0.02	19.67±0.10	57.9±0.6	31.7±0.1
S2	0.45±0.02	22.56±0.14	52.7±0.1	29.5±0.2



(a) Control aciulum (b) S1 aciulum (c) S2 aciulum

(d) Control villi (e) S1 villi (f) S2 villi

Figure 2. SEM of aciulum and villi

Influence on wool fiber

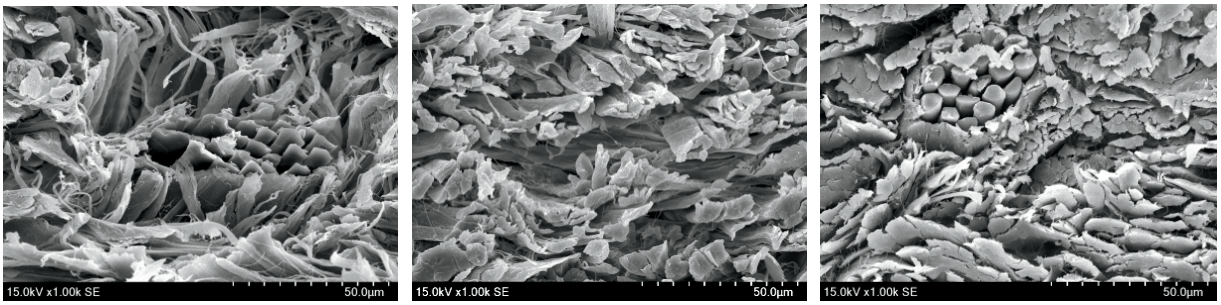
The hair is composed of the scales (cuticula), cortex, and medulla layers. The scales layer is a characteristic surface structure of the hair fiber, which is composed of flaky keratinocytes.[14] Its main function is to protect the hair fibers from the chemical and physical effects of the environment, giving the hair a glossy appearance.

Figure 2 shows the SEM image (X1000) of aciulum and villi respectively. The wool of mink is divided into aciulum and villi. Under the electron microscopy, the aciulum scales are arranged in a hybrid waveform, while the villus scales are arranged in a long petal shape. The structure of aciulum, villi scale layer and leather of mink dry cleaned by subcritical n-pentane showed no significant difference from that treated by traditional dry cleaning technology. The hair fibers were bright, flexible, uniform and even. The structure of hair fiber scale layer was complete, closely arranged and connected with each other.

Influence on leather

The tissue structure of mink fur is composed of three layers of epidermis, dermis and subcutaneous tissue. The characteristics of the tissue structure of the leather are dense collagenous fiber braiding, thin fiber bundles in papillary layer and tightly woven in cross shape, and thick fiber bundles in reticular layer, mainly parallel to skin surface.[15]

Figure 3 shows the SEM image (X1000) of the longitudinal section of the mink fur. It can be observed that after the subcritical n-pentane dry cleaning, most of the oil of mink fur was removed, the inter fibrillar substance was also dissolved. This makes the fiber bundles direction clearer, the collagen fiber bundles well dispersed, the fur firm and thin, soft feel, with good sensory performance.



(h) Control (i) S1 (g) S2

Figure 3. SEM of mink skin

Conclusion

The subcritical fluid has the characteristics of both liquid and gas, low viscosity, easy diffusion and strong solubility, etc. In this paper, the dry cleaning and degreasing process of mink fur with subcritical n-pentane was studied and the results were compared with those of conventional dry cleaning.

(1) The hydrothermal stability analysis shows that the shrinkage temperature of mink fur after dry cleaning with subcritical fluid is increased, which is beneficial to improve the hydrothermal stability and durability.

(2) The analysis of intradermal oil content indicates that the subcritical fluid dry cleaning process can effectively remove the oil.

(3) The analysis of mechanical properties indicates that the tensile strength and elongation of mink fur are improved after dry cleaning with subcritical fluid.

(4) SEM shows that there are no excess lipids on the surface of the hair and scales treated with the subcritical fluid, the structure of the scales of aciulum and villi and the leather are basically consistent with that of the traditional dry-cleaning process, and the dry-cleaning effect is obvious.

Overall, mink dry cleaning process based the subcritical system can effectively reduce the use of harmful chemicals. And dry cleaning solvent can be recycled through condensation recovery, thus reducing production cost, effectively separating uncombined grease and utilizing wastes. This paper provides inspiration for the application of subcritical technology in fur production and processing, hoping to promote the development of clean and environmental protection of fur industry, improve economic benefits and promote the progress of society.

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Metal-Free Combination Tanning with Replenishable Polyphenols and Marine Oil

by

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Abstract

In line with the resurgence of natural products in the global manufacturing industry, the leather industry is also relooking the increased use of organic materials. To exploit the benefits of the vegetable tanning materials and to couple with suitable organic material for overcoming the inherent shortcomings of vegetable tanning materials, studies were undertaken. Tanning materials like raw fish oil have advantageous properties to impart on leather such as softness, lightweight, and washability characteristics. Hence studies were undertaken on polyphenol-fish oil combination tannages.

The quantities of wattle and fish oil and process conditions were standardized. The study indicated that the oxidation of fish oil could take place in the presence of vegetable tannins. The leathers tanned by this combination tanning system could be converted into garment leathers of rich shades and possessed good strength and physical properties. Propelled by encouraging results, investigations were also made on the nature of interaction between vegetable tannins and fish oil with collagen. It was also observed that the vegetable tannins probably do not hinder the oxidation of oil. To sum up, the study leads to the development of a viable, versatile organic tanning system to gain eco-acceptability for the leather manufacturing process.

Introduction

There has been an increasing demand among consumers for metal free garment leathers with improved functional properties such as washability in recent years. Demand for these washable and dry-cleanable leathers continues to increase dramatically and this trend may continue. The latest technological developments in leather research made this increasing market trend possible at affordable production and consumer costs with minimal impact on environment.

Vegetable tannins are extracted from plant leaves, barks, fruits, roots of plants or trees and tannins are water-soluble polyphenolic compounds having molecular weight in the range of 500-3000 Daltons. Besides the usual reaction of phenols, vegetable tannins can convert animal/hides and skins into leather producing relatively dense, firm or solid leather. The primary purpose of tanning is to make collagen resistant to heat, hydrolysis, and resistant to microorganisms' action. Vegetable tannins are colloidal, amorphous, astringent in taste and acidic in nature. They consist of large polyphenol molecules with some acidic groups and numerous secondary functions. The acidic groups may combine with the basic groups of the protein displacing the water by hydration. Generally, acidic conditions (low pH) favor vegetable tannin fixation by increasing the protein basic groups' ionization.

The leathers processed through vegetable tanning have advantages such as compatibility with human skin, comfort and high dimensional stability. The tanning methodology adopted also affords viable treatment and disposal of spent liquors. However, the drawbacks associated with vegetable tanned leathers are lack of softness, poor fastness properties and high susceptibility for fungal growth.[1]

The conversion of skin into leather by fats and oils is undoubtedly one of the most primitive methods used by the early races in different parts of the globe. The oil-tanned leathers are lightweight, soft, air-permeable and resistant to washing.[2-4] Hence in the present work, to take advantage of both tanning agents, fish oil and organic tannins of myrobalan (hydrolysable) and wattle (condensed) are studied in detail.

Materials and methods

Wet salted goat skins of Indian origin in the weight range of one kilogram per skin, industrial grade wattle and myrobalan tannins and fish oil (Cod oil) were chosen for the tanning studies.

Tanning experiments

The skins were processed conventionally up to deliming and tanning experiments were carried out as per the procedure given below. In order to monitor the changes effectively, the skins were cut into two halves, one half was tanned by conventional vegetable tanning and the other using vegetable–oil tanning system, to avoid skin to skin variations. Based on shrinkage temperature, physical properties and

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visual assessment of leathers the quantity and other parameters were standardized.

Tanning process for control

The depickled pelts (pH 4.8-5.0) were processed as below.

Water	50%	
Pretanning syntan	1%	drum for 60 min
Myrobalan or Wattle powder	20%	drum for 6 hrs
Formic acid	1%	3×10+drum for 60 min

The tanned leathers were set, hooked to dry, staked and buffed as being done for vegetable tanned leathers conventionally.

Tanning process for experiments

The delimed pelts (pH 7.5-7.8) were conditioned and processed as below.

Water	50%	
Fish oil	10%	drum for 3 hrs
Myrobalan or Wattle powder	10%	drum for 6 hrs
Formic acid	1%	3×10+drum for 60 min

The tanned leathers were set, hooked to dry, lightly staked and buffed as being done for vegetable tanned leathers.

Determination of iodine value

Industrial grade fish oil was analyzed for iodine value by Hanus method and standard official methods were followed for acid value and saponification value determinations.[5]

Shrinkage temperature

Shrinkage temperature of control and experimental leathers was analysed with Theis shrinkage tester to evaluate tanning efficiency.

Physical properties of leather

Organoleptic properties were evaluated by practising leather technologists for the softness and fullness parameters. In this study, tensile strength, elongation at break and stitch tear resistance of leathers were determined by adopting official procedures.[6,7] The leathers were chosen of even thickness and same region for testing for reliable results.

Scanning electron microscopic analysis

The fiber structure of the tanned leathers was studied using SEM analysis. Leather samples were coated with gold using an Edwards E 306 Sputter coater and analyzed by a Cambridge stereoscan S 150 scanning electron microscope.

Pollution load

The control and experimental process liquors from tanning operation was quantitatively collected and analyzed for BOD, COD, Cl^-, TSS and TDS using standard analytical procedures.[8]

Results and discussion

The combination tannages of both fish oil with myrobalan and fish oil with wattle tanning agents were studied in detail. Preliminary experiments revealed that pre-tannage with fish oil considerably reduces the fixation of vegetable tannins and the degree of tannage is also reduced. Conventionally, vegetable tannins, are fixed to non-ionic groups of collagen. The affinity of keto-imide linkages for vegetable tannins had been indicated as a decisive factor in vegetable tanning. Several researchers had shown the precipitation of tannins by polyvinyl pyrrolidone due to —CO-NH-grouping. Thus, the decreased affinity shown by vegetable tannins (Catechol type) for an oil pretanned protein would indicate that oil tanning also involves the same reactive groups, namely the hydrogen bonding site CO-NH-groups of the polypeptide backbone and others.[9-11]

The possibility of the peroxides or hydroperoxides being bound by the secondary valency forces to the polypeptide backbone seems probable apart from the simultaneous fixation of some of the aldehydic products to the basic protein groups. Similarly, on pre tanning with vegetable tannins followed by oil tannage, less oil fixation is observed. As mentioned earlier, most hydrogen bond sites are blocked with vegetable tannins, the peroxides formed may not have the same number of sites for binding as regular oil tanning.[12-14]

Shrinkage temperature of tanned leathers

Various experiments have been carried out to optimize the quantity of oil and tannins and also to standardize the stage of offer. It has been known that during vegetable tanning, maximum amount of tannins are fixed unipoint and only a small portion fixed bi-functionally as —CO -.OH — V — O.. HO — (Or) — CO.. OH — V — OH...OC — between the — CO of one chain and — OH of hydroxypridine of another chain or between the —CO of one chain and the — CO of another chain as shown above. The results show the oil with wattle combination tanning resulted in higher shrinkage temperature compared with conventional wattle tanned leather (Table I). This could be due to formation of additional cross links by oil during combination tanning. Skins tanned with myrobalan and oil combination exhibited lower shrinkage temperature, less fullness characteristics probably because of inherent nature of hydrolysable polyphenols.[15,16]

Table I

Shrinkage temperature of tanned leathers

S.No	Quantity of Tannins (%)	Quantity of fish oil (%)	Shrinkage Temperature (°C)
1	Myrobalan - 20%	-	65±1
2	Myrobalan - 10 %	5%	70±1
3	Myrobalan - 10 %	10 %	74±1
4	Wattle - 20 %	-	83±1
5	Wattle - 5 %	10%	78±1
6	Wattle - 10 %	10 %	88±1
7	Wattle -15 %	5 %	84±1

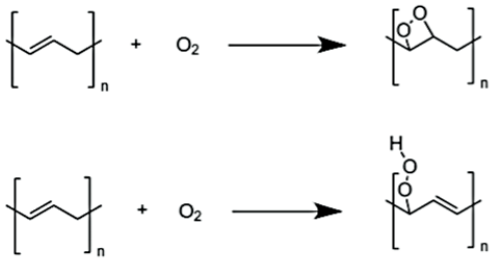

Figure 1. Fish oil degradation process

Wattle 10% and fish oil 10% combination tanned leathers possessed better thermal strength and functional properties when compared with other experimental leathers.

Iodine value

The rate of oxidation of oil is related to the iodine value of the oil. Obviously, the higher the iodine value, the greater would be the number of reactive centres available for oxygen absorption, leading first to the formation of peroxides or hydroperoxides as shown in Figure 1, as a result of chain reactions then to further degradation into other products.

Table II

Iodine value

S.No	Type of tanning	Iodine value
1	Raw fish oil	140
2	Oil tanned leather (Fish oil – 20%)	80*
3	Myrobalan - 10% : Fish oil – 10% tanned leather	70*
4	Wattle - 10% : Fish oil – 10% tanned leather	60*

(*oil extracted from tanned leathers)

The results shown in Table II confirm that the oxidation of fish oil could take place in the presence of vegetable tannins. From the study, it is observed that vegetable tannins do not hinder the oxidation of fish oil, which is probably due to the lower percentage of vegetable tannins offered and thereby providing certain reactive sites of collagen, free to react with the peroxides or hydroperoxides and aldehyde products which formed during the oxidation of fish oil.[17]

Organoleptic properties

The leathers were evaluated for their organoleptic properties and found wattle 10% with fish oil 10% had better properties than other experimental leathers as described in Figure 2. Because of better oil lubrication the fiber matrix have better splitting and resulted in softness and fullness and less tightness compared with wattle tanned leather. The SEM images too confirmed the results.

Physical strength characteristics

The quality of leather is determined by its physical structure, chemical composition, and mechanical stability. The leathers tanned with wattle alone and wattle with fish oil were converted

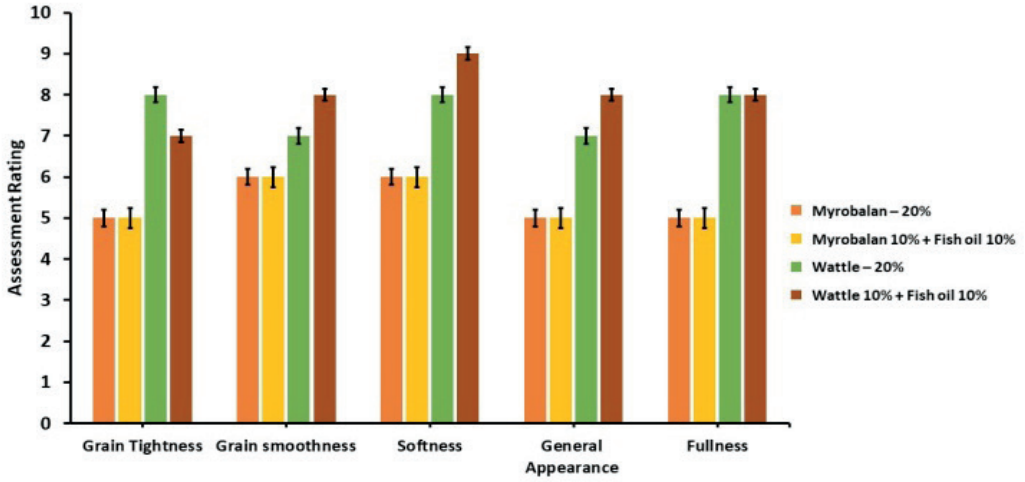

Figure 2. Organoleptic Properties of leathers

Table III

Physical strength characteristics

Tannage	Tensile strength (Kg/cm^2)	Elongation at break (%)	Tear Strength (Kg/cm)
Wattle - 20%	200 ± 3	40 ± 2	25 ± 2
Wattle - 10% Fish oil – 10%	285 ± 2	52 ± 3	60 ± 5

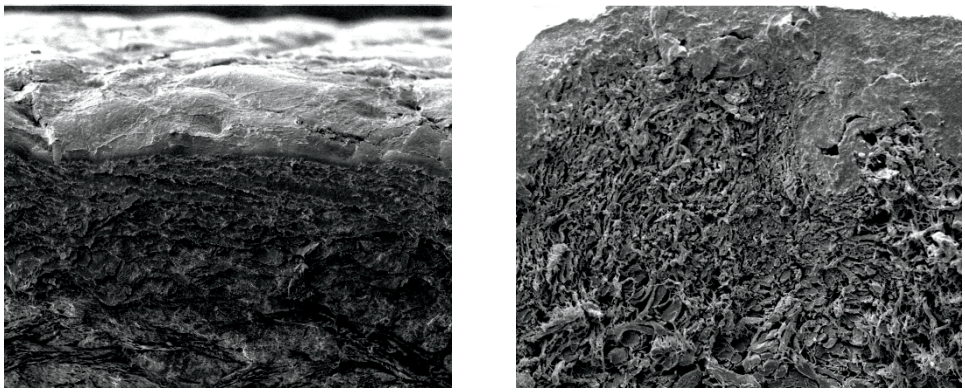

Figure 3. SEM of cross section of tanned leathers. **(3a)** Wattle tanned leather (500X) and **(3b)** Fish oil with wattle tanned leather (500X)

into crust leathers and subjected to mechanical strength testing. From the results of Table III, it is observed that the vegetable-oil combination tanning system had improved mechanical properties and could produce softer types of garment leathers with sufficient drape and softness. The leathers also possessed good appearance and feel with physical properties like tensile strength, tear resistance, etc.

Scanning electron microscopic analysis

A morphological study was carried out for the experimental leathers in comparison with wattle tanned leathers to show the effect of condensed tannin and fish oil combination tanning in the fiber bundles (Figures 3a & 3b).

From the cross-section micrographs, it is clear that the experimental leather fibers were separated from one another, but in the case of conventional wattle tanned leather fiber aggregation can be noticed.

Effluent characteristics

The spent liquors of tanning were analyzed for their impact on environment as expressed by parameters such as BOD, COD, TDS, etc. Conventional vegetable tanning requires pickling and repickling processes which generates huge amounts of chlorides and TDS as shown in Table IV. But in the experimental process, the skins were treated with fish oil after deliming which is at neutral pH. Hence the results indicate huge reduction in effluent parameters of chlorides and TDS. It's proven that fish oil-wattle combination tanning system is eco-friendly and skin friendly.

Table IV

Spent liquor Characteristics

Tannage	Biochemical Oxygen Demand	Chemical Oxygen Demand	Chlorides	Total Suspended Solids	Total Dissolved Solids
Wattle - 20%	6000 ± 30	20000 ± 30	55000± 30	7550± 20	47500 ± 50
Wattle - 10% Fish oil - 10%	3550 ± 25	9750 ± 30	7500± 30	5600± 20	18050 ± 25

Conclusion

Extensive studies have been carried out using vegetable tanning agents - wattle and myrobalan along with fish oil. Based on the analytical results and obtained leathers, it is found that the leathers possessed combined advantage of both the tanning agents. The results showed oil with wattle tanned leathers had higher shrinkage temperature than conventional vegetable tannage. The fringe vegetable tannage probably provided an opportunity for the oil to oxidize even in the presence of vegetable tannins, as inferred from the iodine value of oil extracted from the tanned leathers. Further the amount of vegetable tannins used in the new system is only 50% of the conventional system. Hence the combination tanned leather color has not darkened like conventional leathers. Also, the leathers produced through this tannage were able to be converted into variety of finished leathers, indicating potential versatility of the system with excellent organoleptic and strength properties. The combination tanning system studied could emerge as a viable alternative for conventional tanning systems, as both the tanning materials used organic in nature and are replenishable sources.

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Biocolorant for Leather Dyeing Applications: An Eco-benign Evaluation of Natural Coloring Agent

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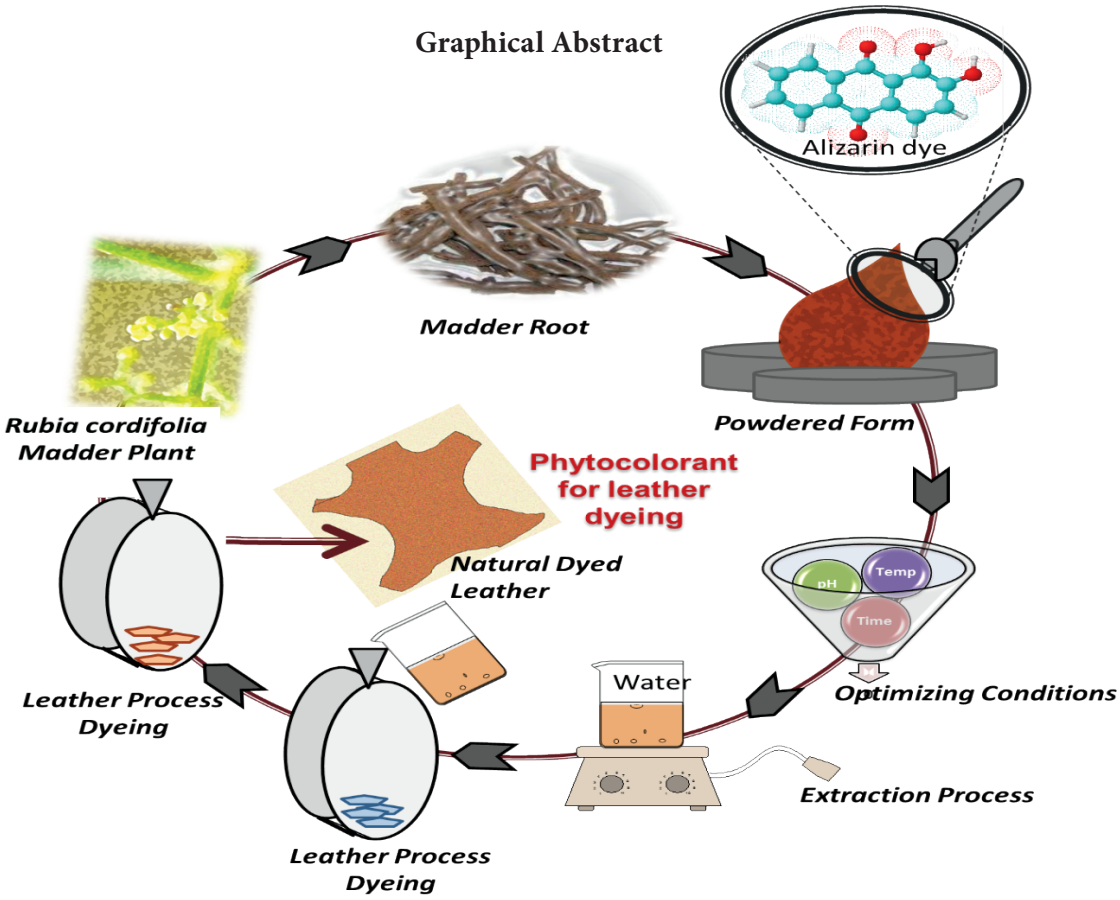

Abstract

Exploration of biocolorant in leather industry is explored widely owing to its environmental limitation. Besides, employing synthetic dyes in leather process requires high end of pipe treatment due to their complex chemical structure. Therefore, an attempt has been made on exploiting madder root dye (*Rubia cordifolia* L.) for leather dyeing application. The effect of varying pretreatment regimen on madder colorant extraction, chemical characterizations (including UV-Vis, IR, particle size, zeta potential value, and thermal studies) and optimum operating leather dyeing conditions are studied. The results revealed dissolving medium pH 5, 100°C, and 60 min duration of extraction is optimum. Thus, obtained dye characteristics showed maximum absorption peak at 460 nm, with an average particle size of 166 nm. The optimum leather dyeing is found at leather pH 5.5, 10% dye concentration and 4 h duration. At optimum dyeing parameters it shows good fastness, perspiration, organoleptic properties without affecting the physical characteristic. Novelty of the present research would lead to develop eco-dyeing method in leather manufacture. Moreover,

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the study unravels a new application of eco-benign dye to achieve sustainable process.

Introduction

Leather sector is one of the highest contributors to the Indian economy. Leather processing involves tanning with pre- and post-tanning operations, with dyeing as one of the post-tanning processes.[1] Dyeing is carried out to impart color to the substrate which is a vital unit activity in leather, textile, and allied industries to enhance aesthetic value.[2] During dyeing, reactive groups of dye molecules react with collagen fibers in the leather substrate by possible adsorption and slow diffusion through the pores.[3] Generally, dyes are chemical structures with attached chromophore conjugate which produce color. The chromophores are diverse based on the functional group such as azo, nitro, carbonyl, anthraquinone, etc.[4] On considering the aesthetic value, several emerged synthetic dyes are employed in leather processing due to their high fastness and lower price. However, using synthetic dyes is prone to serious alarming pollution load and treatment constraints and ultimately toxic to all levels of life forms.[5] Therefore, to combat these paradigms, efficient natural dyes and pigments are emerging as research output to alternate synthetic dyes.

A eco-friendly and renewable dye source is needed in all dyeing industries, including food, textile, and leather sectors. Besides, some plant products possess biological properties, including anti-cancer, anti-oxidant, anti-microbial, anti-viral and larvicidal activity.[6-8] The source of coloring chemical compound is from different plant parts including whole plants, roots, leaves, flowers and fruits.[9-12] Plant metabolite products such as quercetin and lutein was reported as a possible substitute for synthetic dyes by Gulzar et al. (2015) and Adeel et al. (2017), respectively.[13,14]

In the current study, an industrial dye crop plant madder (*Rubia cordifolia*, L.) is used to obtain vibrant reddish colorant towards sustainable leather dyeing process.[15] The vibrancy of madder red can surpass synthetic red color which contains principal coloring component alizarin (1, 2-dihydroxy anthraquinones), an anthraquinone in its root.[16,17] Moreover, recently burgeoning environmental conditions, toxic nature of synthetic dyes and growing awareness on sustainability has posed towards revival of natural dye applications as the success and promises encountered in textile field. Therefore, natural dyes are gaining popularity in other fields with pre-requisite for dyeing process. Many studies pertained to show characterization of natural dyes and chemistry of its dyeing in many non-leather applications. Especially many have been reported for possible utility in applications such as food, textile and health sectors towards eco-benign approach due to their non-toxic nature. Several native plant derived dyes in textile dyeing have been reported extensively and have long been utilized since ancient times.[18,19] A few studies on leather dyeing using plant metabolites are reported by Mohammed et al. (2017); Sivakumar et al. (2009); Musa et al. (2009); Velmurugan et al. (2016); (2017); Tamil Selvi et al. (2013); Vedaraman et al. (2017).[20-24] Considering utilization of natural dye in a large industrial scale operation standardized extraction condition must be optimized to obtain quality of dyeing in leather.

The commercial feasibility of madder dye in the leather application is addressed in this study to increase the demand for natural dye, which is not only beneficial to the environment but also increases the economic feasibility. The main objective is the optimization of madder colorant extraction, chemical characterization, and leather application under optimum fixation condition. The dyeing of leather is optimized at different dye concentrations, initial leather pH value, duration, mordants and analysed the color values. The dyed leather properties, such as color fastness, physical strength, and organoleptic properties were studied.

Materials and Methods

Materials

The madder root powder was purchased from a local buyer, Tindivanam, Tamil Nadu. Undyed chrome-tanned goat crust leather (1.00 mm thickness) was used in the experimental trials. All other chemicals used were of commercial grade.

Optimization on madder dye extraction

An aqueous solution of 1% madder root powder was used for optimizing the extraction and UV-Vis spectrum analysis. The effect of dye extraction at different regimens of temperatures (50, 60, 70, 80, 90 and 100°C) and pH (4, 5, 6, 7, 8 and 9) for 60 min were carried out. Similarly, different time periods (15, 30, 45, 60 and 120 min) on extraction was analyzed for maximum absorption peak and compared.

Preparation and characterization of madder dye

Aqueous dye extraction was carried out at pH 5.0, 80°C for 1 h. The obtained dye extracts were filtered and concentrated to 15-20% solid content. Later, the aqueous extract was dried using a spray dryer apparatus adjusted at a range of 160-170°C and 80-90°C as an inlet and outlet temperature, respectively. The extracted dye was stored at ambient temperature for further characterization.

Spectral characteristics

The extracted dye was scanned for absorption maxima between 200-800 nm using a UV-Vis spectrophotometer. Vibrational spectroscopy was used to determine the functional groups between 4000-400 cm^{-1} wavenumber (JASCO FTIR 4700). Furthermore, the particle size and stability were analyzed using Malvern Zetasizer Nano Instrument.

Thermal property analysis

Thermal stability and its behavior of extracted dye were analyzed from thermograms of TGA (Thermogravimetric analyzer) and DSC (Differential Scanning Calorimetry), respectively. In TGA analysis samples were heated between 25 and 800°C with an increasing temperature of 20°C/min under N_2 atmosphere (TA instruments, Q-50). For DSC analysis samples were heated between 25 to 300°C with an increasing temperature of 10°C/min under N_2 atmosphere (TA Instruments, DSC Q200).

Leather dyeing application and analysis

The dyeing efficiency of dye was evaluated on chrome tanned crust leather as given in Table I. Leather trials were carried out with different parameters such as dye concentrations (2, 5, 10, 15 and 20%), pH (4.0, 4.5, 5.0, 5.5 and 6.0) and durations (2, 4 and 6 h). To understand the mordanting effect on leather dyeing, hence, mordants such as aluminium sulfate, ferrous sulfate and calcium carbonate were used. After dyeing the leathers were subjected to color measurements using reflectance spectrophotometer (Milton Roy ColorMate HDS instrument) and morphological evaluation using optical microscope. The same experimental formulation was used for pre-mordanting experimental trials using 1% aluminium sulfate, ferrous sulfate and calcium carbonate.

To understand the influence of dyeing on leather characteristics rub fastness, perspiration fastness, tear strength, tensile strength, elongation at break and grain crack strength were studied.[25-29] In addition to physical characterization, organoleptic properties such as dye uniformity, dye penetration, grain smoothness, and softness were assessed by four experienced leather tanners.

Results and Discussion

Eco-benign and sustainability are the two critical parameters to assess for the use of chemicals in leather processing. Natural and renewable chemicals are the major characteristic to attain bio-driven processing. Several bio-driven chemicals are exploited for use in leather manufacture. Dyeing is one of the important unit processes in leather making which add aesthetic value to the products for the end use. Natural dyes are exploited as an alternate to synthetic dyes to achieve eco-sustainable and thereby reducing the pollution at the end of pipe treatment. In the present study, dye prepared using madder root was used to dye leather and characterized to understand its possible intervention as a dyeing agent.

Optimization on madder dye extraction

The dyes of natural origin must be extracted from plant material by an eco-friendly manner, which is highly susceptible to degradation, and is majorly influenced by pH, temperature, light, metals, etc.[30] The influence of temperature, pH, and duration of physical disruption factor plays a significant role in the colorant extraction. The absorption spectra of madder dye extracted at different temperatures are shown in Figure 1a. From this data it can be inferred that maximum absorption value is at 100°C. Thus, result showed a hyperchromic shift with increasing temperature. A strong hyperchromic shift is inferred when the temperature increased above 70°C, therefore, dye is extracted at 100°C.

Table I

Post-tanning procedure for dyeing using madder dye

Process	Chemicals	%	Duration	pH adjustment
Wetting back	Water	300		
	Wetting agent	1.0		
	Ammonia solution	0.2	Overnight	
Washing	Water	300	30’	
Neutralization	Sodium formate	1.0	3 × 10’	Different pH***
	Sodium bicarbonate	0.5		
Dyeing	Water	100	15’	
	Madder dye	Different percentage*	Different time interval**	Penetration check
Fixation	Formic acid	1.5	3 × 10’	pH 3.8 - 4.0

Leathers piled overnight, hooked to dry, staked, trimmed and buffed before analysis

* % of dye – 2 to 20; ** Time duration - 2 to 6h; *** pH - 4 to 6

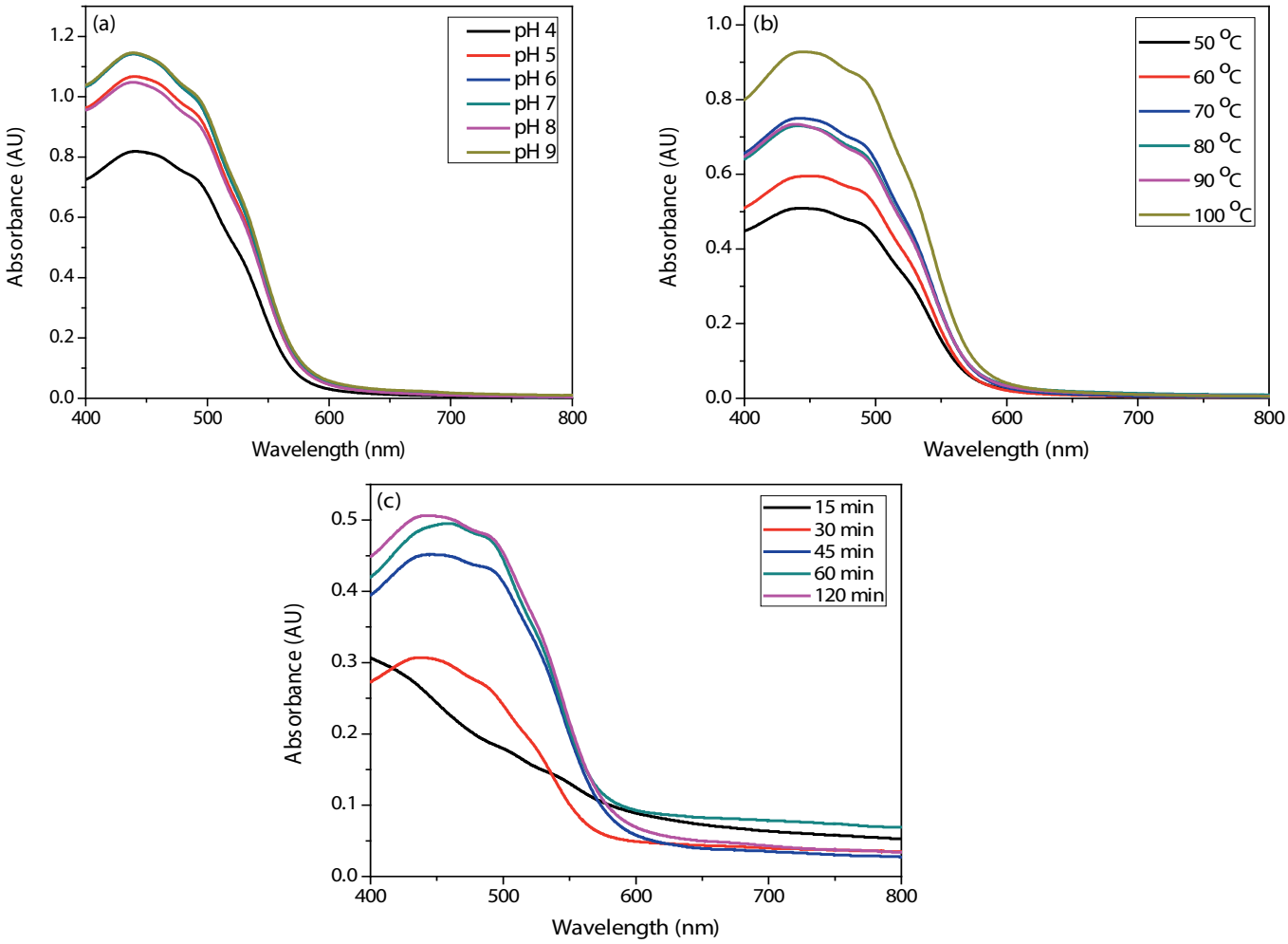


Figure 1. Absorption maximum analysis of dye extracted at different **(a)** Temperatures, **(b)** pH, **(c)** Durations

The absorption spectra of madder dye at different pH levels are shown in Figure 1b. Comparatively, a high pH value towards basic condition has significantly improved the dye extraction process. Thus, dye extracted from the biomass above pH 5 shows maximum peak value. This is a significant hyperchromic shift in absorbance peak value. The absorption spectra of madder dye extracted at different durations is shown in Figure 1c. From this data it can be inferred that the maximum dye extraction has been observed between 30-to-60-minute duration. Therefore, optimum duration for dye extraction is 60 minutes with a hyperchromic shift (Figure 1c). Thus, the overall optimization result shows 60 minutes of extraction duration under 100°C, and pH 5 showed significantly improved colorant extraction. Similarly, Berhanu and Ratnapandian (2017) reported natural dye extracted from *Cassia singueana* at temperature of 95°C and 60 minutes of duration as the optimum dye extraction condition for leather dyeing application.[31]

Spectral characteristic analysis

The UV-Vis spectra of madder dye extract shows a maximum absorption wavelength at 460 nm (Figure 2a). As previously reported alizarin chromophore prominently shows maximum

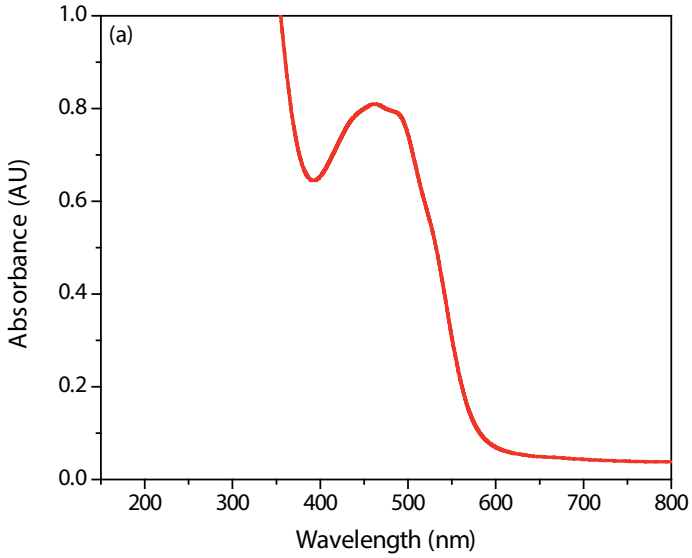


Figure 2a. UV-Vis spectrum of madder dye

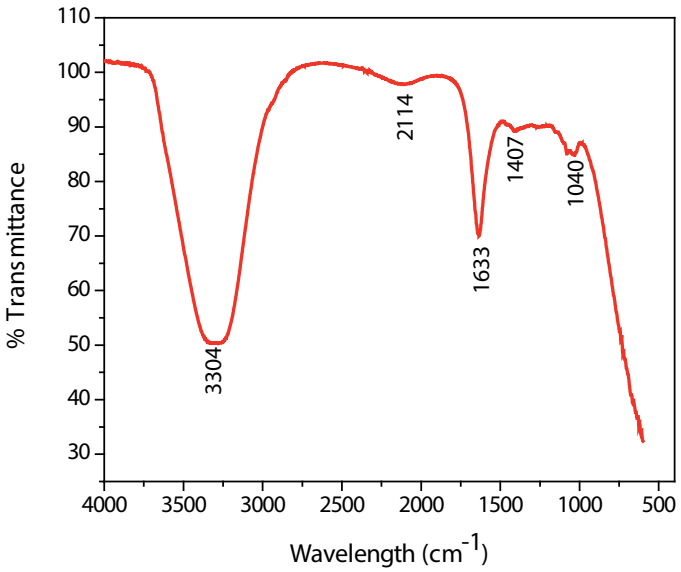


Figure 2b. FT-IR spectrum of madder dye

absorption spectrum at 459 nm.[32] The FT-IR spectra of madder dye extract shows the presence of characteristic peaks at 3300, 2114, 1633, 1407, 1077 cm^{-1} corresponding to OH, C=O, C=C, C-H and C-C group, respectively (Figure 2b). Thus, the vibrant red color of anthraquinone molecule with chromophore can be exploited for leather dyeing applications.

Particle size and stability analysis

The hydrodynamic diameter or particle size of madder dye is measured using DLS method. The result revealed that the distribution range is 166 nm (Figure. 2c). Therefore, madder dye component alizarin within this particle will lead to uniform dye penetration. In an earlier report by Tamil Selvi et al. (2013) and Mohammed et al. (2017), the reported particle size of natural plant dye of *Bixa orellana* and mekmeko dye extract showed good dye penetration in the leather substrate.[3,24] As reported in the previous report, leather dyeing using madder extract shows good penetration through leather pores due to smaller particle size. The obtained colorant showed a zeta potential value of -5.31 (negative) and was found to be highly stable (Figure 2d). The anionic dye property influences the adsorption on the cationic leather surface due to the electrostatic force of attraction. Thus, madder dye is feasible for leather dyeing application.

Thermal stability analysis

The TGA of madder dye shows a weight loss of colorant which indirectly reveals the dye's thermal stability towards increasing temperature (Figure 3a). The colorant decomposing at the high-temperature profile shows a drop in the curve, indicating a loss of sample mass. The TGA curve shows degradation occurs in two distinct regions. Thus, madder dye can be heated up to 100°C as

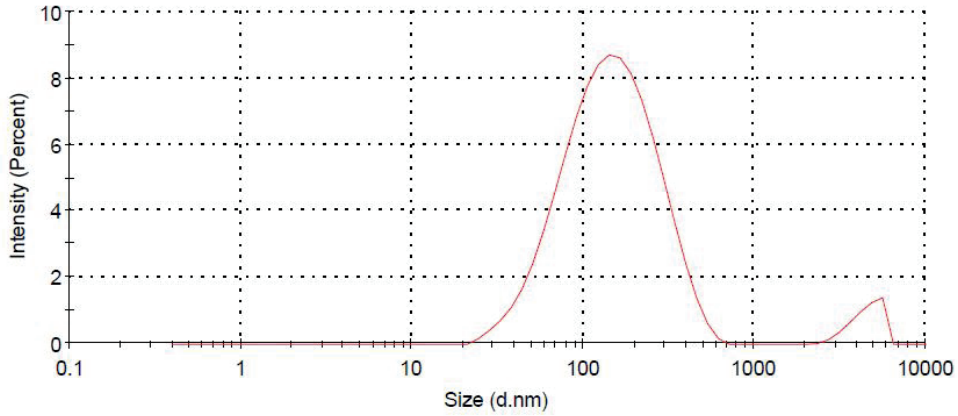


Figure 2c. Particle size spectrum of madder dye

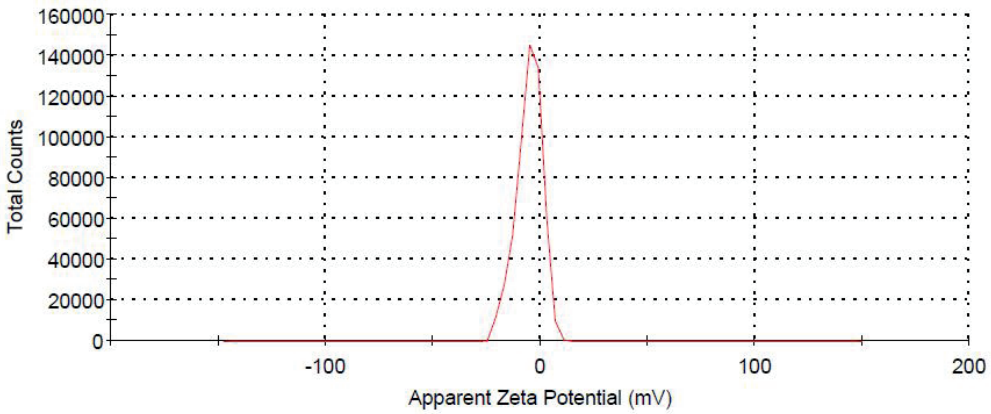


Figure 2d. Zeta potential spectrum of madder dye

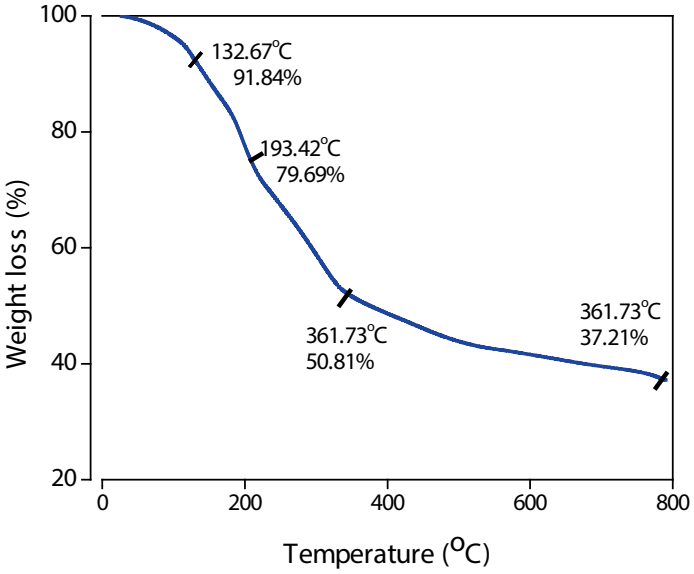


Figure 3a. TGA thermogram of madder dye

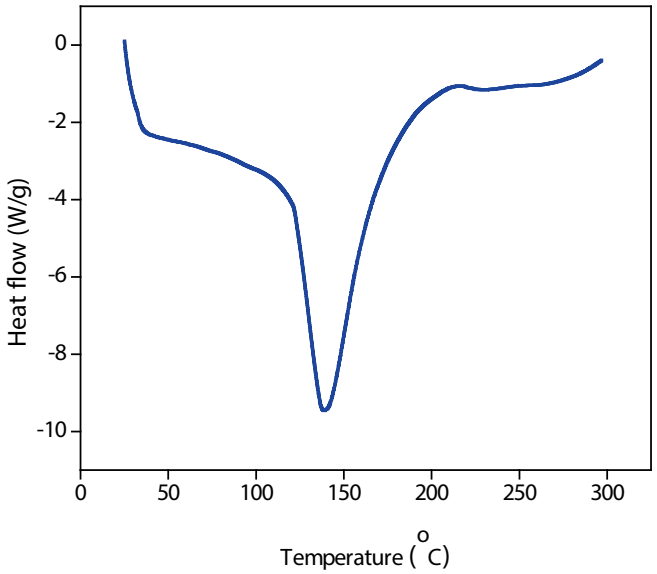


Figure 3b. DSC thermogram of madder dye

revealed in pre-treatment processing. Figure 3b shows the DSC thermogram of madder dye extract. The endothermic reaction at 139.05°C is beyond 100°C due to less moisture content. This indirectly reveals the high heat stability.

Leather dyeing optimization trials

In the following experiments, madder dye was used for wet blue crust leather dyeing at different processing conditions and analysed for the color values.

Effect of concentration (Trial 1)

Color values of different concentrations of dye are given in Table II a. With the increase in the concentration of dye, there is an increase in color values towards the darker shades. From the L*, a*, b* values obtained, it is observed that there is increased darkness towards high dye concentration. Similarly, the more positive values and only marginal difference in a*, b* values show slightly more redness and yellowness. Higher color values are obtained with 10% and 20% dye concentration, but the difference in color values is only marginal; therefore, 10% is taken as an optimized concentration taken for further study.

Effect of pH (Trial 2)

Color values of varied pH leathers were studied and the results given in Table II b. It is observed that pH 5.5 is optimum for high dye uptake by leather. The L*, a*, b* color values at different pH values shows significant changes above pH 5.5 compared to others (Table II b). High fixation at pH 5.5 is due to surface charge alteration towards basic pH, which is influenced by high dye uptake and increased darkness value. Therefore, appropriate surface charge alteration in the leather substrate enhanced the dye fixation. Dye uptake and fixation onto the leather at pH 5.5 were higher than at acidic pH.

Effect of time (Trial 3)

Color values of varied dyed leather at different time intervals is tabulated in Table II c. It is observed that dye uptake increased with increased dyeing time. Thus, optimal duration for dye penetration in the leather substrate is observed at 4 h time duration (Figure 4c). Interestingly color values (L*, a*, b*) in different period trials show significant changes observed between different fixed durations (Table II c).

Effect of Mordants (Trial 4)

Impact of mordants on leather dyeing is given in Table II d. The dyeing effects are varied with different selected mordants and we selected the one which imparts more redness for further studies. In addition, the dye uptake onto leather increased when pre-treated with all mordants with vivid coloration and good penetration. The result showed a significant difference in color values (L*, a*, b*) in the presence of aluminium sulfate mordant. The results show that compared to selected mordants, 1% of alum has more red shade and less saturated compared to control (non-mordanted). This result shows that bio-colorant applied on mordant pre-treated leather is an alternate to different color shades in par with synthetic dye.

Table II

Color value analysis of crust leather dyed using madder dye

a. Effect of concentration

	L*	a*	b*
2.0%	58.638	20.321	9.815
5.0%	56.383	22.629	10.388
10.0%	54.236	23.632	9.495
15.0%	54.018	23.743	9.968
20.0%	52.657	20.495	12.189

b. Effect of pH

	L*	a*	b*
pH 4.0	64.173	17.903	10.559
pH 4.5	60.017	20.732	11.897
pH5.0	55.456	23.875	7.495
pH 5.5	59.622	20.602	10.948
pH 6.0	59.663	19.741	9.037

c. Effect of time duration

	L*	a*	b*
2h	62.654	12.777	9.433
4h	48.986	15.308	11.731
6h	41.398	30.958	14.069

d. Effect of mordants

	L*	a*	b*
Dyed without mordant	62.19	11.17	5.01
Aluminium sulfate	40.43	31.39	13.87
Ferrous sulfate	57.29	18.65	9.48
Calcium carbonate	53.42	15.17	9.98

Grain Surface Analysis

The optical images of dyed crust leather surface imaging were analysed for topographical changes due to dyeing (Figure 4 a-d). From the surface image, it can be ascertained that there was no significant changes in the surface. The dyed leather samples are similar to undyed crust leather samples having compact grain tightness and without any morphological changes. Rather a significant change in color strength is observed prominently.

Characterization of dyed leather

The preliminary studies revealed that 10% of dye concentration, pH 5.5, the period of 4 h, and pre-mordanted with alum yields high coloration and dye penetration.

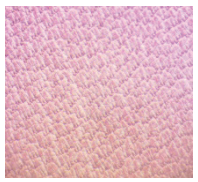
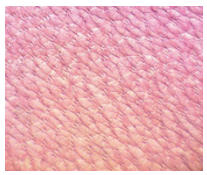
Color fastness analysis

Wet rub, dry rub, and perspiration results of leathers are given in Table III. The testing results show that color fastness characteristic are better and in good acceptable range. From the result, it is evident that rubbing fastness of the bio-colorant dyed leather is good, which is one of the important factors for commercializing the madder dye for leather application.

Organoleptic properties analysis

The organoleptic properties such as dye uniformity, dye penetration, grain smoothness, and grain softness values of the experimental leathers are given in Table III. The visual assessment of the leathers was improved and dyeing was found to have no impact on the leather quality.

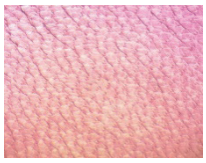
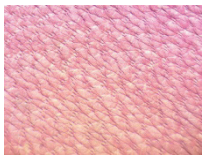
a. Trial 1

2%	5%	10%	15%	20%
				

b. Trial 2

pH 4.0	pH 4.5	pH 5.0	pH 5.5	pH 6.0
				

c. Trial 3

2 h	4 h	6 h
		

d. Trial 4

Aluminium sulfate	Ferrous sulfate	Calcium carbonate
		

Figure 4. Optical images of different trials

Table III

Organoleptic and fastness properties of crust leather dyed using madder dye

S. No.	Properties		Color change values of madder colorant-dyed leather	Recommendation
i	Color fastness to rubbing	Dry 150 rubs	4/5	Min 3
		Wet 50 rubs	4/5	
	Color fastness to perspiration	Cellulose acetate	4/5	
		Bleached cotton	4/5	Min 3
		Spun nylon	4/5	
		Spun polyester	4/5	
		Spun acrylic	4/5	
		Wash spun wool	4/5	
ii	Organoleptic	Dye uniformity	9/10	
		Dye penetration	9/10	
		Grain smoothness	8/10	
		Grain softness	9/10	

Conclusions

The present study focused on developing eco-dyeing from plant wastes. Utilization of plant wastes into a high value product has been presented. The optimum leather dyeing has been optimized at pH 5.5 with 10% dye concentration and required minimum of 4 h duration. Mordants have been used to enhance the dyeing characteristics and the color shades can be varied based on the choice of mordants. The physical characteristics of the dyed leathers met the standard norms. Application of madder root dyes in leather manufacture would be a new insight to achieve sustainable leather products. Moreover, the madder roots are known for biomedical applications. This study could lead to develop medicated properties in leather products. From the preliminary studies, it can be concluded that madder root dyes could be a potential eco-dyeing agent for leather manufacture.

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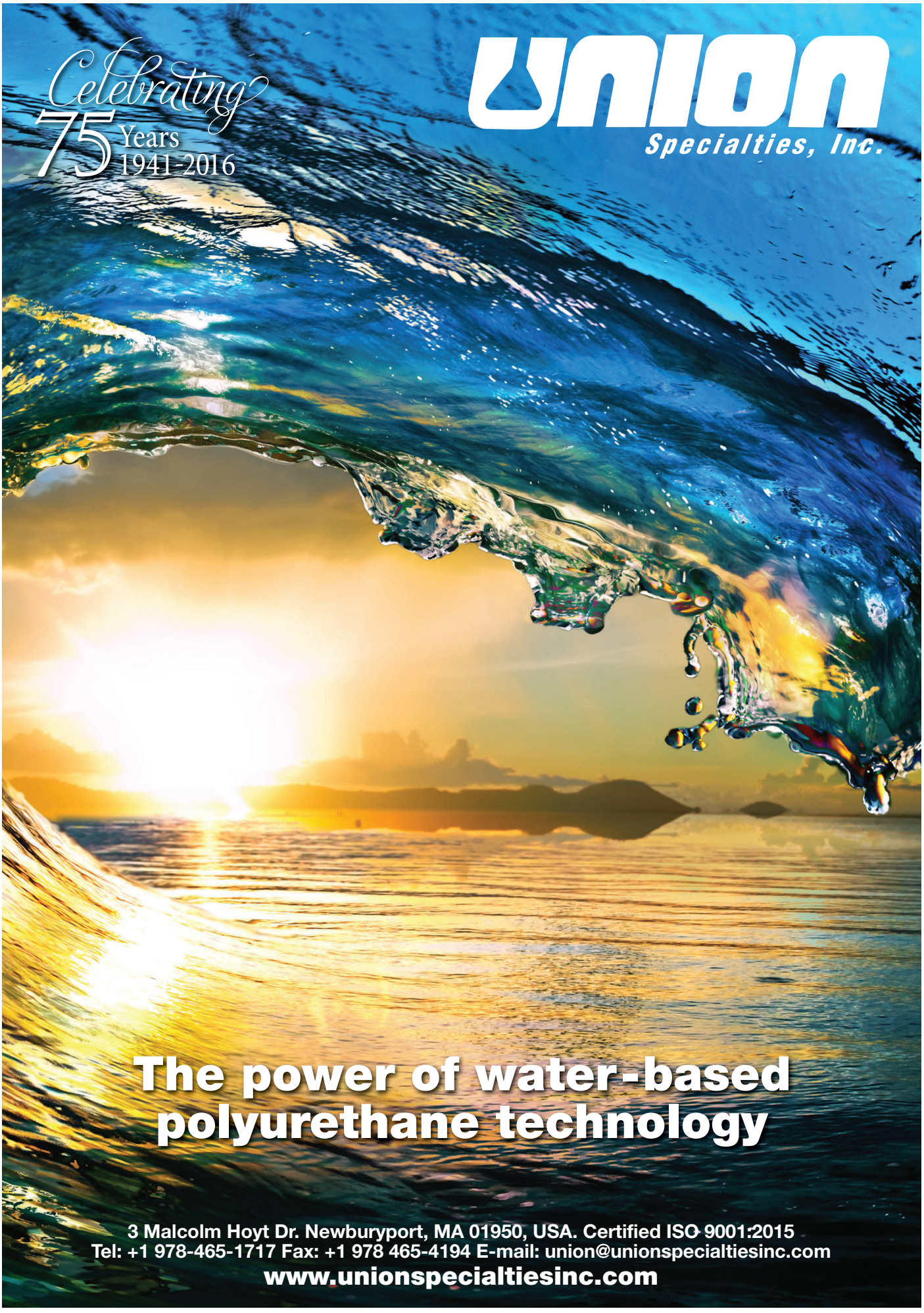
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