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# Effective Removal of Manure/Mud Balls from Cattle Hides using Thioglycolate Salt Containing Formulations

by

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## Abstract

The effective removal of hardened manure/mud balls from cattle hides remains a challenge for the livestock industry. Hardened manure/mud balls must be removed to minimize the risk of microbial meat contamination and hide quality deterioration. To overcome this challenge, we developed thioglycolic acid and its sodium, potassium and ammonium salts containing formulations. In this study, the developed four formulations were compared based on their efficacy in removing adobe type mud/manure balls from the hides in short time. Hide pieces containing hardened manure/mud balls were soaked in the formulations for 5 minutes followed by gentle brushing to remove the debris. The firmly attached mud/manure balls were removed completely from the hide pieces soaked in sodium, potassium and ammonium thioglycolate containing formulations. However, thioglycolic acid containing formulation did not show that much efficacy and the debris remained attached in the hide pieces soaked in water which was used as a control. Moreover, naturally onboard aerobic bacteria count was significantly reduced along with the mud/manure balls removal from hide pieces. After treatment, the hide pieces were processed into crust shoe leather for quality check analysis including mechanical properties, leather surface analysis and general appearance. The crust leathers made from hide pieces treated with the formulation exhibited similar quality to that made from the control. The implementation of this inventive formulations in slaughterhouses or leather industry will drastically reduce the time consuming and labor-intensive operations currently employed to remove firmly attached debris from cattle hide surface.

## Introduction

Formation of hard to remove manure/mud balls on cattle hides is a major problem for both the meat and leather industries. Hardened manure balls form usually during winter season when animals in feedlots get wet and muddy. The problem of hard to remove manure formation is aggravated with long hair cattle breeds. The manure and mud accumulate on the hide hair and hardens as the temperature approaches to freezing. With the addition of more manure, the manure becomes exceedingly attached and entangled with the hide hair leading to the formation of hard to remove manure balls.[1-2] The presence of such type of adobe type mud/manure balls is a major concern to the cattle industry for several reasons. First, they could be a conducive environment for microbial growth leading to increased risk of food safety due to carcass contamination. Second, the adobe type mud/manure balls can create holes on hides during the fleshing process in tannery, as a result the value of the hide will be significantly affected. Third, the integrity of the hide can also be affected because of the enzymes released by the bacteria which will ultimately affect the leather quality.[3-5] To avoid these problems it is important to remove the firmly attached external debris from cattle surface prior to slaughter and leather processing.

Currently, hard-dried manure/mud balls are manually raked or mechanically removed from the animals either by washing the animals with water or using electric shaver. These current practices are labor intensive and suboptimal because of the need to use large amount of water under high pressure for hours and the discomfort experienced by the animals as well as the manual handling of animals by workers.[2,6]

There has been effort to develop formulations that can remove hardened manure. Auer et al. reported[7] that hardened manure balls are mainly composed of lignocellulosic material (cellulose, hemicellulose and lignin) and other minor components, like feed proteins, hair, lipids, carbohydrates and minerals. To that effect solutions containing mixtures of enzymes were developed to break down the components of the hardened manure on cattle surfaces. The enzymes utilized include cellulase, xylanase or hemicellulase and laccase. Even though the formulation of enzyme mixtures was reported to aid in removing the hardened manure but in a proof of concept study the enzyme mixtures were not found to be effective when applied in live animals. In another study Ramos et al reported a soaking formulation that can soften hardened manure and facilitate their removal from the hide surface. The soaking formulations containing sodium carbonate and glycerol with or without biodegradable detergent sophorolipid were

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**Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture (USDA). USDA is an equal opportunity provider and employer applied on hide samples containing hard-dried manure for 2 hrs. The soaking formulation was reported to be effective in softening and subsequent removal of manure from hide surface. It was also reported that the soaking formulation did not negatively affect the quality of the finished leather.[6] Marsico et al also reported the use of sodium percarbonate as an oxidizing agent in combination with sodium hydroxide in removing hardened manure from hide surface. This combination was reported to remove hardened manure in less than 30 minutes by weakening the hair.[8] Recently Navone et al reported[2] manure removing formulations which contained protease enzymes that attack the interaction between the hardened manure and the hair. Protease enzymes weaken the framework of hairs at the point of attachment between the hair and the manure while degrading adhesive protein that may hold the manure structure together. However, these soaking formulations require long time to be effective in terms of industrial application and can only be applied on hides not carcass, therefore, no use in meat processing plant prior to hide removal. Thus, there is still a need to develop cost effective, labor efficient and fast method of removing hardened debris from hide surface without damaging the hide.

In our previous study,[9] we developed a formulation combining potassium thioglycolate with sodium hydroxide. The formulation was effective in removing mud/manure balls from the hide surface in 5 to 8 minutes depending on the level of concentration. The formulation disrupts the disulfide bonds of keratin protein in hair where the mud/manure balls are firmly attached to on cattle surface. An aqueous soluble weakly toxic antimicrobial agent, sodium dichloroisocyanurate dehydrate[10-12] was also added into the formulation to improve its efficacy on limiting microbial population on hide. Both spraying and soaking methods of dispensing the formulation were found equally effective in performance. However, in this study three more formulations have been developed using thioglycolic acid, sodium and ammonium thioglycolate. The efficacy of these formulations has been compared in removing mud/manure balls from the bovine hide. The impact of the formulations on the quality of the finished leather was evaluated by assessing the grain structure and measuring the mechanical properties of leather produced out of the treated hide samples.

## Materials and Methods

Fresh bovine hides were collected from the local meat packing company, JBS Packerland (Souderton, PA). The manure containing part of the hide was cut into smaller pieces of approximately equal size (12 in × 12 in) that weighed around 1kg. Potassium thioglycolate solution (40-44%) was purchased from Acros Organics. Thioglycolic acid, sodium thioglycolate and ammonium thioglycolate were purchased from Sigma Aldrich. All the chemicals were of laboratory grade at the time of use.

**TABLE I**

**Composition of manure removing formulations**

| Formulations | Composition |
|---|---|
| **F-A** (control) | Tap water |
| **F-B** | 7.5% Potassium thioglycolate + 7.5% NaOH |
| **F-C** | 7.5% Sodium thioglycolate + 7.5% NaOH |
| **F-D** | 7.5% Ammonium thioglycolate + 7.5% NaOH |
| **F-E** | 7.5% Thioglycolic acid + 7.5% NaOH |

### Preparation of Mud/manure Removing Formulation

The formulations were prepared as described in Table I by dissolving the required amount of the chemicals in tap water at room temperature (~22°C) and ~24 h prior to conducting the experiments.

### Determination of pH of the Developed Formulations

Three readings have been taken to determine the pH of each formulation at room temperature. A laboratory pH meter, YSI 1200 Laboratory pH Instrument with a range of 0.00 to 14.00 units and ±0.01 units accuracy has been used for the measurement.

### Manure/Mud Removing Method

Picture of the hide pieces containing manure/mud balls were taken before soaking them within the formulations. The hide pieces were soaked in 100% (w/w) float of the manure/mud removing formulations for 5 minutes. The soaked hide pieces were spread on a flat surface and gently brushed with a polymer brush to remove the debris from the hide panels. After brushing off the debris, pictures of the hide pieces were taken again, and finally the hide panels were directly used for leather processing.

### Microbial Testing

A 10in × 5in surface of hide area were aseptically and independently swabbed with a sterile sponge before and after brushing and placed into a bag with 25 mL of buffered peptone water from a sampling kit for analysis (Nasco Meat and Turkey Carcass Sampling Kit, Salida, California). Sample bags containing the buffered peptone and the swabbed sponges were hand massaged for ~2 min. Samples were subsequently diluted and spread-plated on Tryptic Soy Agar (TSA). The TSA was obtained from Fisher Scientific, Pittsburg, PA. Samples were incubated between 24-48 hours at 37°C and bacterial colonies were enumerated for aerobic bacterial recovery with the lowest detection level at 1 CFU (colony forming unit) per 10in × 5in area. All assays were carried out in triplicate, and the results are presented as the mean standard deviation as described by Steel et al (1997).[13] GraphPad software was used to perform a one-way analysis of variance with a post hoc Turkey's test (GraphPad Prism 7.0, GraphPad Software, Inc., San Diego, CA).

**Table II**
**pH of the Formulations**

| Sample | R1 | R2 | R3 | Average | St. Dev. |
|---|---|---|---|---|---|
| F-A (Tap water) | 7.2 | 7.15 | 7.23 | 7.19 | ± 0.040 |
| F-B | 12.3 | 12.29 | 12.34 | 12.31 | ± 0.026 |
| F-C | 12.07 | 12.08 | 12.08 | 12.07 | ± 0.005 |
| F-D | 12.67 | 12.68 | 12.74 | 12.69 | ± 0.037 |
| F-E | 9.56 | 9.61 | 9.56 | 9.57 | ± 0.028 |

### Tanning and Leather Quality Analysis

Following the manure removing operation, the hide pieces were washed with water individually and put together in one hair removing drum. The dehairing process was carried out in accordance to the established USDA tanning procedure.[14-16] After the dehairing process, all the hide samples were put into a single drum for pickling, tanning, re-tanning steps. The hide samples were processed into crust upper shoe leather and stored in a controlled environment, where the temperature and humidity are maintained at 21°C and 50% (relative humidity) respectively, until the mechanical tests, organoleptic and microscopic analysis were performed.

The impact of the developed manure removing formulations on leather quality was determined by measuring the mechanical properties of the finished crust leather. The mechanical properties which include tensile strength, elongation ("stretchability"), Young's Modulus ("stiffness") and fracture energy ("energy required to open unit area of crack surface") were determined as per the procedures mentioned in previous article.[17-19] Five dumbbell shaped samples were cut from each experimental leather piece according to the protocol in ASTM D2209. Leather samples with an average thickness range of 1.86 to 2.58 mm was observed. An Insight-5 test frame and Testworks-4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used to determine the mechanical properties of the leather samples. The strain rate and the grip distance for this study were set to 24.5 cm/min and 10.16 cm respectively. Subjective tests (break, handle, fullness, and color) on the finished leather products were conducted by an in-house (USDA) leather expert. Crust leather panels produced from the control and formulation treated hides (F-A to F-E) were also analyzed under a stereo microscope (Nikon Digital Microscope SMZ-2T, Melville, NY) to determine if there is any difference in the grain structure of the experimental leather panels comparing to the control. The stereo microscope images were taken according to the published procedures.[16-18]

## Results and Discussion

### pH of the Developed Formulations

The pHs of the formulations have been listed in Table II. The formulations, F-B, F-C, F-D are basically the mixture of a neutral thioglycolate salt and sodium hydroxide therefore, the pH of these three formulations is found at the high end of ~12 as expected. However, the pH of F-E is found lower because some of sodium hydroxide is consumed to neutralize the thioglycolic acid in the formulation but still remains basic in nature.

### Efficacy of Different Manure/Mud Removing Formulation

Figure 1 shows the pictures of the fresh hide pieces before and after the manure removing operation. For comparison purposes the pictures are displayed side by side as before and after treatment for each manure removing formulation. As it can be seen from the pictures, the manure was removed completely from the hide pieces treated with formulations F-B, F-C and F-D. Adobe type mud/manure balls are still firmly attached to the control sample (F-A) and also the manure was barely removed by the formulation F-E. The debris were dislodged from the attachment site after 5 minutes of soaking followed by gentle brushing. The easy removal of the hard-ball manure can be attributed to the effect of the reducing agents on the hairs where the manure is attached. That means the disulfide bond of the keratin which is the main component of the hair is being reduced and the hair is breaking apart.[20-21] It was also observed that some part of the hardened manure ball was getting decomposed and that may be because of the effect of the reducing agent on the protein component of the manure. Out of all formulations it was easier to remove the debris from the hide pieces soaked in sodium and potassium thioglycolate containing solutions than other formulations and that could be because of the differences in the rate of diffusion of the reducing agents into the hair structure as a whole. The rate of diffusion depends on the chemical nature of the reducing agents (Ogawa et al 2008).[22] Thus sodium/potassium thioglycolate solutions should have higher diffusion rate to cleave the disulfide bond in a short period of time compared to the other reducing agents used in other manure removing formulation.

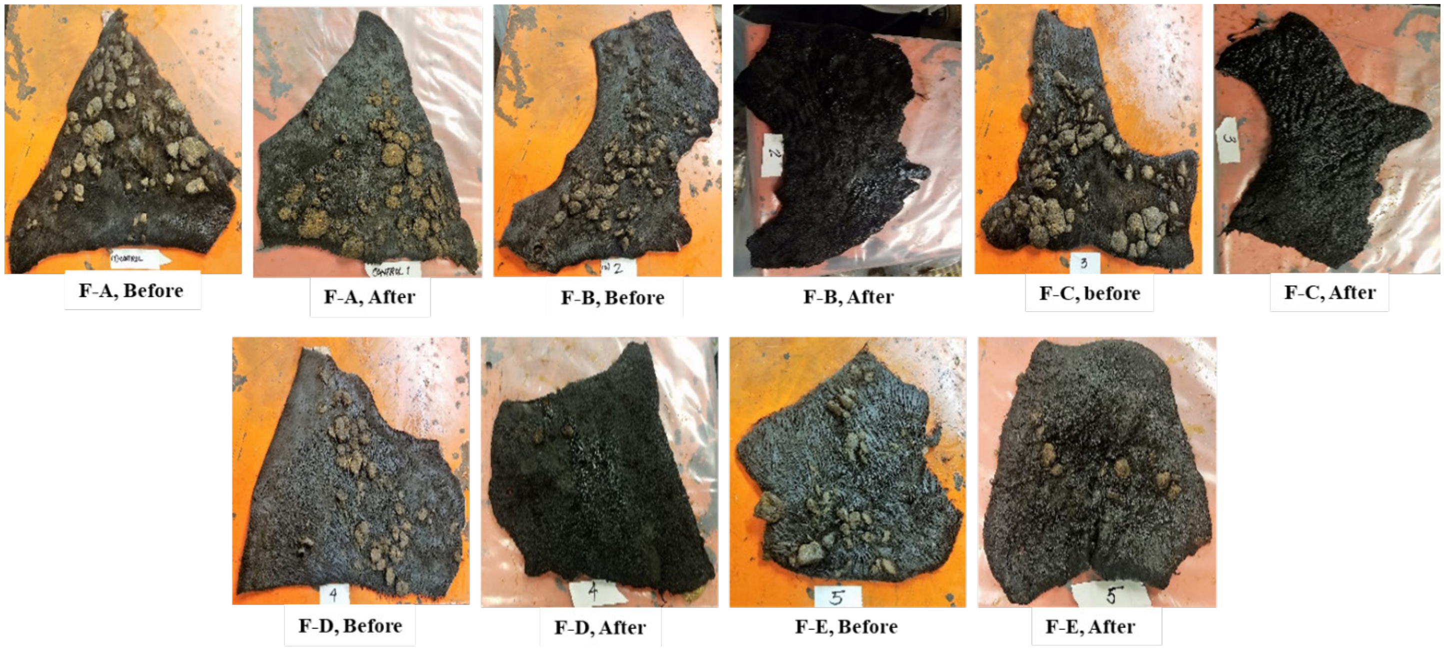


**Figure 1.** Picture of hide pieces before and after mud/manure balls removing treatment using different formulations. **F-A**, **F-B, F-C**, **F-D**, **F-E** represent formulation composition as described in Table 1.

**Aerobic Bacterial Count**

Generally, underlying meat surface of the carcass is sterile,[23-27] but it can be contaminated with microorganisms transferred from the hide surface during the hide removal process. Also, excessive bacteria present on raw hide leads to its deterioration quickly. Therefore, hide surface decontamination plays an important role for both meat and hide processing operations. Aerobic bacteria count analysis was carried out to see if the removal of external debris including manure/mud balls helps to reduce the naturally onboard bacteria from the hide surface.

As it is shown in Figure 2, before treatment all the hide pieces carried almost similar number of aerobic bacteria naturally. However, after removing mud/manure balls or debris F-B, F-C and F-D treated hide samples got in reduction of aerobic bacteria by 3.09, 1.87, 4.13 log CFU/50 in$^2$ respectively. On the contrary, control (F-A) and F-E treated samples got in reduction of only 0.51 and 0.1 log CFU/50 in$^2$ respectively. This data establishes a co-relation between Figure 1 and 2, where Figure 1 shows F-B, F-C and F-D perform better than the control (F-A) and formulation F-E in removing mud/manure balls from hide surface: less debris result in more reduction in bacteria counts. This experiment overall indicates that by only removing the external debris, a significant reduction of bacteria on hide surface can be achieved as those debris mainly harbor those microorganisms.

**Quality Analysis of Crust Leather**

Following the USDA standard tanning protocol**,** the hide pieces were processed into crust upper shoe leather. The impact of the developed manure removing formulations on leather quality was

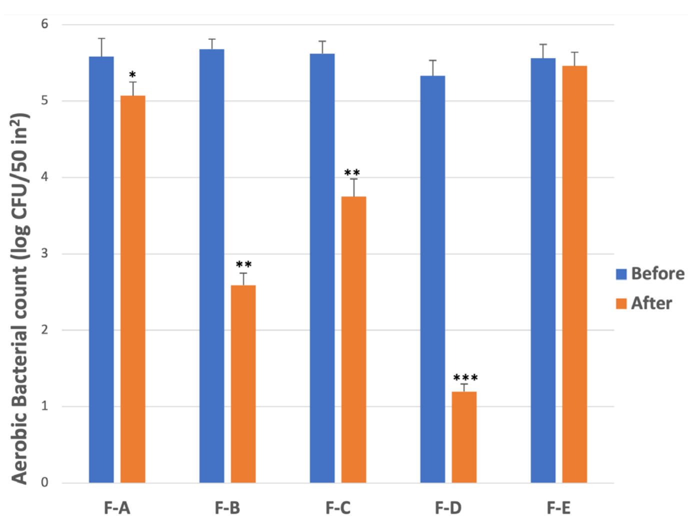


**Figure 2.** Aerobic bacterial count on hide surface before and after mud/manure removing treatment with different formulations. Asterisks indicate that the differences between the means of various treatments are statistically significant (**P* 0.05; ***P* 0.01; ****P* 0.001).

**Table III**
**Mechanical properties of the finished leather product after treating with the manure removing formulations**

| Sample | Tensile Strength (MPa) | Elongation (%) | Young's Modulus (MPa) | Fracture Energy (J/cm^3) |
|---|---|---|---|---|
| **F-A** | 7.9 ± 0.9 | 40.1 ± 8.8 | 12.2 ± 4.9 | 1.1 ± 0.2 |
| **F-B** | 6.7 ± 2.1 | 26.0 ± 4.3 | 23.1 ± 11.6 | 0.7 ± 0.2 |
| **F-C** | 6.6 ± 1.7 | 27.8 ± 5.2 | 20.7 ± 10.9 | 0.7 ± 0.1 |
| **F-D** | 9.8 ± 0.4 | 38.1 ± 3.1 | 15.4 ± 2.5 | 1.3 ± 0.2 |
| **F-E** | 7.1 ± 2.2 | 34.6 ± 7.2 | 13.3 ± 3.4 | 0.9 ± 0.3 |

determined by measuring the mechanical properties which include tensile strength, elongation to break, Young's Modulus (stiffness) and fracture energy (the energy required to fracture the leather sample). In addition to measuring the mechanical properties, the grain surface of the finished crust leather was also analyzed. Moreover, the quality of the finished leather was also verified by a subjective test where in-house USDA leather expert assessed the break, handle, fullness, and color of the finished leather product.

### Mechanical Properties

Even though the hardened manure is a major source of hide quality deterioration, it is also important that the manure removing formulations do not decrease the performance of the final leather products. As shown in Table III, it is evident that there is some variation in some aspects of the mechanical properties of the finished crust leather obtained from the treated hides with different manure removing formulations. Compared to the control, there is no significant difference observed in the tensile strength among the crust leather products. However, the stretching and stiffness properties of F-B and F-C are different in comparison with the control (F-A) and this is due to the fact that raw hide pieces are collected from the different parts of a bovine hide where natural variation of hide thickness exists. In fact, 1.86 to 2.58 mm range of variation in thickness was found among the dumbbell shaped leather samples (cut from the experimental leather panels) prepared for the mechanical studies. It is very unlikely that only 5 min exposure of formulations with similar pH values (~12) can create such a significant change, rather it is more obvious that, leather products produced from hide pieces of different thicknesses show differences in mechanical properties.

### Grain Surface Analysis of Leather Panels

The grain structure of each finished leathers was analyzed under a stereo microscope. The analysis was conducted to see the effect of each formulation on the surface fineness or coarseness of the crust leather. As shown in Figure 3, there is no noticeable difference between the grain structure of leather produced from the hide treated with the manure removing formulations and the control, suggesting that the

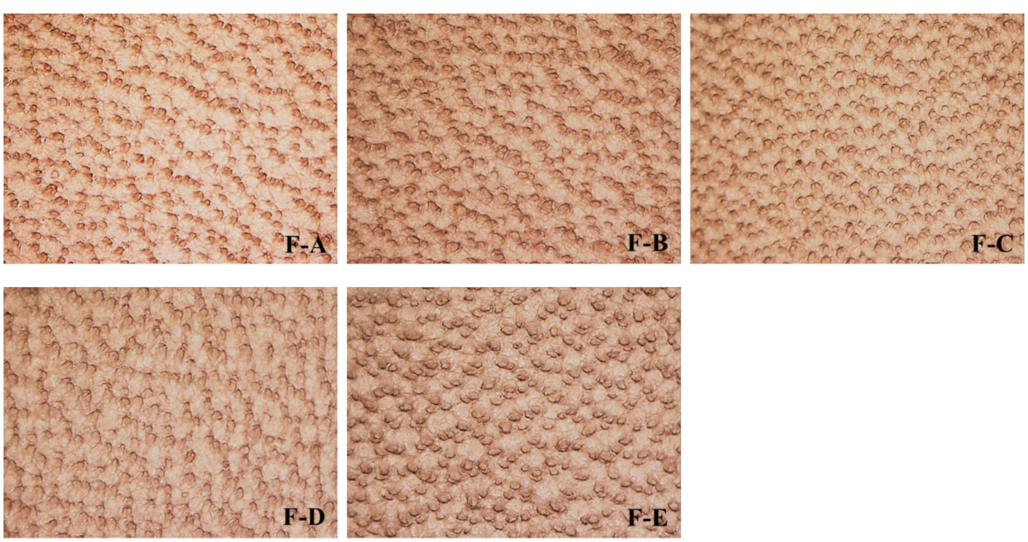


**Figure 3.** Stereo microscopic images of the crust leather made from hides treated with water (control) and different formulations.

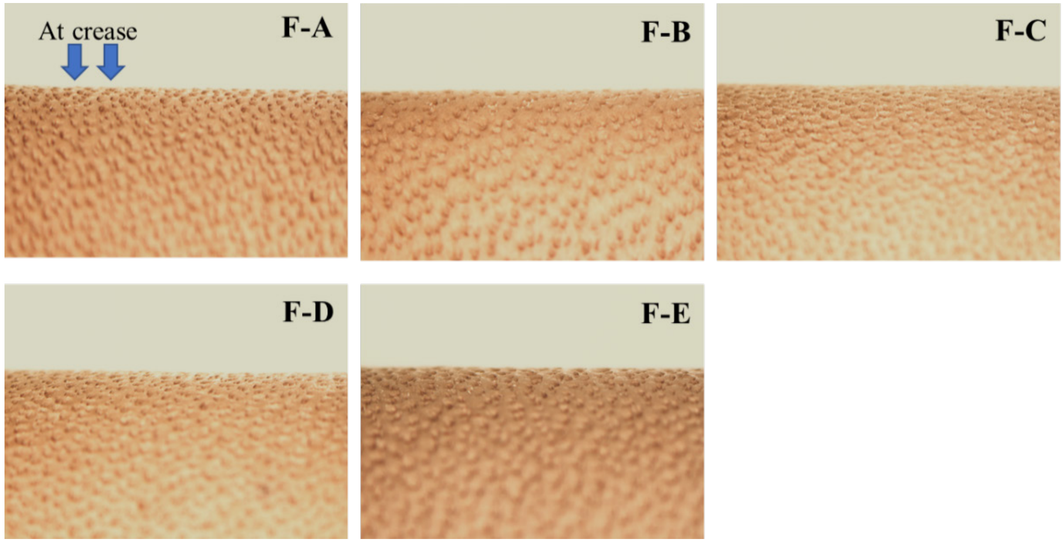


**Figure 4.** Stereo microscopic images of the finished leathers at the crease.

formulations did not adversely affect the hide pieces in the process of removing hardened manure. To further evaluate the surface feature of the crust leather, stereo microscopic images were captured at the crease upon folding the leather panels (Figure 4). Again, there was no fraying (broken fiber) was observed at the crease on any of the leather pieces indicating no damage on collagen network.

**Subjective Test Analysis of Leather Panels**

In-house expert on leather assessed the crust leather panels for their fullness, softness, color, grain tightness (break) and general appearance by hand and visual examination (Table IV). The subjective test results were expressed on a scale of 0-5 points with 0 being the worst and 5 being the best outcome. The leathers produced from the control and hide pieces treated with the manure removing formulations displayed similar fullness, grain, handle, color and general appearance. Overall, the subjective test results indicate that the manure removing formulations did not damage the hides as there is no significant difference between the control and the leather produced from treated hides.

Thioglycolic acid, sodium thioglycolate, potassium thioglycolate and ammonium thioglycolate are safe to humans and to the environment because they are commonly used chemicals in permanent wave, hair straightening, hair color preparations and depilatories.[28-30] The use of up to 5% of thioglycolic acid and its salts in cosmetic preparations is generally considered to be safe which is close to the concentrations used in this study. Therefore, the use of these chemicals in mud/manure removing formulation will not present any unreasonable risk to humans and the environment.

## Conclusion

To remove firmly attached adobe type mud/manure balls or external debris from the cattle surface is essential but challenging task for the meat and hide industries as it relates to meat safety and byproduct quality. In previous study, we reported the efficacy of potassium thioglycolate based formulation in removing debris from the hide surface. In this study the effectiveness of four formulations containing thioglycolic acid and its potassium, sodium and

**Table-IV**

**Subjective properties for leather samples made after treating with the manure removing formulations**

| Formulation | Break | Fullness | Handle | Color | Grain | Appearance |
|---|---|---|---|---|---|---|
| **F-A** | 5 | 3 | 3 | 3 | 3 | 4 |
| **F-B** | 5 | 3 | 3 | 4 | 4 | 3.5 |
| **F-C** | 5 | 3 | 3 | 3 | 4 | 3.5 |
| **F-D** | 5 | 3 | 3 | 4 | 4 | 3.5 |
| **F-E** | 5 | 4 | 4 | 3 | 2 | 4 |

ammonium salt respectively has been compared. Although, all developed formulations have been found effective in removing debris from hide surface to some extent but sodium and potassium thioglycolate based formulations exhibited better performance than others. Mud/manure balls can be easily removed from the hide panels soaked in those formulations for 5 minutes. The removal of debris also facilitates the reduction of onboard natural bacteria count significantly. From the stereo microscopic analysis and mechanical properties, the developed manure removing formulations do not appear to have any negative effect on the finished crust leather. This study will provide a wide option for meat and hide industries to choose the appropriate mud/manure removing formulation based on cost and the availability of chemicals. Application of the developed formulations in slaughterhouses will minimize the likelihood of meat contamination and avoid the ineffective and labor-intensive work required to remove manure/mud balls from cattle hides.

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## Conflict of Interest

The authors declare that there is no conflict of interests on the work published in this paper.

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# Remediation of Spent Vegetable Tannins from Waste Tanning Liquor through Coagulation and Ultrasound Pre-Treatment: A Sustainable Approach

by
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## Abstract

Vegetable tanning is one of the oldest methods of tanning. Vegetable tannins present in spent tanning liquor necessitates suitable remediation measures for sustainable solution. Vegetable tanning agent, wattle extract powder and vegetable tanning process spent liquor collected from a commercial tannery were used for the experiments. In the present approach, natural clay has been employed for the coagulation of spent vegetable tannins. Various other suitable precipitating agents such as zinc chloride ($ZnCl_2$), barium chloride ($BaCl_2$), ferric alum, lime and poly-electrolyte have also been studied for their efficacy in the treatment process and their requirement optimized. The efficacy of coagulation was monitored through settling characteristics of precipitation process and % settled volume for a given time. In the case of wattle powder, better settling of tannins was obtained due to combined use of optimized amount of clay and $ZnCl_2$. Whereas, ultrasound pre-treatment provided further enhancement. In the case of spent tannery vegetable tanning liquor, ultrasound pre-treatment of polyelectrolyte along with optimized amount of normal lime, clay and ferric alum provided rapid settling behavior, with steady state achieved in 20 minutes with settled volume of ~10 ml. Similar trend was also achieved (10 ml, 8 min.) for ultrasound pre-treated optimized clay with the use of other agents as normal. There was a significant reduction in particle size of clay (from 539 nm to 298 nm) through ultrasound pre-treatment (20 min.), leading to more surface area facilitating the coagulation process. This method could be useful for remediation of vegetable tannins present in spent vegetable tanning liquors using available natural material clay and shall also be extended to other streams. The present study has explored the ultrasound assisted coagulation science and technology for remediation of wastewater in general, whereas, spent vegetable tanning liquor in specific.

## Introduction

Tanning industry is one of the oldest industries in the world.[1] Tanning process consists of three basic steps a) beam house operations b) tanning c) finishing process. Leather tanning process is classified mainly into two categories such as chrome tanning and vegetable tanning. Manufacturing of leather generates numerous by-products, solid wastes and wastewater containing different loads of pollutants and emissions.[2] Nearly 70% of the pollution loads of Bio-chemical oxygen demand (BOD), chemical oxygen demand (COD), and Total Dissolved Solids (TDS) are generated from operations such as soaking, liming, degreasing, pickling and tanning processes.[3]

Vegetable tanning is one of the oldest methods of tanning and the waste spent tanning liquor has high BOD and COD values. Physical, chemical and biological characteristics of spent tannery vegetable tanning liquor has been analyzed and reported recently.[4] Even though vegetable tannins are natural materials, one of the refractory groups of chemicals in tannery effluents are derived from tannins.[5] Study on leaching of pollutants from vegetable tanning residue.[6] Treatment of refractory organic pollutants in industrial wastewater by wet air oxidation has been studied earlier.[7] About 30% of vegetable tanning extracts (% based on skin/hide weight) are normally employed in main tanning process for conversion of animal skins/ hides into leather. A significant amount of these vegetable tannins are underutilized in tanning process and available in spent liquor, they subsequently enter waste streams causing pollution load. In this regard, suitable remediation measures are beneficial after separating the spent vegetable tanning liquor as sectional streams, before mixing into another wastewater stream. Since, vegetable tannins are natural materials, available in spent liquors, the same could be used for some useful purpose such as enhancement of soil, if separated from the wastewater through suitable methods such as coagulation. Before going into details of the present study, the following section provides the brief details of vegetable tannins employed in tanning process of leather industry.

### Chemistry of vegetable tannins

There are two types of vegetable tannins, viz., hydrolysable and condensed tannins (*Con-Tan*).[8] Generally, hydrolysable tannins (*Hyd-Tan*) are only used as a supplementary agent for main (*Con-Tan*) used in tanning, in order to prevent oxidation and to provide lighter color to tanned leather. Hydrolysable tannins are esters of

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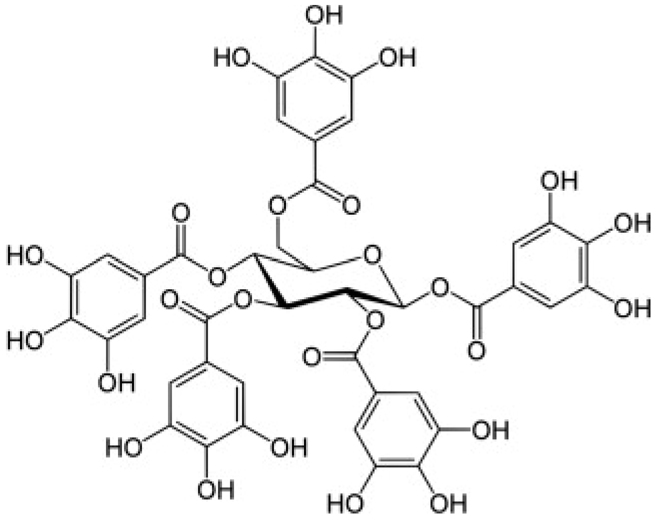


**Figure 1.** Schematic representation of hydrolyzable tannins 1,2,3,4,6 Penta galloyl glucose as esters of phenolic acids and glucose.

phenolic acids and glucose such as 1,2,3,4,6 Penta galloyl glucose as schematic representation shown in Figure 1. Typical examples of *Hyd-Tan* are Myrobalan, Divi-Divi etc.

*Con-Tan* are widely used as a main vegetable tanning agent. Typical examples of Con-Tan are wattle, mimosa etc. Condensed tannins are built from catechin units, flavon 3-ol. Schematic representation of a *Con-Tan* molecule is shown in Figure 2. Condensed tannins can be linear (with 4 to 8 units) or branched (with 4 to 6 units shown as dotted line).

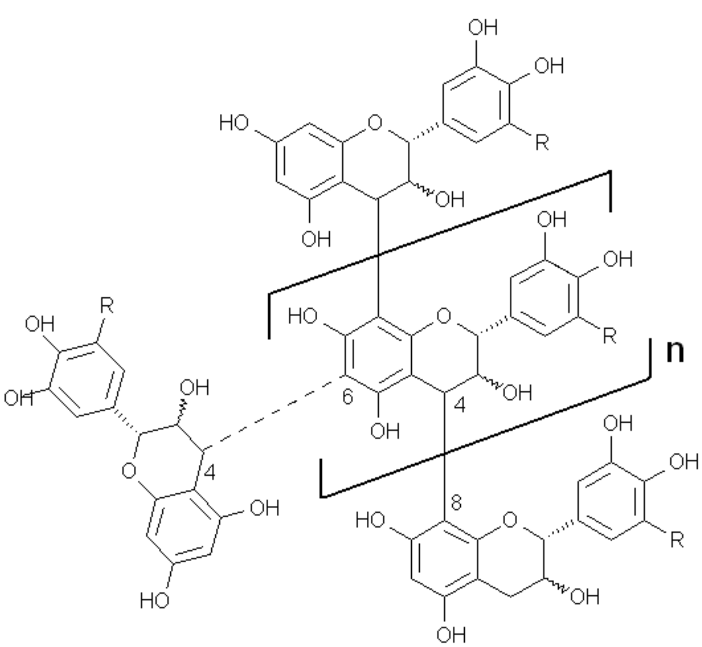


**Figure 2.** Schematic representation of Condensed tannins with catechin (flavon 3-ol) units

**Coagulation treatment for vegetable tannins**

**Use of soil clay in coagulation process:**

**Originality of the present work**

Coagulation process occurs when cations and anions in aqueous solution combine to form an insoluble ionic solid called a precipitate. In the present approach, another natural material, viz., soil clay having surface charge properties has been employed for the coagulation of spent vegetable tannins. Basics of clay minerals with their types and their characteristic properties such as Ion-exchange capacity as well as general specific surface area ($m^2/g$) has been reported.[9] The clay materials comprise hydrous phyllosilicate having silica, alumina and water with variable number of inorganic ions like $Mg^{2+}$, $Na^{+}$, $Ca^{2+}$ find useful in coagulation process. An approach for the treatment of vegetable tan liquor containing hydrolysable tannins using zinc sulfate and zerolite iron catalyst has been reported earlier.[10] Use of salts like ferric chloride to provide interaction with plant tannins with formation of colored complex has been widely studied for qualitative determination of presence of tannins.[11,12]

However, there is a need to enhance the process using natural materials such as clay in the area of soil enrichment.[13] In this regard, application of bentonite clays in suspension fertilizer formulations and use of Bentonite based clay as organic amendment, which enriches microbial activity in agricultural soils have been studied earlier.[14] Spectroscopic and mineralogical characterization of bentonite clay from Ghardaïa, Algeria for heavy metals removal in aqueous solutions has been made.[15] A recent study has been reported on the understanding the impact of soil clay mineralogy on the adsorption behaviour of zinc.[16]

The precipitate of the coagulation process yields suspended materials or fall to the bottom of the solution. The remaining fluid is called supernatant liquid. The two components of the mixture (precipitate and supernatant) of tannins and clay can be separated by various methods, such as filtration, centrifuging, or decanting and subsequently used for different applications.

However, tannins separated only from vegetable tanning sectional stream through this approach for soil enrichment purpose need to be studied separately for their applicability and efficacy in this regard, which is not the part of the present study, the same would be investigated as future work.

**Use of ultrasound in coagulation process**

Another important feature of the present study is to enhance the coagulation process by physical activation method, viz., ultrasound. Ultrasound is a sound wave having frequency above the human audible range of 16 kHz and widely studied for enhancing the physical as well as chemical processes.[17,18] Schematic representation of ultrasound pre-treatment using clay and other precipitating agents for vegetable tanning spent liquor, further settling and clarification is shown in Figure 3. Ultrasound could be employed in pre-

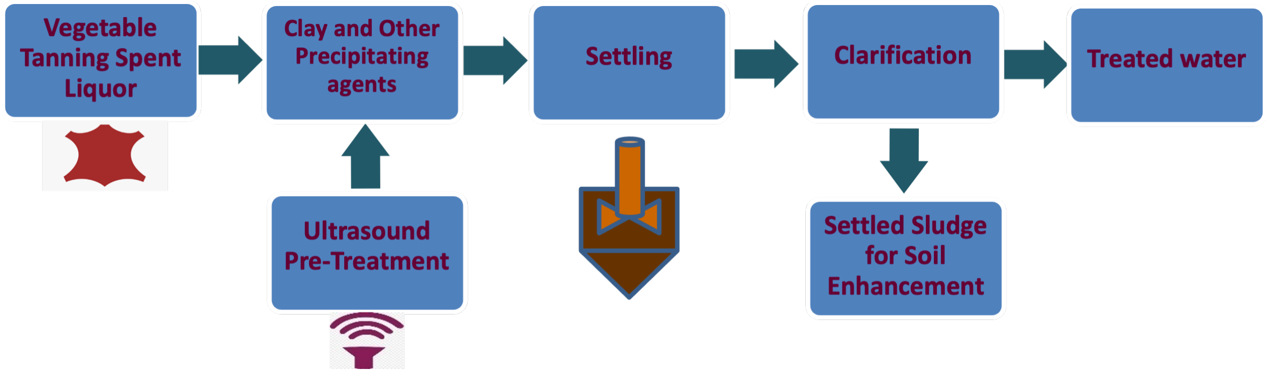


**Figure 3.** Schematic representation of ultrasound pre-treatment using clay and other precipitating agents for vegetable tanning spent liquor, further settling and clarification.

treatment disintegration and particle size reduction of coagulants employed and increase the surface area for better coagulation. In this regard, earlier studies on the use of ultrasound in chrome recovery process from spent chrome liquor through precipitation of chromium present as chromic hydroxide has been reported.[19] Whereas significant improvement was obtained in settling rate of chromic hydroxide precipitate with the use of pre-ultrasound pre-treated MgO as compared to control (no ultrasound pre-treatment) and considerable decrease of Cr in the supernatant liquor after precipitation leading to better Cr recovery due to better dispersion and particle-size reduction of MgO with ultrasound pre-treatment has been reported.[19] In another study, effect of ultrasound pre-treatment on sedimentation of suspended solids in water has been studied earlier.[20] Earlier study on particle-size reduction of dickite by ultrasound treatments and the effect on the structure, shape and particle-size distribution has been reported.[21] Use of ultrasound in the preparation of nanocomposites based on fibrous clay minerals and nano cellulose from microcrystalline cellulose has also been studied.[22]

### Effect of other coagulating agents

Effect of other suitable coagulating agents need to be studied in the process. The present study also involves the treatment of vegetable tanning spent liquor using different precipitating agents such as barium chloride ($BaCl_2$), zinc chloride ($ZnCl_2$), ferric alum, lime and flocculating agent and their opulent effect upon ultrasound treatment in order to improve the removal of color and total solids and thereby reducing the sludge level. This is a simple sedimentation technique using precipitating agents to make the process easy and effective removal of color and total solids in tannery effluent. In the present study, ultrasonic pre-treatment on clay and other agents has been performed in view of better coagulation process. The experiments were also carried out using combination of alum, poly-electrolyte and lime. The present study tries to explore the possibility of ultrasound assisted coagulation science and technology for remediation of wastewater in general and spent vegetable tanning liquor in particular. This study is expected to provide better settling rate and useful remediation of tannins present in vegetable tanning spent liquor.

## Materials and Methods

### Materials used

Chemicals reagents (AR Grade), Zinc chloride ($ZnCl_2$), Barium chloride ($BaCl_2$), Alum were procured from SD Fine, Chemicals, Ltd., India. Clay sample was collected from sub soil surface of CSIR-CLRI garden. Lime (CaO) powder (commercial grade), Poly electrolyte (commercial grade) were also used. Vegetable tanning agent (condensed type), Wattle extract GS powder (Tanext chemicals, India) was employed in various experiments. Whereas, spent vegetable tanning process liquor was collected from a commercial tannery M/s. C. Kalyanam & Co. Pallavaram, Chennai, India.

### Ultrasound equipment

Ultrasound assisted experiments were carried out using ultrasonic probe (VCX 400, Sonics and Materials, USA) operating at frequency: 20 kHz with variable ultrasound power: 0– 400 W, with provisions to set required output power and process time as described earlier.[23]

## Methods

### Preparation of synthetic vegetable tanning liquor (SVT)

In order to avoid other contaminants in the experiments for optimization studies, synthetic vegetable tanning liquor (SVT) was prepared by taking 0.5 g of wattle tannin GS powder and mixing well with 100 ml distilled water in a magnetic stirrer in order to make SVT and used for various experiments for optimization of coagulation and settling process. Whereas, in order to analyze application of the present approach, separate studies were also carried out using spent vegetable tanning process liquor as collected from a commercial tannery.

### Settling characteristics and % Settled Volume

The component of materials which are settled after the coagulation process, at any given time period is a good measure of coagulation efficacy. This implies the lower the settled volume, the better the coagulation process, with clearer supernatant with less contaminants. Usually, denser precipitates yield lower settled volume. For this purpose, in each experiment, the respective experimental solution, with vegetable tannins and respective coagulating agents were mixed well in a clean beaker and 100 ml of this solution was taken in a 100 ml graduated measuring jar and allowed to settle. Percent settled volume could be measured by noting the settled layer below the clear supernatant layer by visual observation in the measuring jar graduations at any given point of time. As time progress, the settling process also proceeds with percent settled volume decreasing and clear supernatant layer at the top increases. The optimization of different coagulants has been made from the settling characteristics of precipitation process and percent settled volume for a given time.

**Optimization of Zinc chloride, Barium chloride and Clay**

Barium chloride and Zinc chloride have been studied at different amount (0.1 g to 0.6 g) along with 100 ml of SVT was added to each amount and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

To enhance the efficiency of $ZnCl_2$, clay was used to increase settling rate. Clay sample was washed thoroughly with distilled water and dried. This dried clay was taken in different amount such as 0.2 –1.4 g and optimized amount of zinc chloride (0.3 g) was added to it. Then 100 ml of SVT was also added to the above solution and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded. The amount of clay was optimized from the settling rate.

**Effect of ultrasound pre-treatment on optimized zinc chloride**

To enhance the coagulation process, effect of ultrasound pre-treatment was employed on optimized zinc chloride. For this purpose, optimized amount of zinc chloride was taken and dissolved in 100 ml water and ultrasound pre-treatment was carried out for 30 minutes using 80 W power. Optimized amount of ultrasound pre-treated zinc chloride (100 ml solution) with 0.5 g tannin powder was used for the experiment. Then the sample solution was mixed well and kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

**Effect of combination of zinc chloride and clay**

In addition, effect of combined use of optimized amount of zinc chloride and clay has also been performed using 100 ml SVT with tannin powder 0.5 g for the experiment. Then the sample solution was mixed well and kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

**Optimization of Ferric alum and Clay**

Having optimized the amount of clay, zinc chloride in settling of tannins, other coagulating agent's ferric alum, lime, polyelectrolytes and clay were studied as an industrial practice of treating wastewater. Various amounts of alum (0.08 –0.2 g) were taken and 100 ml of spent tannery vegetable tanning liquor collected from tannery was added to it, mixed well and the solution was allowed to settle. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Optimized amount (0.15 g) of ferric alum was added to various amount of clay such as 0.2– 1 g and 100 ml of spent tannery vegetable tanning liquor was added to it and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

**Optimization of poly electrolyte**

For further enhancement of settling rate, the effect of commercial flocculants, poly electrolyte was also studied. The optimized value of ferric alum and clay such as 0.15 g and 0.8 g were added to the various amount of poly electrolyte (4 –15 mg). Then 100 ml of spent tannery vegetable tanning liquor was also added to it and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

Then the optimized quantity of reagents clay, ferric alum and poly electrolyte as arrived from the above experiments were used for remediation treatment purpose of spent tannery vegetable tanning liquor as collected from a commercial tannery and the effect of ultrasound pre-treatment on different reagents used was studied as follows:

**Effect of ultrasound pre-treatment on clay with optimized normal ferric alum and polyelectrolyte**

For this experiment ultrasound pre-treatment on 0.8 g of clay was performed using 80 W power for 30 minutes and employed in coagulation process. The ultrasound pre-treated clay was mixed with optimized amount of 5 mg polyelectrolyte and 0.15 g of ferric alum. Then 100 ml of spent tannery vegetable tanning liquor was added to it and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

**Effect of ultrasound pre-treatment on polyelectrolyte with optimized normal clay ferric alum**

For this experiment, ultrasound pre-treatment on 5 mg of polyelectrolyte was performed using 80 W power for 30 minutes and employed in coagulation process using optimized amount of 0.8 g of clay and 0.15 g of ferric alum. Then 100 ml of spent tannery vegetable tanning liquor was added to it and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

**Effect of lime on ultrasound pre-treated optimized polyelectrolytes in spent tannery vegetable tanning liquor**

The optimized polyelectrolytes (5 mg) were ultrasound pre-treated for 30 minutes using output power 80 W. Then optimized amount of

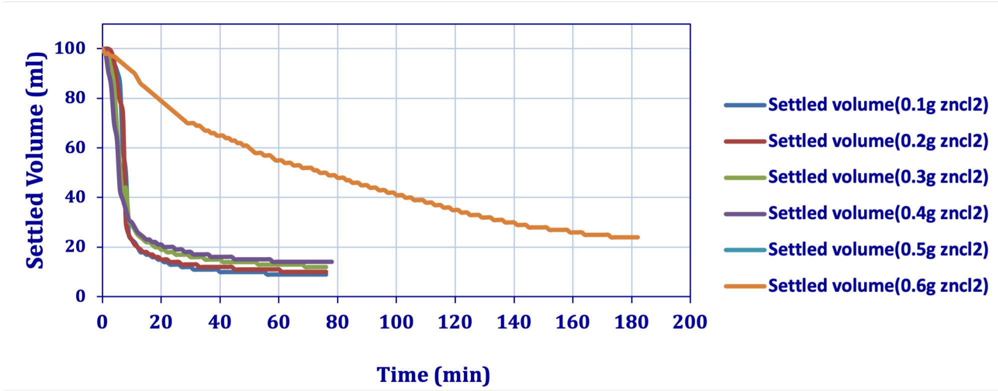


**Figure 4.** Effect of amount of Zinc chloride used in SVT tannins coagulation and settling rate characteristics during the settling process.

0.6 g lime, 0.8 g clay and 0.15 g ferric alum was added to it. Then 100 ml of spent tannery vegetable tanning liquor was also added to it and mixed well. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

**Effect of lime on ultrasound pre-treated optimized clay in spent tannery vegetable tanning liquor**

Optimized amount of clay 0.8 mg was ultrasound pre-treated for 30 minutes using output power 80 W. Then optimized amount of quick lime (CaO) 0.6 g and 0.15 g ferric alum was added to it and mixed well. Then 100 ml of spent tannery vegetable tanning liquor was also added to it. Then the sample solution was kept standing and allowed to settle. During settling process, percent settled volume for a given time was monitored and recorded.

**Particle size analysis of clay samples**

The particle size distribution of clay sample was analyzed using particle analyzer operating with dynamic light scattering principle (Malvern Instruments Ltd). The particle size of normal clay, and ultrasound pre-treated clay sample was analyzed. For ultrasound pre-treatment, 1 g of clay sample was dissolved in 100 ml distilled water and the sample was ultrasound pre-treated at 150 W at 20 kHz. The ultrasound pre-treated sample was collected at 10 and 20 minutes for particle-size analysis.

## Results and Discussions

**Optimization of Barium chloride and Zinc chloride**

When barium Chloride was used as precipitating agent, samples were analyzed after treatment and found a decent settling rate. But the color removal of treated water didn't satisfy as per the requirements. Moreover, it is not eco-friendly while considering in the case of disposing of the sludge. Barium chloride is a heavy metal, and it precipitates when it comes in contact with the chromium in the wastewater.

Zinc chloride gave better results and effective color removal when compared to Barium Chloride. The optimization of amount of $ZnCl_2$ for 100 ml of SVT could be derived from Figure 4, which indicates better settling characteristics for 0.2 – 0.5 g of $ZnCl_2$ other than 0.6 g. Whereas, keeping in view of materials and cost savings as well as for establishing better settling performance for scale-up with a possible margin of deviation, the optimized amount of $ZnCl_2$ has been considered as 0.3 g for 100 ml of SVT. Hence, further studies were carried out using zinc chloride as precipitating agent. Figure 4 shows the effect of amount of $ZnCl_2$ used in SVT tannins coagulation on the settling rate characteristics during the settling process. The results indicate continuous settling process with steady state achieved at about 80 min. with settled volume of ~20 ml using $ZnCl_2$.

**Optimization of clay with optimized Zinc chloride**

Figure 5 shows the effect of amount of clay used in SVT tannins coagulation on settling rate characteristics during the settling

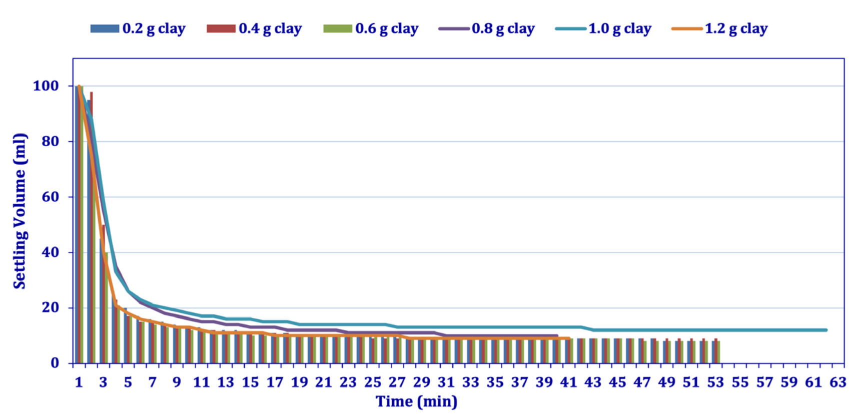


**Figure 5.** Effect of amount of clay with optimized amount of 0.3 g Zinc chloride used in SVT tannins coagulation and settling rate characteristics during the settling process.

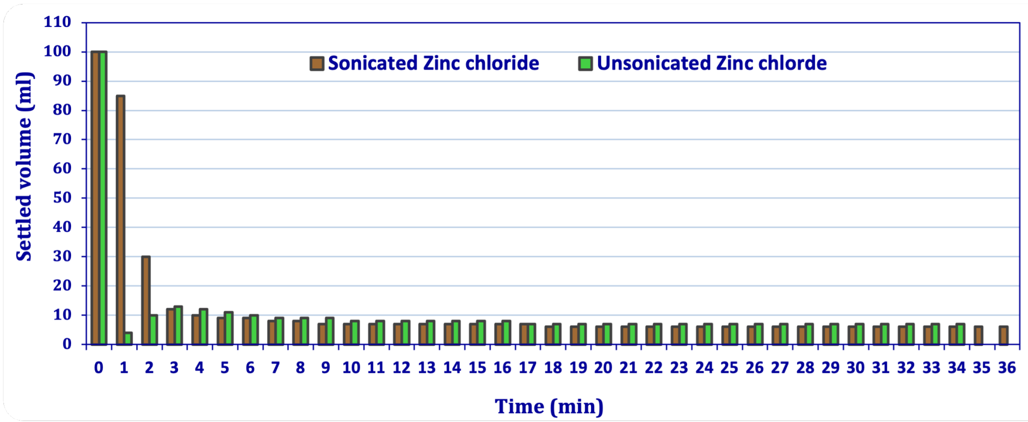


**Figure 6.** Effect of ultrasound pre-treatment on optimized Zinc chloride used in SVT tannins coagulation and settling rate characteristics during the settling process.

process. The optimization of the amount of clay along with optimized 0.3 g zinc chloride for 100 ml of SVT could be obtained from Figure 5, which indicates better settling characteristics for different amounts of clay used other than 1 g, which has shown longer settling times, perhaps due to exceeding the optimized amount of clay; which also indicates the optimized amount should be lower than 1 g for 100 ml of SVT. Whereas, keeping in view of this aspect as well as materials and cost savings for establishing better settling performance for scale-up with a possible margin of deviation, the optimized amount of clay has been considered as 0.8 g for 100 ml of SVT, containing 0.5 g of tannin powder along with optimized amount of 0.3 g zinc chloride. Therefore, the optimized amount of clay was found to be 0.8 g. The results indicate faster settling process with steady state achieved at about 53 min. with settled volume of ~10 ml, providing better coagulation for optimized clay & $ZnCl_2$ with as compared to $ZnCl_2$ alone. Table II shows the optimization of different coagulants on SVT tannins and the amount required for 100 g tannins in SVT for facilitating the settling process.

**Effect of ultrasound pre-treatment on optimized Zinc chloride**

Figure 6 shows the effect of ultrasound pre-treated (80 W, 30 min.), optimized 0.3 g of zinc chloride used in SVT tannins coagulation and settling rate characteristics during the settling process, which indicates better settling rate for ultrasound pre-treated optimized zinc chloride. The results also indicate that during initial 1–2 min, settled volume is higher for sonicated zinc chloride as compared to un-sonicated sample. The reason for this behavior may be due to initial drag for well dispersed nature of $ZnCl_2$ upon ultrasound pre-treatment. Whereas the same effect could subsequently lead to better binding with tannins and better performance in settling observed for ultrasound pre-treated $ZnCl_2$ as compared to that of normal case leading to steady state settled volume of 7 ml achieved in 17 min.

**Effect of combined use of Zinc chloride and Clay**

In addition, combined use of zinc chloride and clay has also been performed and the results show there is a significant improvement in settling characteristic. Whereas, Figure 7 shows the effect of combined use of optimized zinc chloride and clay as compared to the use of optimized zinc chloride alone employed in SVT tannins coagulation and settling rate characteristics during the settling process.

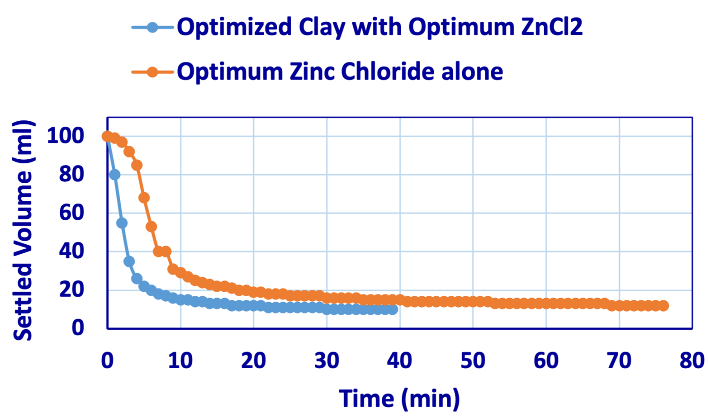


**Figure 7.** Effect of combination of optimized Zinc chloride and Clay used in SVT tannins coagulation and settling rate characteristics during the settling process.

**Optimization of ferric alum**

Having optimized the amount of clay, zinc chloride in settling of tannins, other coagulating agent's ferric alum, lime, polyelectrolytes and clay were studied as an industrial practice of treating wastewater. The optimized value of ferric alum was found to be 0.15 g for 100 ml of spent tannery vegetable tanning liquor collected from the tannery. Figure 8 shows the effect of the amount of Ferric alum in tannins coagulation and settling rate characteristics during the settling process. The results indicate gradual and continuous settling process with steady state achieved at about 106 min. with settled volume of ~5 ml.

**Optimization of clay with optimized ferric alum**

Further studies were carried out to optimize the value of clay with optimized ferric alum. The amount of clay was optimized by analyzing the settling rate. Figure 9 shows the effect of the amount of clay in coagulation and settling rate characteristics during the settling process. The optimized amount of clay was found to be 0.8 g

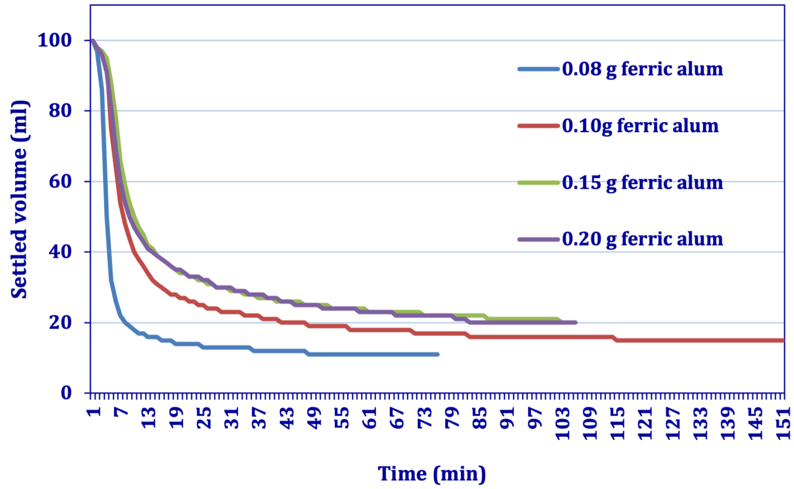


**Figure 8.** Effect of amount of Ferric alum used in spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process.

with 0.15 ferric alum for 100 ml of spent tannery vegetable tanning liquor. The results indicate gradual and continuous settling process with steady state achieved at about 60 min. with settled volume of ~5 ml.

**Optimization of poly electrolyte**

In order to achieve further enhancement in settling rate, the use of commercial flocculants, poly electrolyte was also studied. The optimized value of ferric alum and clay such as 0.15 g and 0.8 g were added to the various amount of poly electrolyte (4–15 mg). Then 100 ml of spent tannery vegetable tanning liquor was also added to it and mixed well. The settling rate was analyzed. This optimized amount was used for further studies. Whereas, Figure 10 shows the effect of amount of polyelectrolyte with optimized value of ferric alum and clay used in tannins coagulation and settling rate characteristics during the settling process. The optimized amount of polyelectrolyte was found to be 5 mg. The results indicate gradual and continuous settling process with steady state achieved at about 50 min. with settled volume of ~5 ml.

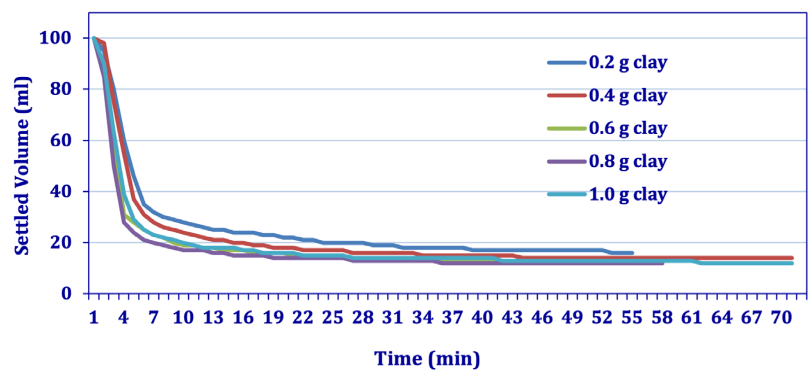


**Figure 9.** Effect of amount of clay with optimized ferric alum used in spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process.

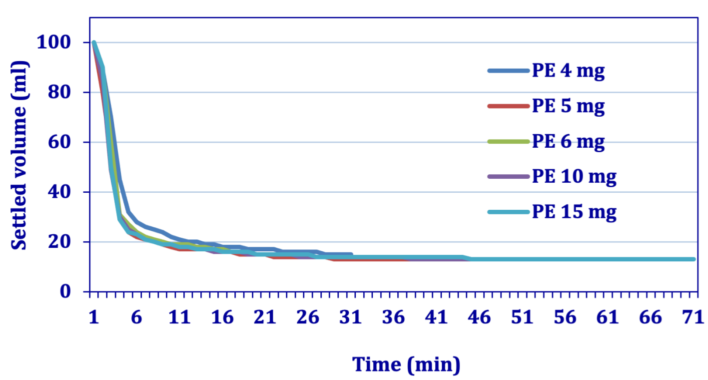


**Figure 10.** Effect of amount of polyelectrolyte (PE) with optimized value of ferric alum and clay used in spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process.

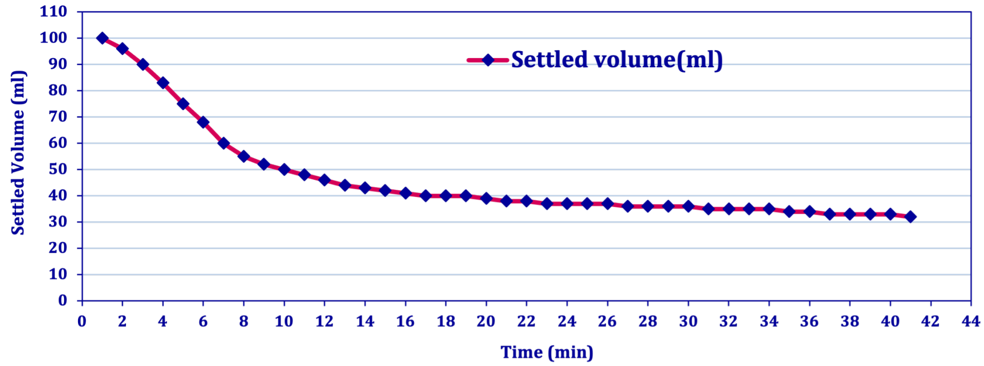


**Figure 11.** Effect of ultrasound pre-treated clay with normal optimized ferric alum and polyelectrolyte used in spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process.

**Effect of ultrasound pre-treatment on optimized clay with normal optimized ferric alum and polyelectrolyte**

Ultrasound pre-treatment on optimized 0.8 g of clay was performed using 80 W power for 30 minutes with normal optimized amount of 5 mg polyelectrolytes and 0.15 g of ferric alum and employed in coagulation process. Then 100 ml of spent tannery vegetable tanning liquor was added to it and mixed well. Effect of ultrasound on optimized clay in spent tannery vegetable tanning liquor was analyzed to increase the settling rate. The results indicated that settling rate was higher in ultrasound pre-treated clay when compared to normal clay as shown in Figure 11, with continuous settling process with steady state achieved at about 42 min. with settled volume of ~30 ml.

**Effect of ultrasound pre-treatment on optimized polyelectrolyte with optimized normal clay ferric alum**

Ultrasound pre-treatment on 5 mg of optimized polyelectrolyte was performed using 80 W power for 30 minutes and employed in coagulation process using optimized amount of 0.8 g of clay and 0.15 g of ferric alum. Then 100 ml of spent tannery vegetable tanning liquor was added to it and mixed well. Then the settling rate was analyzed.

The effect of ultrasound pre-treated polyelectrolyte and normal optimized amount of clay and ferric alum were used with spent tannery vegetable tanning liquor tannins to determine coagulation and settling rate characteristics during the settling process is shown in Figure 12, which indicates better settling rate of tannins with steady state achieved at about 15 min. with settled volume of ~15 ml.

**Effect of lime on ultrasound pre-treated polyelectrolytes in spent tannery vegetable tanning liquor**

Effect of lime on ultrasound pre-treated polyelectrolytes in spent tannery vegetable tanning liquor was analyzed. In order to enhance the pH of in spent tannery vegetable tanning liquor, lime was used. The amount of lime was optimized by analyzing the pH in spent tannery vegetable tanning liquor with lime as shown in Table I. Whereas, 0.6 g of lime provided neutralization for pH – 7 and taken as optimized value. The optimized polyelectrolyte (5 mg) was ultrasound pre-treated for 30 minutes using output power 80 W. Then the optimized amount of 0.6 g lime, 0.8 g clay and 0.15 g ferric alum was added to it and mixed well. Then 100 ml of spent tannery vegetable tanning liquor was also added to it. Settling rate characteristics during the settling process is shown in Figure 13. The results indicate rapid settling in 2 min. with settling process steady state achieved at about 20 min. with settled volume of ~10 ml.

**Effect of lime on ultrasound pre-treated clay in spent tannery vegetable tanning liquor**

Optimized amount clay 0.8 mg was ultrasound pre-treated for 30 minutes using output power 80 W. Then optimized amount of quick lime (CaO) 0.6 g and 0.15 g ferric alum was added to it. Then 100 ml of spent tannery vegetable tanning liquor was also added to it and mixed well. Figure 14 shows the effect of lime on ultrasound pre-treated clay in spent tannery vegetable tanning liquor with optimized amount of normal polyelectrolyte and ferric alum used in spent tannery vegetable tanning liquor tannins coagulation and

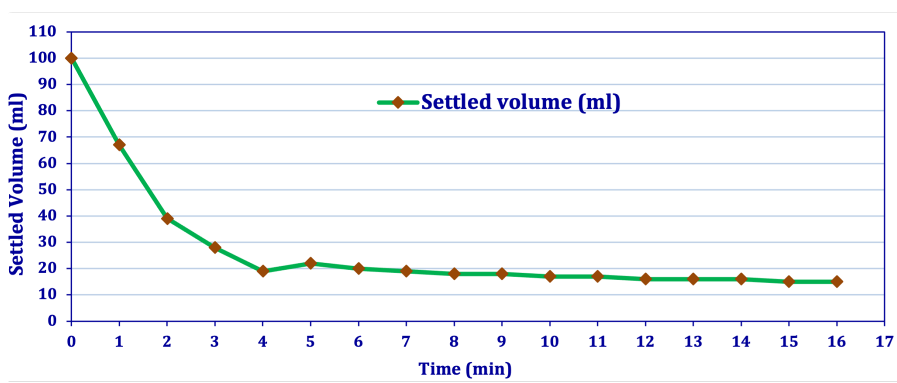


**Figure 12.** Effect of ultrasound pre-treated polyelectrolyte and normal optimized amount of clay and ferric alum used in spent tannery vegetable tanning liquor tannins coagulation and settling rate characteristics during the settling process.

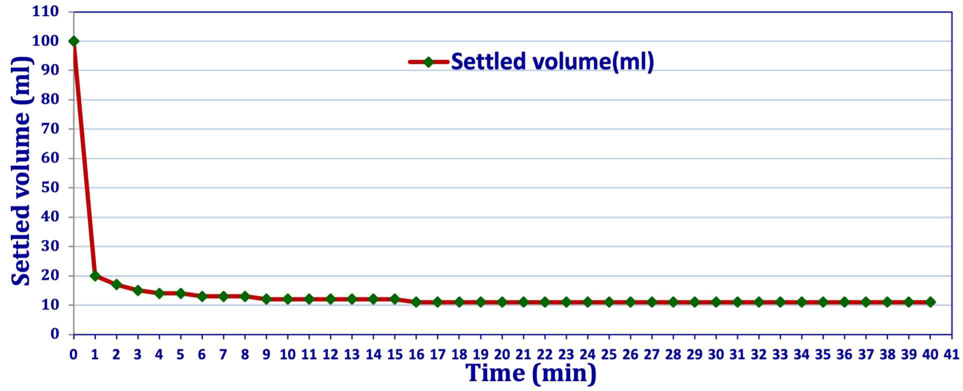


**Figure 13.** Effect of lime on ultrasound pre-treated optimized polyelectrolyte with optimized amount of normal clay and ferric alum used in spent tannery vegetable tanning liquor tannins coagulation and settling rate characteristics during the settling process.

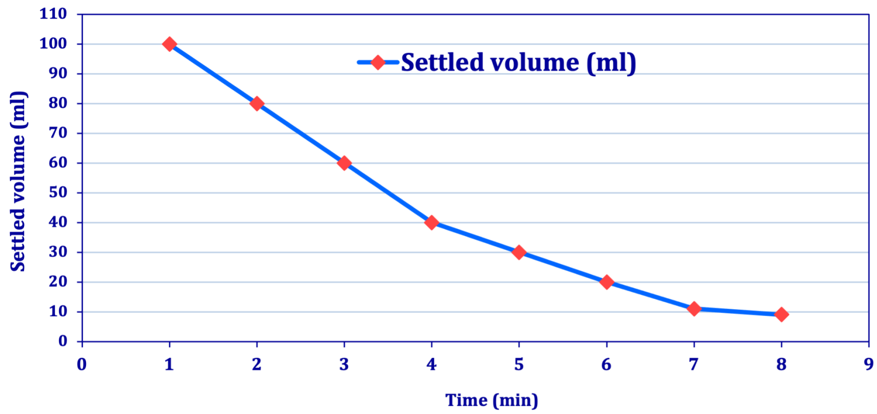


**Figure 14.** Effect of lime on ultrasound pre-treated optimized clay with optimized amount of normal polyelectrolyte and ferric alum used in spent tannery vegetable tanning liquor tannins coagulation and settling rate characteristics during the settling process.

**Table I**

**Optimization of Lime in spent tannery vegetable tanning liquor and corresponding pH values**

| Exp. No. | Amount of Lime (g) | pH |
|---|---|---|
| 1 | 0.2 | 5.5 |
| 2 | 0.4 | 5.5 |
| 3 | 0.6 | 7.0 |
| 4 | 0.8 | 10 |
| 5 | 1.0 | 10.5 |

settling rate characteristics during the settling process. The results indicate rapid settling rate, with steady state achieved at about 8 min. with settled volume less than 10 ml.

Table II shows the optimization of different coagulants on SVT tannins or spent tannery vegetable tanning liquor coagulation for facilitating the settling process and the amount required for 100 g tannins in SVT or 10 L of spent tannery liquor.

Whereas, Table III shows the effect of different optimized coagulants and influence of ultrasound pre-treatment on SVT tannins or spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process. Table III shows that in case of spent tannery vegetable tanning liquor (100 ml), optimized amounts of Ferric Alum (0.15 g) along with clay have achieved (5 ml, 60 min.); whereas addition of polyelectrolyte (5 mg) provided (5 ml, 50 min.). Settling rate was higher for ultrasound pre-treated clay with normal optimized ferric alum (0.15 g) and polyelectrolyte (5 mg) provided (30 ml, 42 min.); while in the case of ultrasound pre-treated polyelectrolyte has given (15 ml, 15 min.) with other agents as normal. Whereas, addition of lime (optimized 0.6 g) in this process along with ultrasound pre-treatment of either optimized clay or polyelectrolyte provided rapid settling in 8-10 min. with 10-20 ml settled volume.

**Particle size analysis of clay and effect of ultrasound treatment**

The particle size of clay samples after ultrasound treatment and without ultrasound employed in the coagulation process was analyzed. For ultrasound treatment, 1 g of clay sample was dissolved in 100 ml distilled water using ultrasound power 150 W. The ultrasound pre-treated sample was collected at 10 min and 20 min after ultrasound pre-treatment and particle sizes of clay samples were measured and the results shown in Table IV. Figure 15a shows the particle size distribution of normal clay sample without ultrasound pre-treatment. Figures 15b and 15c shows the particle size distribution of clay sample after ultrasound pre-treatment for 10 and 20 min respectively. The results indicate that there exist two distinct particle size segments for clay before and after ultrasound treatment and there has been a significant reduction of mean particle size (peak

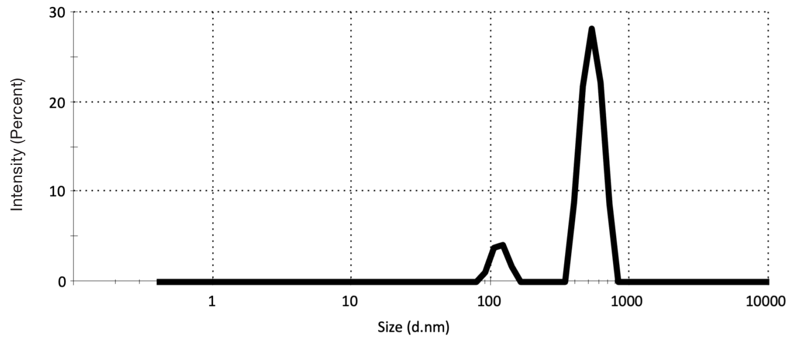


**Figure 15a.** Particle size distribution of normal clay sample without ultrasound pre-treatment

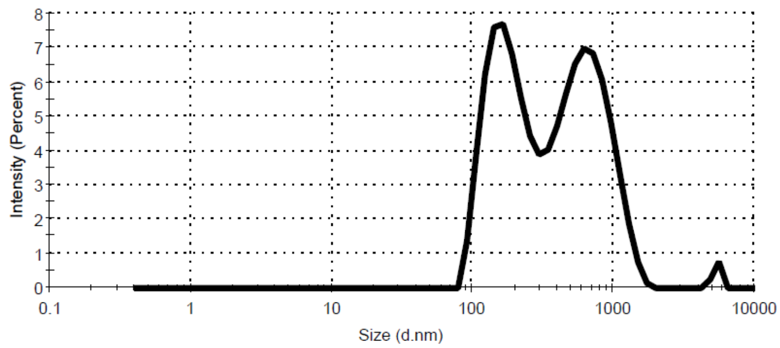


**Figure 15b.** Particle size distribution of clay sample after ultrasound pre-treatment for 10 min.

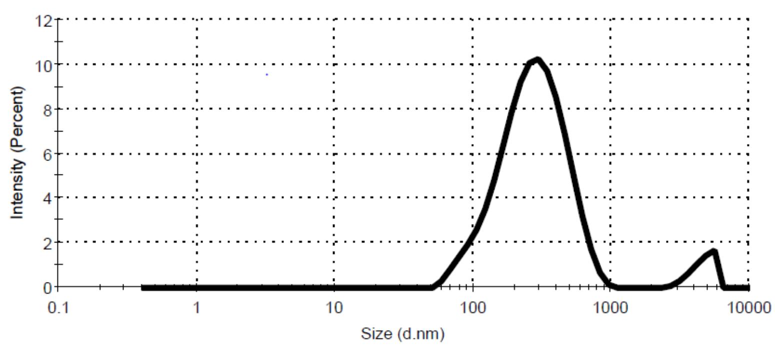


**Figure 15c.** Particle size distribution of clay sample after ultrasound pre-treatment for 20 min.

**Table II**

**Optimization of different coagulants on SVT tannins or spent tannery vegetable tanning liquor coagulation for facilitating the settling process**

| Exp. No. | Coagulants Employed | Optimized Amount of Coagulant (g) | | | |
|---|---|---|---|---|---|
| | | Vegetable Tannins Source and Amount | | | |
| | | Synthetic Spent Liquor SVT (0.5 g Wattle extract in 100 ml water) | Spent Tannery Vegetable Tanning Liquor (100 ml) | 100 g of Tannins from SVT (or % of Coagulant required on wt. of Tannins) | 10 L of Spent Tannery Vegetable Tanning Liquor |
| 1 | Zinc Chloride | 0.3 | | 60 | |
| 2 | Clay | 0.8 | | 160 | |
| 3 | Ferric Alum | | 0.15 | | 15 |
| 4 | Poly Electrolyte | | 0.005 | | 0.5 |
| 5 | Lime | | 0.6 | | 60 |

**Table III**

**Effect of different optimized coagulants and influence of ultrasound pre-treatment on SVT tannins or spent tannery vegetable tanning liquor coagulation and settling rate characteristics during the settling process.**

| Exp. No. | Optimized Number of Coagulants with Ultrasound (US*) or Without US Pre-treatment | | Vegetable Tannins Source | | | |
|---|---|---|---|---|---|---|
| | | | Synthetic Spent Liquor SVT (0.5 g Wattle extract in 100 ml water) | | Spent Tannery Vegetable Tanning Liquor (100 ml) | |
| | | | % Settled Volume | Time (min) | % Settled Volume | Time (min) |
| | Coagulant used | Optimized Amount (g) | | | | |
| 1 | $ZnCl_2$ | 0.3 | 20 | 80 | | |
| 2 | Clay + $ZnCl_2$ | Clay – 0.8<br>$ZnCl_2$ – 0.3 | 10 | 53 | | |
| | Clay + $ZnCl_2$ US* | | 7 | 17 | | |
| 3 | Clay + Ferric Alum (F.A) | Clay – 0.8<br>F.A – 0.15 | | | 5 | 60 |
| 4 | Poly Electrolyte (P. E) + Clay + Ferric Alum (F.A) | P.E – 5 mg<br>Clay – 0.8<br>F.A – 0.15 | | | 5 | 50 |
| 5 | Clay US* +<br>P. E + Ferric Alum F.A | Clay US* – 0.8<br>P.E – 5 mg<br>F.A – 0.15 | | | 30 | 42 |
| 6 | P.E US* +<br>Clay +<br>F.A | P.E US* – 5 mg<br>Clay – 0.8<br>F.A – 0.15 | | | 15 | 15 |
| 7 | Lime +<br>Clay +<br>F.A +<br>P.E US* | Lime – 0.6<br>Clay – 0.8<br>F.A – 0.15<br>P.E US* – 5 mg | | | 10 | 2/20 |
| 8 | Lime +<br>Clay US* +<br>F.A +<br>P.E | Lime – 0.6<br>Clay US* – 0.8<br>F.A – 0.15<br>P.E – 5 mg | | | 8 | 10 |

**Table IV**

**Effect of ultrasound (150 W at 20 kHz) on the particle size distribution of clay samples (1 g in 100 ml)**

| Sample | Particle size (nm) | | |
|---|---|---|---|
| | Peak 1 | Peak 2 | Peak 3 |
| Un ultrasound pre-treated clay | 538.6 | 116.5 | 0 |
| Ultrasound pre-treated clay (10 min) | 659.1 | 177.7 | 5375 |
| Ultrasound pre-treated clay (20 min) | 298.2 | 4630 | 0 |

1) of clay from 539 nm to 298 nm for 20 minutes treatment. This significant reduction in particle size provided more surface area for clay and could be attributed to the better performance of ultrasound pre-treated clay in coagulation process of vegetable tannins.

## Conclusions

In the present approach, the remediation of tannins available in spent vegetable tan liquor using another natural material, soil clay has been employed for the coagulation of spent vegetable tannins. Commercial condensed vegetable tanning agent, Wattle GS powder (SVT) as well as vegetable tanning process spent liquor collected from a commercial tannery were used in the experiments. Various other precipitating agents have been investigated and their amounts optimized (Table II). The efficacy of coagulation is monitored through settling characteristics and %Settled volume for a given time. Table III shows the summary of the results obtained through the present study. The results indicate that for 100 ml SVT (0.5 g tannins), the combined use of optimized $ZnCl_2$ (0.3 g) and clay (0.8 g) has provided enhancement as compared to individual use, whereas ultrasound pre-treatment of $ZnCl_2$ has given further improvement. In case of spent tannery vegetable tanning liquor (100 ml), optimized amounts of Ferric Alum (0.15 g) along with clay have achieved (5 ml, 60 min.); whereas addition of Poly electrolyte (5 mg) in the same process and ultrasound pre-treatment of either optimized clay or polyelectrolyte has provided further enhancement. Whereas, the best performance was achieved due to addition of lime (optimized 0.6 g) along with ultrasound pre-treated optimized polyelectrolyte (5 mg), normal clay (0.8 g) and ferric alum (0.15 g) with rapid settling in 2 minutes, with settling steady state achieved at ~20 minutes, with settled volume of ~10 ml; whereas (10 ml, 8 min.) obtained for ultrasound pre-treated optimized clay (0.8 g) with other agents as normal in the same process.

There is a significant reduction in particle size of clay from 539 nm to 298 nm for 20 minutes ultrasound pre-treatment, which provided more surface area for clay and attributed to the better performance of ultrasound pretreatment for clay sample in coagulation process of vegetable tannins. This method could be useful for remediation of vegetable tannins as natural materials, available in spent vegetable tanning liquors as sectional stream, using another available natural material clay through coagulation process with ultrasound pre-treatment for possible use such as enhancement of soil. However, separate study in this regard for the applicability and efficacy is very much essential, which would be investigated in future work. The coagulation method *per se* (not soil enrichment) as per the present shall be extended to other streams with suitable modifications. Thus, the present study has demonstrated the ultrasound assisted coagulation science and technology for beneficial remediation of wastewater in general, whereas, spent vegetable tanning liquor in specific.

## Acknowledgements

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# Synthesis and Characterization of Large Particle Size Self-Matting Core-shell Acrylic Resin

by

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## Abstract

Acrylic resin plays an important role in leather-making, such as finishing agent, filler and tanning agent. Acrylic resin can be easily fabricated via conventional emulsion polymerization, but how to prepare large particle size with self-matting effect has always been a challenge. In this paper, a continuous three-stage polymerization method: seed-polymerization coupled core-polymerization and shell polymerization was employed to prepare large particle size self-matting acrylic resin emulsion. Simultaneously, the effect of feeding methods on particles size and the effects of latex particle size, shell structure and cross-linking degree on the morphology and gloss of coating were investigated. The Z-average size of PBA seed latex particles was 213.4 nm for semi-continuous feeding method but 82.3nm for batch feeding method. After three-time continuous growth, the seed emulsion turned into core emulsion, and the particle size of core latex reached about 700nm. In third stages of shell polymerization, the core emulsion was changed into core-shell emulsion, and the latex particle size increased further to 804nm. The latex particle size, core-shell structure and cross-linking degree of shell layer were found to influence the gloss of the coating. Large latex particle size imparted the film spherical micro-rough surface, soft-core combined with hard-shell structure led to deformation resistant during film formation and cross-linking of shell layer increased the densification of shell layer, all contributed to the coating rough surface, as a result, increasing the matting effect of the coating. Finally, the leather gloss was reduced from 5.8° to 1.2°.

## Introduction

The preparation method of acrylic resins was invented by the German scientist Rohm in the early 20th century and used as a leather finishing agent in Germany in the 1930s.[1] Acrylic resin has good oxidation resistance and medium resistance because the C-C single bond in its main chain is difficult to be oxidized and hydrolyzed. At the same time, the main absorption peak of C-C single bond to electromagnetic wave is not in the range of solar spectrum, so it has good outdoor weather resistance. In addition, acrylic resin emulsion has the advantage of simple production process, safety, environment friendly, and low cost.[2-4] Therefore, it has been widely used in leather finishing, textile laminating, interior and exterior wall coating, adhesive, papermaking, automobile, construction, aerospace and other fields.[4-5]

As a coating material, acrylic resin plays a special role in protection, decoration and other aspects such as hydrophobicity and antifouling.[6] The gloss of the coating can be divided into matting coating and bright coating determined by their reflectivity to light. Bright coating has a crystal clear and beautiful appearance, so it is a popular choice for young consumers. With the changed aesthetic concept, people begin to pay more attention to the introverted fashion beauty. In recent years, the matting coating with soft luster has been widely used in automotive interior leather, sofa leather, wood painting, etc, which greatly promotes the development of matting coating materials.[7]

According to the Bennet-Porteus rough surface light reflection model,[8] the relationship between light reflectivity R of the rough surface with the mean square roughness $R_q$ of the coating surface is shown as in formula 1,

$$R = R_0\, exp\left[-\left(\frac{4\pi R_q cosi}{\lambda}\right)^2\right] \quad (1)$$

Where $R_0$ represents the reflectivity of absolutely flat surface, i is incident angle and $\lambda$ is the wavelength of incident light.

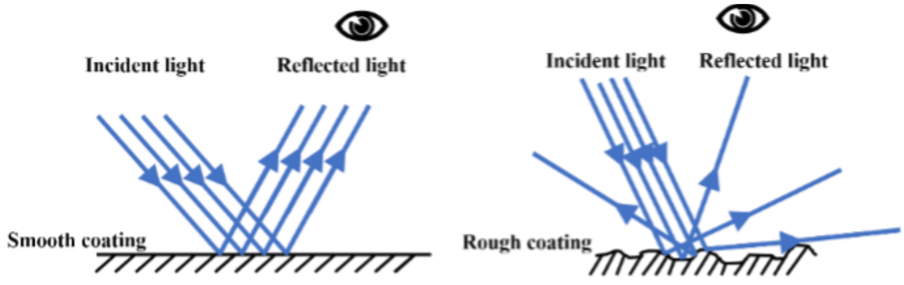


**Figure 1.** Effect of coating surface roughness on light path

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The propagation path of light on surface is shown in Figure 1. When a beam of incident light is emitted to the coating surface, light interacts with the coating, some will be absorbed, and some will be reflected and refracted. For the extremely smooth surface, the angle of incident light is the same as that of reflected light, which leads to a complete reflection and a high-gloss coating. In turn, for the rough surface, due to different normal directions of each point on the surface, many light beams diffuse on the surface, so the light intensity entering eyes becomes weaker and the matting effect is obtained.[9,10]

The conventional matting coating is obtained by adding matting fillers into polymer bulk. These matting fillers are usually inorganic silica powder or organic wax powder, and their particle sizes are larger than the latex particles, which will produce uneven surface after film-forming.[11,12] However, the poor compatibility between them will inevitably bring a series of problems, such as poor stability of emulsion, poor appearance of coating, rough handle and low transmittance.[7,11,12] Therefore, self-matting acrylic resin and polyurethane have become a research hotspot.[10,13,14] Such polymers are usually prepared into larger particle size emulsions, forming rough surfaces when film forming, resulting in matting effect. As well known that the preparation of acrylic resin emulsion is classical emulsion polymerization, the latex particle size synthesized by this method is too small (50-150nm) to meet the requirement for extinction. Therefore, how to prepare large size latex through special emulsion polymerization is the key issue to the preparation of self-matting acrylic resin.

According to the film-forming mechanism of polymer emulsion as illustrated in Figure 2, the film formation process of acrylic resin emulsion can be divided into three steps. (1)Firstly, moisture volatilization in the polymer emulsion, the latex particles gradually accumulate, water and other soluble substances are dispersed in the gap between the latex particles. (2) With the further volatilization of water, the gap between latex particles becomes smaller until a capillary is formed. The capillary action forces the latex particles to deform, resulting in disappearance of the interface between particles. (3) Finally, the polymer chains diffuse and entangle at the interface of raw latex particles, and the particles fuse with each other to form a continuous and flat polymer film.[15-17] In the film-forming process, the soft latex particles are prone to deformation in the second stage of film formation and fusion in the third step, resulting in a relatively smooth and high gloss surface. However, as a matting coating, the deformation and fusion of latex particles should be avoided as much as possible in the process of film formation, so as to improve the roughness of the coating and obtain the matting effect. Therefore, hard latex particles are more suitable for matting coating.

For this reason, a large particle size self-matting acrylic resin emulsion with soft core and hard shell was prepared by three-stage-method. Firstly, butyl acrylate (BA) was used as soft monomer to prepare PBA seed emulsion with particle size of about 200nm. Then, the core latex was prepared by three-time core polymerization on the basis of seed emulsion to enlarge the particle size of latex to approximately 700nm. Finally, P (BA-MMA/AN) soft core-hard shell latex with latex particle size of 800nm was obtained by shell polymerization with methyl methacrylate (MMA) and propylene cyanide (AN) as hard monomers. At the same time, the effects of feeding method of monomer and emulsifier and the growing method of seed latex particle on latex particle size and the effects of latex particle size, shell hardness and crosslinking on the gloss of the coating were also investigated.

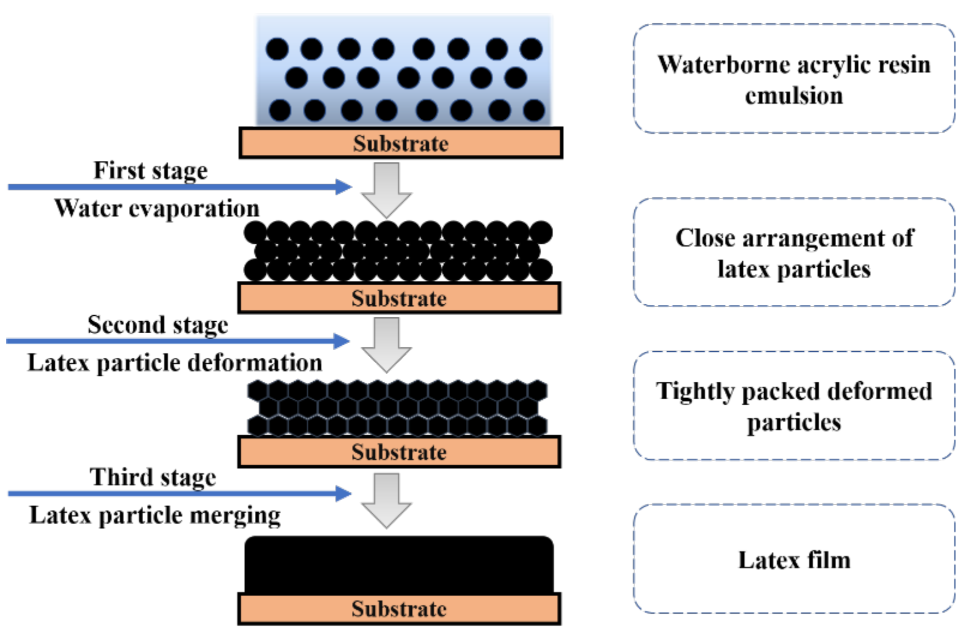


**Figure 2.** Film formation process of acrylic resin emulsion

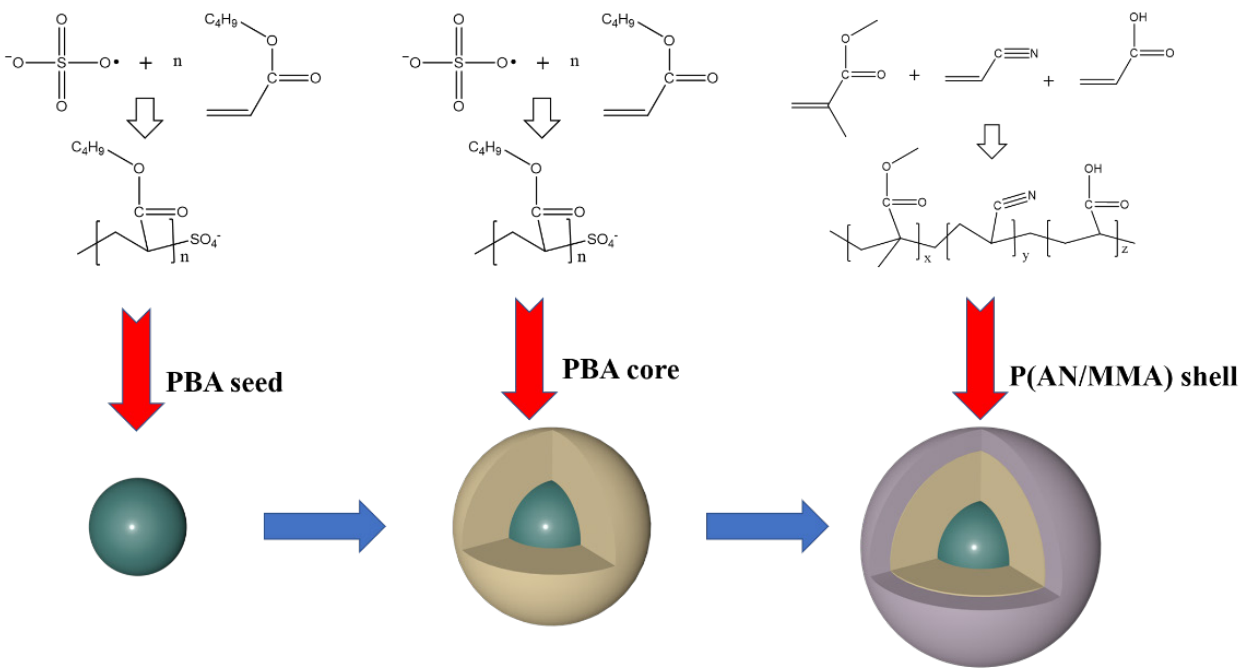


**Figure 3.** Synthesis of acrylic resin emulsion latex particle

## Experiment

### Raw materials

Butyl acrylate (BA) was purchased from Greagent. Methyl methacrylate (MMA), acrylic acid (AC), allyl methacrylate (AMA) and sodium dodecyl sulfate (SDS) were purchased from Adamas. Acrylonitrile (AN) was purchased from TCI. Deionized water (DDI) was self-made in the laboratory as the synthesis medium.

### Preparation of acrylic resin emulsion

The preparation of acrylic resin emulsion was divided into three stages. Firstly, the PBA seed emulsion with relatively large particle size was prepared. Then the seed emulsion grew for three times to fabricate large particle size core emulsion. Finally, core-shell emulsion was fabricated by shell polymerization on the basis of core emulsion. In experiment, BA was used as soft monomer and MMA/AN was used as hard monomer, the amount of emulsifier SDS was low to prevent the formation of new micelles and latex particles. The specific reaction process was shown in Figure 3.

### Preparation of PBA seed emulsion

The reaction was carried out in four-necked round bottom flask equipped with condensing pipes, nitrogen protection devices and mechanical stirrer. In the reaction, four-necked round bottom flask was placed in a water bath with thermostatic control. The polymerization temperature was 78°C and the stirring rate was 125rpm. According to the formula of reactants listed in Table I, the seed emulsion was first prepared. The seed emulsion was synthesized by two feeding methods under the conditions mentioned above: batch feeding method and semi-continuous feeding method. Batch feeding method, that is, all reactants were one-time poured to the reactor at the beginning polymerization. After heating to the reaction temperature, the initiator APS was added. While for semi-continuous feeding method, the pre-emulsion (BA monomer, half of the total amount of deionized water, emulsifier SDS and initiator APS) was pre-emulsified at ambient temperature for 1h firstly, then the pre-emulsion was dropped into reactor for 2h, and the seed emulsion was obtained.

### Preparation of PBA core growth emulsion

Core emulsion was fabricated by three times growth of seed emulsion. According to the reactant formula listed in Table II, firstly, all BA, deionized water, SDS and APS were magnetically stirred at ambient temperature for 1h to prepare the pre-emulsion. Then the seed emulsion was poured into reactor simultaneously and heated to the reaction temperature to 75°C. After that, the pre-emulsion was dropped to the reaction system in a period of 2 h. Finally, a core emulsion with once growth of latex particles

**Table I**

**Recipes for the preparation of PBA seed latexes**

| Ingredients | BA(g) | $H_2O$(g) | SDS(g) | APS(g) | $NaHCO_3$(g) |
|---|---|---|---|---|---|
| Seed | 80 | 240 | 0.24 | 0.24 | 0.5 |

**Table II**

**Recipes for the preparation of PBA core latexes**

| Ingredients | Seed (g) | Core1 (g) | Core2 (g) | BA (g) | $H_2O$ (g) | SDS (g) | APS (g) | $NaHCO_3$ (g) |
|---|---|---|---|---|---|---|---|---|
| Core1 | 120 | - | - | 80 | 240 | 0.24 | 0.24 | 0.5 |
| Core2 | - | 120 | - | 80 | 240 | 0.24 | 0.24 | 0.5 |
| Core3 | - | - | 120 | 80 | 240 | 0.24 | 0.24 | 0.5 |

was obtained (named core 1). Similarly, core 1 was used as mother liquor, core 2 emulsion with twice growth of latex particles was prepared. In the same way, core 3 emulsion with large particles size could be achieved

**Preparation of P(BA-MMA/AN) core-shell emulsion**

The formulation of P(BA-MMA/AN) core-shell emulsion was shown in Table III. Firstly, the shell monomer (MMA and AN), AMA (crosslinker), deionized water, SDS and APS were magnetically stirred at ambient temperature for 1h to prepare the pre-emulsion. Then the quantitative core 3 emulsion was charged into reactor simultaneously and heated to the reaction temperature to 75°C. Finally, the pre-emulsion was dropped to the reaction system for 2 h and the P(BA-MMA/AN) emulsion with soft core and hard shell was obtained.

**Preparation of leather coating**

Appropriate amount of core-shell acrylic resin emulsion, leveling agent and thicker were mixed together with viscosity of 1000-1500mPa·S. Then the thickened acrylic resin was applied on leather by using 8μm rod coater. Finally, the coated leather was dried in an oven at 120°C for 5 minutes to obtain the coated leathers.

## Characterization

**Coating gloss test**

According to the standard ISO 2813-2014, the gloss of leather coated with different acrylic resins was measured by 60° gloss meter (REFO 60, German). All samples were measured 5 times and the average value was recorded.

**Measurement of latex particle size distribution**

The latex particle size distribution (PSD) of acrylic resin emulsion was observed by dynamic light scattering particle size analyzer (DLS Malvern Zetasizer Nano ZS, England). The sample was diluted 500 times by deionized water in glass cuvette to determine the Z-average particle size and particle size distribution.

**Characterization of surface morphology and roughness**

The surface morphology and roughness of self-matting acrylic resin coating were characterized by scanning electron microscope (SEM Helios G4 UC, German) and atomic force microscope (AFM SPM-9500, Japan) respectively. The emulsion was dripped onto the silicon wafer and dried at ambient temperature and ventilation condition to obtain the coating. After spraying gold, the surface morphology of the coating was obtained by secondary electron signal of SEM. In addition, the three-dimensional surface topography and surface roughness of coating can be observed by AFM with 5μm × 5μm scanning area. The samples were prepared by spin coating self-matting acrylic resin emulsion on the silicon wafer substrate.

**Characterization of glass transition temperature**

The glass transition temperature ($T_g$) of PBA core latex and core-shell latex were characterized by differential scanning calorimetry (DSC 214 F1, NETZSCH Instrument, German). The experiment was

**Table II**

**Recipes for the preparation of P(BA-MMA/AN) core-shell latexes**

| Ingredients | Core3 (g) | MMA (g) | AN (g) | AA (g) | AMA (g) | $H_2O$ (g) | SDS (g) | APS (g) | $NaHCO_3$ (g) |
|---|---|---|---|---|---|---|---|---|---|
| Core-shell without AMA | 60 | 15 | 20 | 0.105 | 0 | 105 | 0.105 | 0.105 | 0.2 |
| Core-shell with AMA | 60 | 15 | 20 | 0.105 | 0.25 | 105 | 0.105 | 0.105 | 0.2 |

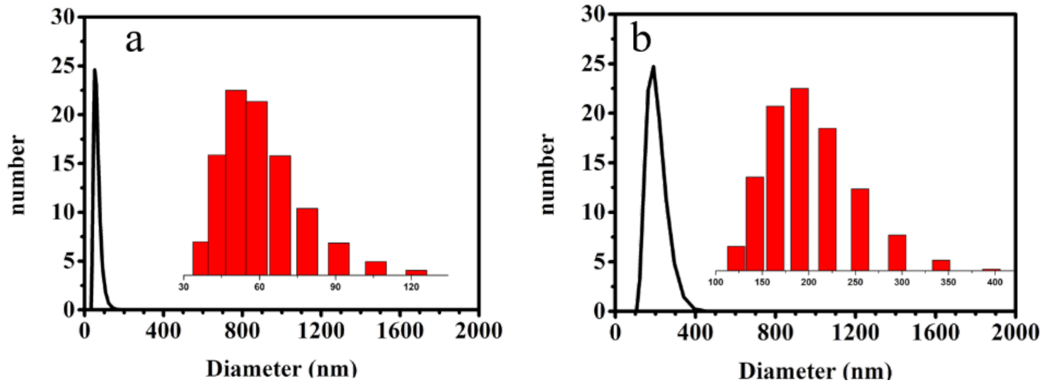


**Figure 4.** Particle size distribution of PBA seed latex particles: **(a)** batch **(b)**semi-continuous

carried out in nitrogen atmosphere. After eliminating the thermal history, the sample was scanned from -80°C to 160°C at a heating rate of 10°C/min.

## Result and Discussion

**Effect of feeding mode on particle size of seed emulsion**

The particle size of the seed emulsions synthesized by two different feeding methods are shown in Figure 4. The Z-average particle size of PBA seed emulsion synthesized by batch feeding method was 82.3nm, as shown in Figure 4(a). Meanwhile, this value for semi-continuous feeding method was 213.4nm, as shown in Figure 4(b), which indicates that semi continuous feeding method is more conducive to the formation of large size seed emulsion.

The conventional free radical emulsion polymerization includes three stages according to the monomer conversion rate. Stage I: latex particle formation stage, stage II: latex particle growing stage, stage III: polymerization completion stage.[20,21] In stage I, the nucleation mechanism of latex particles can be divided into the following three types: a) micelle nucleation mechanism, b) monomer droplet nucleation mechanism and c) oligomer nucleation mechanism.

In this study, the concentration of emulsifier (SDS) in the reaction system and pre-emulsion was lower than its critical micelle concentration ($CMC_{(SDS)}$=8mmol/L). Therefore, micelles would not be formed and micelle nucleation would not occur in the reaction system.[18] For conventional radical emulsion polymerization, when the monomer droplet concentration was too low, the free radical would be hard to diffuse into monomer droplets, so monomer droplet nucleation is also difficult to occur.[19] In the aqueous phase, there were a small amount of free monomers existing as true solution, these monomers can be initiated by free radicals. Because the solubility of this polymer in aqueous phase decreased sharply with the increase of relative molecular mass, the free radical chains were precipitated before they grow to a relatively large relative molecular mass. The precipitated oligomers absorbed emulsifier from the surrounding so that it could stably exist in the aqueous phase, thus forming new latex particles. This nucleation mode is called oligomer nucleation mechanism. The formation of PBA latex particles in this experiment should follow this nucleation mechanism.

As described above, when the concentration of emulsifier (SDS) was lower than $CMC_{(SDS)}$, there were almost no micelles in the reaction system, that means the polymerization reaction went directly to stage 2 without going through stage 1, in which latex particle nucleation and latex particle growth occurred simultaneously. a) BA monomer dissolved in aqueous was initiated by free radicals in the aqueous phase to form oligomers, once their relative molecular mass became large, they would precipitate from the aqueous phase and adsorbed emulsifiers to form latex particles, i.e., oligomer nucleation. b) the radical chain formed after the reaction between APS and BA is hydrophobic at one end and hydrophilic at the other end, so the radical chain exhibited surface active, and the hydrophobic end of this surface-active radical chains entered the latex particles and triggered the monomers swelling inside the latex particles, leading to the growth of the latex particles. In above both reactions, reaction a) led to the formation of new latex particles while reaction b) led to the growth of latex particles. Therefore, if the polymeric parameters could be adjusted to make reaction b) more likely to occur, then a larger particle size emulsion could be obtained.

The possibility of oligomer nucleation can be predicted according to the number density of BA monomers in the aqueous phase. For batch feeding method, the concentration of the low water-soluble monomer BA remained constant at the beginning of the reaction, i.e., the saturation concentration of BA ($1.4\times10^{3}$g·mL$^{-1}$). These monomer molecules in the aqueous phase could be triggered by free radicals for polymerization, and then the monomers in the monomer droplets would continuously diffuse into the aqueous phase to replenish the monomers consumed by polymerization, thus keeping the monomer concentration in the aqueous phase constant at the saturation concentration of BA. In the case of batch feeding method, the molecular number density $N_m$(batch) of BA in the aqueous [22] phase can be calculated from Equation 2:

$$N_m(\text{batch}) = \frac{1.4\times10^{-3}}{M_{BA}} \times N_A = 6.576\times10^{18} mL^{-1} \quad (2)$$

Where $M_{BA}$ is the BA molecular mass (128.17 g/mol) and $N_A$ represents Avogadro constant.

For semi-continuous feeding method, the number density of monomers in the aqueous phase of reaction system depended on the addition rate of monomer in the pre-emulsion. After the dropwise addition of a small amount of BA monomer, the concentration of BA monomer in the reaction system was lower than the saturation concentration of BA monomer in the aqueous phase, which means that any slowly added monomer would diffuse and be consumed rapidly in the reaction system without causing monomer enrichment. In the case of semi-continuous feeding method, the molecular number density $N_m$(semi-continuous) of BA[22] in the aqueous phase can be calculated from Equation 3:

$$N_m(\text{semi-continuous}) = \frac{\text{FR}_{\text{BA}}}{V_{H_20}M_{BA}} \times N_A \leq 2.617 \times 10^{17} mL^{-1} \cdot s^{-1} \quad (3)$$

Where the $FR_{BA}$ is the feeding rate of BA monomer in pre-emulsion, and the  is the volume of deionized water initially added in the semi-continuous method.

The results obtained from the above two equations show that the molecular number density of monomer BA in semi-continuous feeding method was significantly lower than that in batch feeding method. Moreover, as the volume of the aqueous phase in the reaction system increased, the number density of BA molecules decreased further, which reduced the probability of oligomer nucleation in the semi-continuous feeding method. Therefore, the number of latex particles produced in semi-continuous feeding method was smaller and the latex particle size was larger compared to batch feeding method.

Based on the latex particle size D measured by DLS (Figure 4), the individual latex particle mass m and the latex particle number density N could be calculated by Equation 4 and Equation 5 as follows [22]

$$m = \rho\left[\frac{4}{3}\pi(D/2)^3\right] = \frac{\rho\pi D^3}{6} \quad (4)$$

$$N = \frac{M}{mV} \quad (5)$$

Where ρ is polymer density ($\rho_{PBA} = 1.08 g \cdot mL^{-1}$) and M is the total mass of monomer fed to the reactor in this stage. When the monomer conversion is 100%, the N obtained from the calculations was shown in Table IV.

The data of latex particles number density in Table IV show that in the seed emulsion preparation stage, the number density of latex particles using batch feeding method was greater than that of semi-continuous feeding method, which also confirmed the theoretical prediction in the foregoing.

**Growth of Core latex particle size**

In the latex particle growing stage from seed emulsion to core emulsion, the continuous feeding method was used to increase the latex particle size. After three times growth, the particle size and size distribution of the core emulsion obtained for each time is shown in Figure 5.

It can be seen that the latex particle size gradually increased with the increase of growing times, and the resultant Z-average particle size reaches about 700nm after three times of growth, which is three times that of seed latex particles. And with the increase of latex

**Table IV**
**Diameter and number density of PBA seed latex particles at termination stage of polymerization**

| Seed latex particle | | |
|---|---|---|
| **Feeding Method** | **Diameter(nm)** | **Number density(nm)** |
| Batch | 82.3 | $1.06\times10^{15}$ |
| Semi-continuous | 213.4 | $6.07\times10^{13}$ |

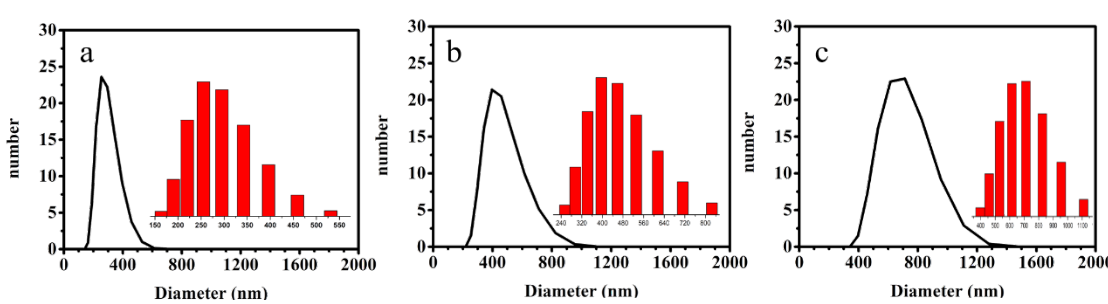


**Figure 5.** Particle size distribution of PBA core latex particles: **(a)** core1 **(b)** core2 **(c)** core3

**Table V**
**Variation of diameter and number density of PBA after growth**

| Core latex particle | | |
|---|---|---|
| **Code** | **Diameter(nm)** | **Number density** |
| Core-1 | 312.3 | $1.94\times10^{13}$ |
| Core-2 | 480.4 | $5.32\times10^{12}$ |
| Core-3 | 695.0 | $1.76\times10^{12}$ |

**Table VI**
**The number of PBA particles at initiation and termination stage of polymerization**

| Code | The number of latex particles | |
|---|---|---|
| | Initiation of polymerization | Termination of polymerization |
| Core-1 | $5.46\times10^{15}$ | $6.4\times10^{15}$ |
| Core-2 | $1.75\times10^{15}$ | $1.76\times10^{15}$ |
| Core-3 | $4.79\times10^{14}$ | $5.81\times10^{14}$ |

particle size, the latex particle size distribution (PSD) became wider. The diameter and number density of latex particles for each growth shown in Table V.

It can be seen that the number density of latex particles decreased with each latex particle growth, which also led to the increase of latex particle size. The reason for this phenomenon was that when the continuous feeding method was adopted, some of the newly added monomers entered the interior of the latex particles and some monomers were dissolved in the aqueous phase, forming a dynamic balance of monomer concentration. According to the rule of "the likes dissolve each other", hydrophobic BA was more likely to enter the latex particles, therefore, the BA concentration in aqueous phase was very low, and the probability of new oligomer nucleation was very rare. At this time, latex particle growth become dominate, which caused the increase of particle size for each growth. Since the probability of each latex particle growing up was random, so the latex particle size distribution became wider.

The number of latex particles at the initiation and termination of polymerization are compared in Table VI. The results showed that although the number density of latex particles decreased after latex particles growth, the number of particles at the termination of polymerization was increased slightly, which indicated that some secondary particles were generated. Although oligomer nucleation and particle growth reactions occurred simultaneously during the latex particle growth process, the number of newly generated latex particles is small, again indicating the dominance of the particle growth reaction.

**Effect of hardness of shell polymer on the surface morphology of coating**

MMA-AN and BMA-AN were used as co-polymerization monomers, the effect of shell hardness of core-shell latex particles on the glass transition temperature ($T_g$), surface morphology and gloss of

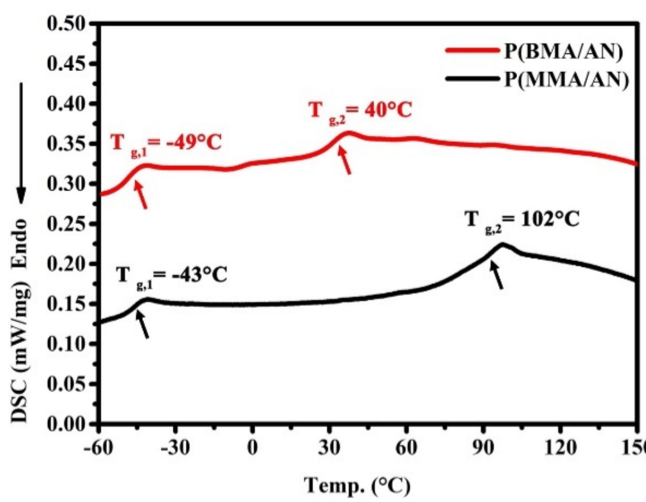


**Figure 6.** DSC curve of acrylic resin from different shell polymer

**Table VI**
**Glass transition temperature and gloss of films with soft shell and hard shell**

| Shell structure | Soft shell P(BMA/AN) | Hard shell P(MMA/AN) |
|---|---|---|
| Homopolymer $T_g$ (°C) | 20(BMA)/96(AN) | 105(MMA)/96(AN) |
| Copolymer theoretical $T_g$ (°C) | 50 | 100 |
| Copolymer practical $T_g$ (°C) | 40 | 102 |

coating were investigated. DSC curves are shown in Figure 6 and the SEM image are shown in Figure 7, and gloss and glass transition temperature data are shown in Table VII.

DSC was utilized to analyze the glass transition temperature of both acrylic resins with different shell structure. For P(BA-BMA/AN) emulsion, the $T_{g,1}$of core polymer is -49°C, and the $T_{g,2}$ of shell copolymer is 40°C, whilst for P(BA-MMA/AN), the corresponding $T_{g,1}$ and $T_{g,2}$ are -43°C and 102°C. The glass transition temperature of homopolymer PBA, PMMA, PBMA and PAN are -56°C, 105°C, 20°C and 96°C, separately. The glass transition temperature of shell copolymers ($T_g$) can be calculated by the given FOX[23] formula Equation 6.

$$\frac{1}{T_g} = \frac{W_A}{T_{g,A}} + \frac{W_B}{T_{g,B}} \tag{6}$$

Where $T_g$ is the glass transition temperature of A and B monomer copolymer; $W_A$ and $W_B$ are the mass proportion of A and B monomer in all monomers, respectively; $T_{g,A}$ and $T_{g,B}$ are the glass transition temperatures of A and B monomer homopolymer, respectively.

The $T_{g,1}$ obtained from the practical test deviated from the theoretical value $T_g$ of PBA. The reason for this phenomenon was that the synthesized latex particles were core-shell structure, and the hard-shell structure with higher glass transition temperature outside enveloped the soft core of PBA, so it would make the $T_g$ of PBA core have a certain elevation. The glass transition temperature of copolymers could be calculated by FOX formula. The deviation of the calculated results from the practical results might be due to the actual ratio of the two copolymer monomers deviating from the feed ratio in the continuous polymerization. The observed lower glass transition temperature peak $Tg,_1$ corresponded to the PBA core, and the higher $Tg,_2$ was similar to the glass transition temperature of the copolymer obtained from theoretical calculations, which showed a better fit with the core-shell model.

The surface morphology of latex film with different shell structure was observed by SEM (Figure 7). It can be seen that latex film with relative soft shell shows smooth surface, whilst latex film with hard shell shows an uneven "pebble-like" surface. Just as mentioned above, the harder shell layer could prevent the latex particles from deformation and fusion in process of drying, which was beneficial for achieving the roughness of coating surface. Compared with MMA, the side chain of BMA was longer and its glass transition temperature was lower. The copolymer composed of BMA and AN had formed a soft-shell layer, which appeared in a rubbery state during film formation, in this case the deformation and fusion of latex particles occurred easily during the film formation process, thus forming a smooth surface of coating. While the copolymer composed of MMA and AN had formed a hard-shell layer, and this hard shell was difficult to move and could fully resist the deformation and fusion of the latex particles during the film formation process, so the latex particles were forced to form the pebble-like shape after film formation.

**Effect of cross-linking on the surface morphology and gloss of the coating**

Crosslinking of shell copolymer is closely related to latex particle size, glass transition temperature of polymer as well as apparent

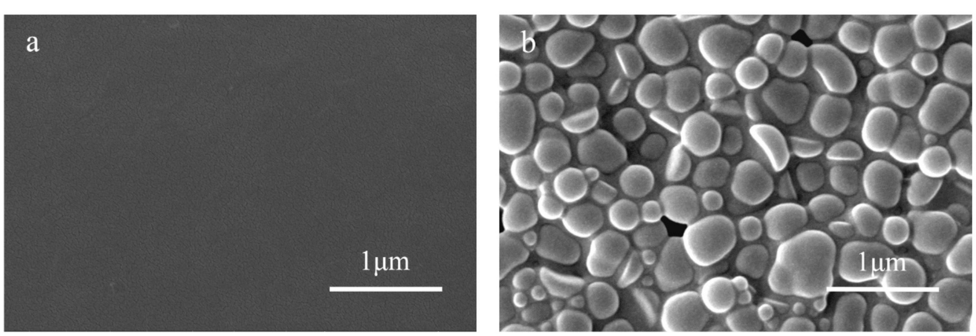


**Figure 7.** SEM images of acrylate resin films: **(a)** soft shell, **(b)** hard shell

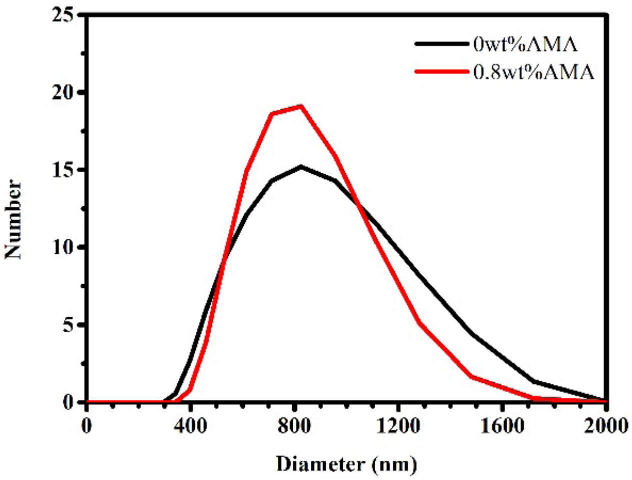


**Figure 8.** Particle size distribution of P(BA-MMA/AN) core-shell latex particle with or without AMA cross-linking

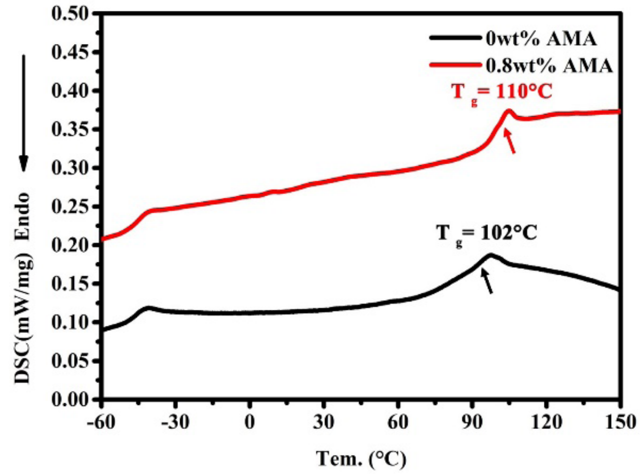


**Figure 9.** DSC curve of acrylic resin films with or without AMA cross-linking

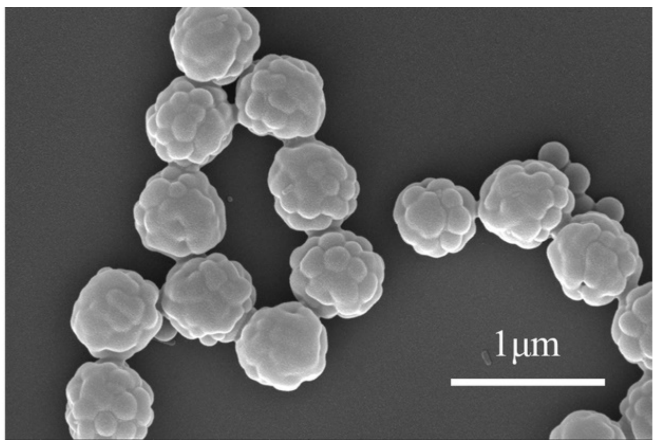


**Figure 10.** SEM images of acrylic resin films with AMA cross-linked

morphology and gloss of coating. Figure 8 shows the change in particle size of P(BA-MMA/AN) core-shell latex before and after cross-linking, the changes in glass transition temperature of shell copolymer and morphology of P(BA-MMA/AN) coating surface are shown in Figure 9 and Figure 10, Table VIII lists the relative data.

As can be seen from Figure 8 and Table X that the latex particle size shows little changes except the narrowing down of particle size distribution after cross-linking. From Figure 9 it was found that the glass transition temperature of the shell copolymer increased from 102°C to 110°C with the addition of the cross-linking agent, which will further hinder the deformation and fusion of latex particles during the film formation process and thus form a higher roughness of coating surface.

The change of morphology of film surface also proves the above inference. As could be seen from Figure 10, the original pebble-like particles evolved into spherical shape, and separated from each other. The cross-linking also imparts the coating surface sulcus and gyrus structure due to difference in internal stress.

Figure 11 are the AFM images showing the apparent roughness of coating surface. It can be seen that the coating roughness $R_q$ increased rapidly with the increase of particle size of emulsion. For example, the $R_q$ is 144.96nm for emulsion a with particle size 243.98nm but are 173.2 nm, 207.8 nm, 243.98 nm for emulsion b, c, d with increased particle size. This enhanced roughness of coating surface was believed to further improve the diffuse reflection of light, which was conducive to the improvement of the matting property of the coating.

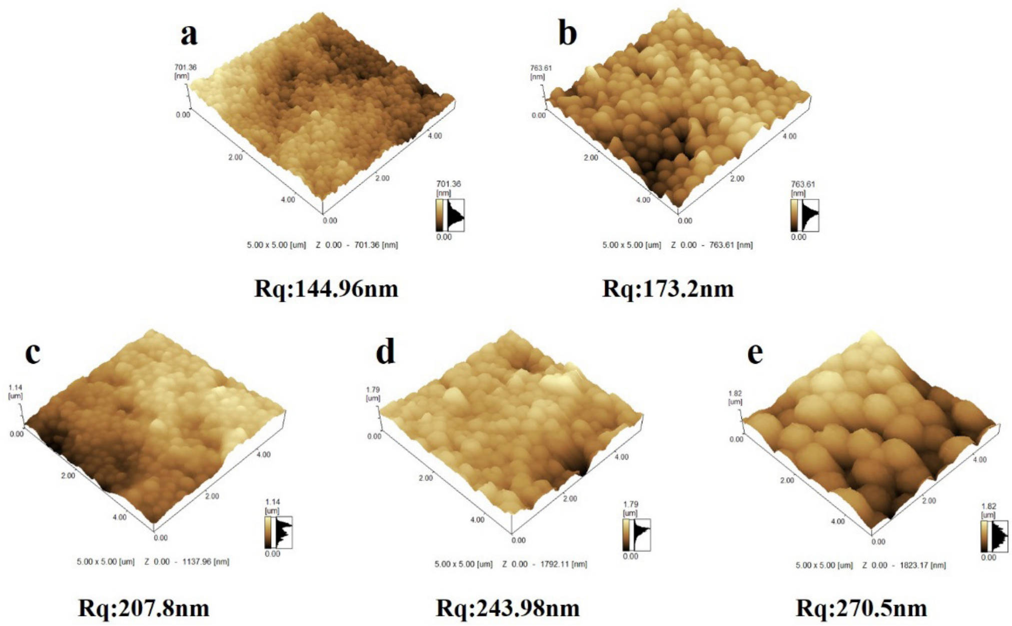


**Figure 11.** Effect of latex particle diameter and cross-linking on coating roughness: particle size of emulsion (**a**)245.8nm (**b**)359.4nm (**c**)555.8nm (**d**)802.4nm (**e**)804.7nm with AMA cross-linking

**Table VIII**

**Coating roughness, Theoretical light reflectivity and Gloss with different acrylic resin coating**

| | 0wt%AMA | | | | 0.8wt%AMA |
|---|---|---|---|---|---|
| **Acrylic resin coating** | **a** | **b** | **c** | **d** | **e** |
| Particle diameter of emulsion (nm) | 245.8 | 359.4 | 555.8 | 802.4 | 804.7 |
| Coating roughness(nm) | 144.96 | 173.2 | 207.8 | 243.98 | 270.5 |
| Theoretical light reflectivity(R) | 22.29 | 12.65 | 5.71 | 2.04 | 0.90 |

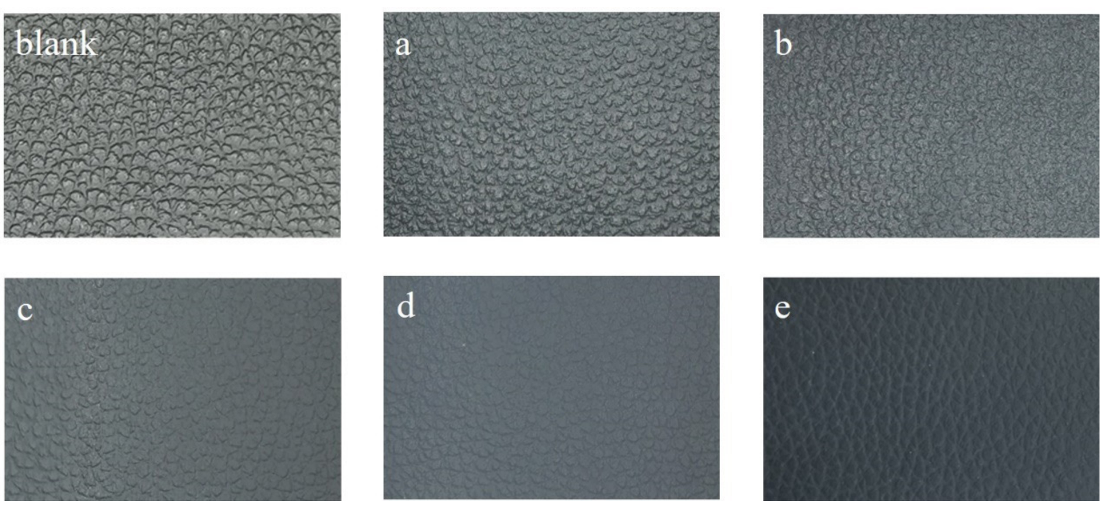


**Figure 12.** Effect of latex particle diameter and cross-linking on coating gloss: particle size of emulsion (**a**)245.8nm (**b**)359.4nm (**c**)555.8nm (**d**)802.4nm (**e**)804.7nm with AMA cross-linking

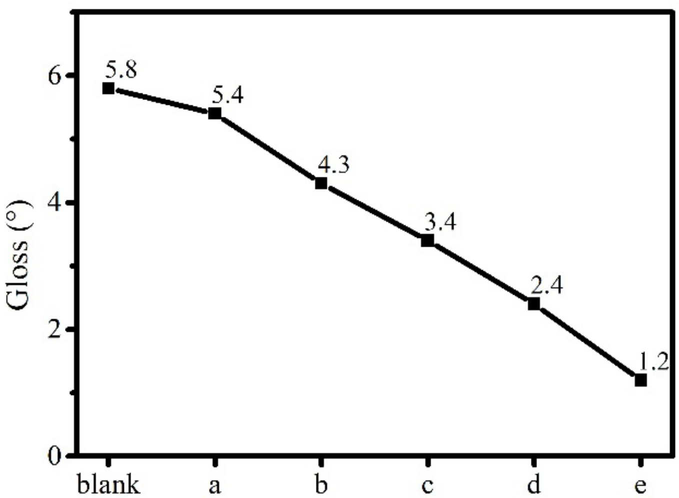


**Figure 13.** Gloss of finished leather corresponding to Figure 12; particle size of emulsion **(a)**245.8nm **(b)**359.4nm **(c)**555.8nm **(d)**802.4nm **(e)**804.7nm with AMA cross-linking

Based on the $R_q$ measured by AFM, the theoretical light reflectance R of the coating can be calculated by the Equation 1, and its value was shown in Table VIII.

As described in Table VIII, with the increase of surface roughness from 144.96 nm to 270.5 nm, the theoretical light reflectance of the coating calculated by Equation 1 decreased from 22.29 % to 0.9%, showing a significantly decreasing tendency.

Figure 12 and Figure 13 shows the comparison of the gloss of leather coating. It can be seen that the coating exhibits good matting properties. And the gloss of the coating decreased from 5.4° to 2.4° with the increase of the latex particle size form 245.8 nm to 802.4 nm, showing a decreasing tendency. Emulsion d (802nm) and emulsion e (804nm) had similar particle sizes, but the latter exhibited lower gloss (1.2°) and higher matting effect, this is attributed to the crosslinking of shell copolymer. The shell copolymers without crosslinking were looser to each other, after cross-linking, the linear copolymers became network copolymers, which led to the increase of the shell layer densities. As a result, the latex particles were not easily deformed and fused when the coating were drying. Therefore, the coating gloss was further decreased from 2.4° to 1.2°, variation of coating gloss keeps good consistent with the trend of the surface roughness.

## Conclusion

In this study, the methods of acrylic latex particle size growth, the effects of different feeding methods on the latex particle size as well as the effects of latex particle size, core-shell structure and crosslinking degree on the apparent morphology and gloss of the coating were investigated. In comparison with batch feeding method, the particle size of PBA seed emulsion prepared from semi-continuous feeding method increased from 82.3nm to 213.4nm. The latex particle size can be further enlarged to 700nm after three-time consecutive growths. More interestingly, the core polymerization still follows the oligomer nucleation mechanism, the newly generated latex particles are less, and the particle growth reaction is the dominant. After shell polymerization, the particle size of resultant emulsion can be increased to 804 nm. Larger latex particle size makes the coating surface present a spherical rough structure after drying, and designable matting effect of the coating can be obtained. The gloss of the coating can also be regulated by changing the hardness and crosslinking of shell copolymer. Compared with P(MBA-AN) with soft-shell structure or without crosslinking, P(MMMA-AN) with hard-shell structure and crosslinking was found to possess lower gloss and higher matting effect. Higher hardness and crosslinking will hinder the deformation and fusion of latex particle during the drying process of the coating, as a result, the surface roughness of the coating will be increased and the leather gloss can be further reduced to below 1.0°.

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**Authors' contributions**

Hao Peng: Conceptualization, Methodology, Formal analysis, Writing - Original Draft, Data curation, Formal analysis, Huan Wei: Validation, Investigation, Jun Xiang: Writing- Reviewing, Editing, Validation, Yi Chen: Visualization, Validation, Haojun Fan: Writing - Review & Editing, Supervision.

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**Availability of data and materials**

All data generated or analyzed during this study are included in this article.

## Declarations

**Competing interests**

The authors declare no competing interest.

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# Potential of Water Hyacinth Leaves Extract as a Leather Tanning Agent

by
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## Abstract

Water hyacinth (Eichhornia crassipes) is listed as one of the worst aquatic plants in the world and its presence in Lake Tana in Ethiopia has been recognized since 2011. Currently, the plant coverage in the lake is increasing and very limited studies have been conducted in the country on practical application of water hyacinth. The aim of this study was to determine the phytochemicals, functional groups and Tannin content of the water hyacinth plant found in the Lake, which could serve as a vegetable tanning agent. Both qualitative and quantitative approaches were used to assess the quality tannin in the plant stem and leaves. On phytochemical analysis of the dried material, the tannin content was found to be 4.1% for leaves and 2.7% for stem parts. As the tannin content of the leaves was higher than the stem parts, leather tanning conducted using the 10% wt and 20% wt leaves and the quality of tanned leathers was evaluated and compared with the leather made from quebracho vegetable tanning material as a control. Most properties of leathers tanned using the leaves met the minimum specified standards for leather product manufacturing, which includes tearing strength > 45 N, percent elongation at break > 42% distension at grain crack > 6.5 mm, and distension at burst >7.8 mm. Even though shrinkage temperature is one of the most important parameters in determining the thermal stability of leather, the leather tanned with leaves extract had a shrinkage temperature of 52°C, which is lower than the standard limit (75°C) for leather product manufacturing. This indicated that, the crosslinking reaction between the hide (collagen fibers) and tannins (leaves) was weaker, implying that the leather would not be as durable or of higher quality. Similarly, the maximum tensile strength of tanned leather was 7.2 N/mm$^2$, which is lower than the standard requirement (20 N/mm$^2$) for leather product manufacturing. Therefore, water hyacinth leaves extract has limited potential as a vegetable tanning agent, and the tanned leather will not be used to make leather products that requires good thermal resistance and strength. On the other hand, the tanned leather may be utilized for leather products that need minimal tensile strain and thermal property requirements such as leather photo frames, sketchbook leather bound, etc. Since water hyacinth tannin is less than ideal as a tanning agent due the minimum shrinkage temperature and tensile strength of the tanned leather, the potential of the plant as a retanning agent should be studied in future.

## Introduction

Leather production is a long and complex process that involves a number of chemical and mechanical processes. Tanning is a chemical method that converts a putrescible organic material into a stable material that can withstand biochemical attack by addition of crosslinks to collagen in order to link active tanning agents to protein functional groups.[1] Tannins are phenolic compounds that bind to collagen proteins in the hide, creating insoluble complex compounds that are more resistant to bacterial attacks.[1] Tannins are most commonly obtained from plants, but certain tannins can also be obtained from minerals. Depending on the type of animal and the intended use of the leather, hides and skins are normally tanned using either a mineral or a vegetable tanning technique.[2]

Chrome tanning is a mineral tanning technique which accounts for more than 90% of global leather production.[3] Currently, Ethiopia has more than 20 tanneries and a majority of tanneries in the country use a chromium-based tanning method that uses lots of water and chemicals. At present, approximately 90% of the tanneries in the country discharge their effluents into water bodies and land without proper treatment mechanisms.[4] Nevertheless, concerns about pollution-related issues in the global scenario have persuaded all tanneries to treat their effluents and to follow more environmentally friendly vegetable production methods.

In line with this, vegetable tanning has been identified as a viable alternative to chrome tanning, with the industry moving toward eco-labeling and green tanning chemistry.[1] However, vegetable tanning is not as widely used as chrome in Ethiopia due to the high cost of Mimosa, which is the only available vegetable tanning agent for commercial tanning purpose. Similarly, in the country there is limited knowledge and awareness about indigenous plants that could be used as vegetable tanning agents. The aim of this study was to determine the tannin content in the water hyacinth plant (stems and leaves parts), which are a threat to Lake Tana in Ethiopia, and to investigate the plant potential applications as a source of vegetable tanning agent.

**Water hyacinth infestation in Lake Tana, Ethiopia**
Lake Tana is the Ethiopia's largest lake and the Blue Nile's second largest sub-basin, having a surface area of 15,114 km$^2$.[5] Fishing,

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**Figure 1.** Water hyacinth leaves and stems parts outdoor and oven drying

electric power generation, transportation, common grazing land and drinking water for humans and animals, and a site for various birds are some of the multidisciplinary uses of Lake Tana. However, this multi-purpose lake is currently plagued by several issues. On the shores of this sensitive Lake, one of the most ecologically dangerous weed infestations has been recognized since 2011, and the weed coverage continues to escalate from 20 ha in 2012 to more than 50,000 ha in 2014.[5-6] Even if a tremendous amount of human labor, time and money has been employed each year by both surrounding community and government, the infestation coverage continues to escalate in the range of 278.3 ha and 2504.5 ha from 2015 to 2019.[7]

In the recent past, this aquatic plant has received a lot of attention as a potential source of income in many parts of the world.[8] However, there are few studies and reports on the functional use of water hyacinth plant in Ethiopia. The aim of this research was to investigate the potential of water hyacinth extracts as a vegetable tanning agent.

## Methodology

### Methods

Secondary data collection techniques were applied and the data was gathered by reviewing different articles, books and reports. Similarly, both qualitative and quantitative approaches were used to assess the quality of water hyacinth plant tannin and the tanned leather properties. The research work was carried out at Ethiopian Institute of Textile and Fashion Technology found in Bahir Dar and Leather Industry Development Institute found in Addis Ababa.

### Plant collection and drying

The leaves and stems of healthy water hyacinth plant were collected from Lake Tana, next to Kirstos Samra Monastery in Gonder in Ethiopia. The plant's roots section was cut off and the plant leaves and stems were cleaned, washed repeatedly with water, and cut into small chips for faster drying. As shown in Figure 1, the plant leaves and stems parts were dried outdoors for seven days at temperatures ranging from 25°C to 35°C, and then oven dried for one hour at 104°C.

### Percentage yield of dried water hyacinth plant leaves and stems parts

A 2 kg of fresh sample leaves and 2 kg of fresh sample stems were weighed separately before drying. Then, the oven dried samples weighed separately, and yielded 145 g of leaves and 167 g of stem. The yield percentage of the plant leaves and stem parts were calculated as following:

$$\text{Yield \%} = \frac{\text{Dried Final Weight}}{\text{Original Weight}} \times 100$$

$$\text{Leaves Yield \%} = \frac{\text{Dried Final Weight}}{\text{Original Weight}} \times 100 = \frac{145\text{ g}}{2000\text{ g}} \times 100 = 7.25\%$$

$$\text{Stems Yield \%} = \frac{\text{Dried Final Weight}}{\text{Original Weight}} \times 100 = \frac{167\text{ g}}{2000\text{ g}} \times 100 = 8.35\%$$

### Plant powder preparation

The dried leaves and stems were individually weighed and ground in a high-speed multifunction grinder with a mesh size of 50 - 300 shown in Figure 2. The fundamental idea behind grinding the plant parts was to maximize the surface area available for extraction, thereby raising the extraction rate. The powdered samples were placed in small plastic bags for later experimental usage.

### Extract preparation

The form of solvent used in the extraction process has a big impact on the success of determining biologically active compounds from plant content.[9] Thus, three different solvents (distilled water, acetone, and ethanol) were used for phytochemical analysis. Separate extracts were obtained by dissolving 50 g of leaf powder and 50 g of stem powder in 500 mL distilled water, acetone, and ethanol solvents. The mixtures were then stirred for 1 hour at room temperature using a magnetic stirrer shown in Figure 3. Solids were removed using a Whatman

**Figure 2.** Water hyacinth leaves and stems part grounding

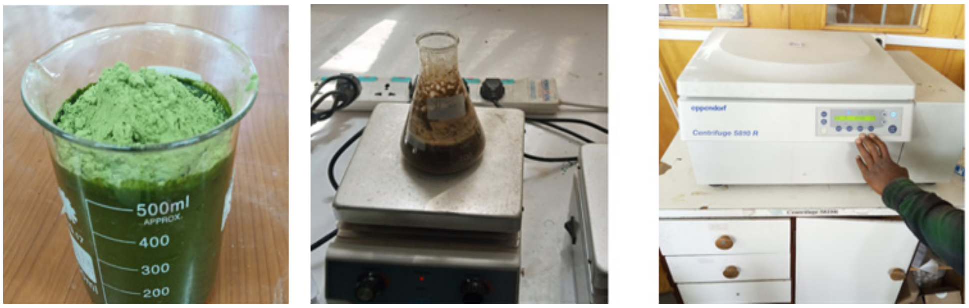


**Figure 3.** Water hyacinth leaves and stems extract preparation using magnetic stirrer and centrifugation.

filter 1 paper, 24 cm disc separately.[10] Each filtrate portion was then put in a glass beaker with aluminum foil on top and left to stand at room temperature for 48 h. The extracts were further purified using a centrifuge 5810 with 4000 rpm centrifugation for 15 minutes at room temperature. Each extract was then preserved in volumetric flasks in a refrigerator at 20°C, for later phytochemical analysis.

**Phytochemical tests**

Phytochemicals are non-nutritive plant chemicals that have defensive or disease-preventive properties. These chemicals are generated by plants to protect themselves, but studies have shown that certain phytochemicals can also protect humans from disease. Steroids, terpenoids, carotenoids, flavanoids, alkaloids, tannins, and glycosides are some of the examples of such plant bioactive constituents.[11]

Qualitative phytochemical screening helps to explain a range of chemical compounds generated by plants, and quantification of those metabolites will help to extract, purify, and identify the bioactive compounds for useful aspects to the tanning process. The extract was subjected to preliminary qualitative phytochemical screening for alkaloids, flavonoids, tannins, saponins, collagen, and phenol analysis following standard methods.

**Beam house operations**

Since the tannin content of water hyacinth leaves (4.1%) is higher than that of stems (2.7%), tanning experiments were conducted using the leaves extract, with quebracho vegetable tanning material used as a control. Separate and combination tanning were carried out using water hyacinth leaves powder and quebracho (control) powder. As shown in Table I, the beam-house operation carried out (i.e., soaking, liming, deliming, bating, degreasing and pickling) in the drum and the operation were same for all batches.[38]

**Vegetable tanning operations**

For laboratory investigation, fresh raw hides were purchased from hide and skin market in Addis Ababa. Vegetable tanning operations were done using laboratory drums having a diameter of 800 mm. Based on shown recipe in Table I, [39] separate tanning operations

**Table I**
**Beam house operations recipe and procedure**

| Process | Amount (%) | Materials /Chemicals | Time/min | Remark |
|---|---|---|---|---|
| Soaking | 300 | Water | 30 | Drain/wash |
| | 300 | Water | | |
| | 0.4 | NaoH | | PH = 8.0 - 8.5 |
| | 0.05 | Bactericide | 60 | LON 5'/h for 18 h & Drain |
| Liming | 80 | Water | | |
| | 1 | Na2s | | |
| | 0.5 | NaHS | 60 | Hair removal checked. |
| | | | | LON 5'/90' and morning Fleshing |
| De-liming | 200 | Water | 20 | Drain wash |
| | 80 | Water | | |
| | 0.75 | Amm sulphate | 30 | Temp 30°C, drain |
| | 80 | Water | | |
| | 0.75 | Amm sulphate | 40 | PH = 8.0 - 9.0 drain and wash |
| Bating | 80 | Water | | Temp 37°C |
| | 0.2 | TD15 | 40 | Check temp test, D/W/2x |
| Degreaser | 20 | Water | | |
| | 0.3 | GT 01 | 60 | |
| | 300 | Water | 10 | D/W/3x |
| Pickling | 40 | Water | | |
| | 5 | Salt | 2 | Be = 6.5 - 7.0 |
| | 0.5 | HCOOH | 60 | PH = 4.8 - 5.0 |

**Table II**

**Vegetable Tanning operations recipe and procedure**

| Process | Amount (%) | Materials /Chemicals | Time/min | Remark |
|---|---|---|---|---|
| Tanning- Hide weight ratio (Batch 1: 10% Water hyacinth leaves; Batch 2: Combination (5% Water hyacinth leaves and 5% Quebracho); Batch 3: 10% Quebracho (Commercial vegetable tanning agent) | 12 | Veg Tan x | | |
| | 12 | Quebracho | 180 | |
| | 5 | Veg Tanx x | | |
| | 5 | Quebracho | | |
| | 2 | Fish oil | 300 | Penetration |
| | 100 | Water | 20 | |
| | 0.8 | Tanigal BL | 60 | PH = 4.0 |
| Wet back | 200 | Water | | Temp 40°C |
| | 0.5% wetting agent | | 40 | |
| Neutralization | 100 | Water | | Temp 30°C |
| | 0.2 | Formic Acid | 10 | |
| | 2 | LSF 100 | 30 | |
| | 2 | Sodium Formate | 30 | |
| | 1.5 | Sodium Bicarbonate | 60 | Check PH = 4.8/5.0 |
| Retanning/Dyeing and Fatliquoring | 50 | Water | 30 | Temp 40°C |
| | 2 | Acrylic resin | 30 | |
| | 4 | Retanal MD 80 | 60 | |
| | 4 | LSF-100 | | |
| | 4 | Mimosa/WH | 60 | |
| | 3 | Black dye | | |
| | 100 | Water | | Temp 60°C |
| | 4 | Lipsol J-622 | 60 | |
| | 1 | Neopristol SW | 60 | |
| | 2 | Formic Acid | 40 | Check PH = 3.8/4.2 |

for all batches were conducted based on the weight of the sample cow hide. Each batch was separately soaked for three days in 10 wt% water hyacinth leaves, 20 wt% water hyacinth leaves, and a combination (5 wt% water hyacinth leaves and 5 wt% Quebracho) and 10 wt% Quebracho (Control). Changes in liquor color and penetration across the pelt cross-section were used to monitor tanning progress. Meanwhile, the hides were left in it overnight, and rotated for 30 minutes before being removed from the drum and horsed up. Cutting a small piece of the pelt in the neck area was used to check for tannin penetration, and color uniformity around the pelt cross-section was used to determine tanning completion. Subsequently, fatliquoring was achieved with warm water, greasing, and toggle drying carried out.

## Results and Discussion

As shown in Table III, Flavonoids, saponins, phenols, tannins, alkaloids, starch, and proteins were detected in distilled water, ethanol, and acetone extracts of water hyacinth leaves and stems.

**Table III**

**Phytochemical analysis of water hyacinth leaves and stems parts**

| No | Compound | Detection Method | Distilled water extract (Leaves) | Distilled water extract (Stems) | Ethanol extract (Leaves) | Ethanol Extract (Stems) | Acetone extract (Leaves) | Acetone Extract (Stems) |
|---|---|---|---|---|---|---|---|---|
| 1 | Flavonoids | Alkaline reagent test[12] | + | ++ | - | ++ | + | + |
| 2 | Saponins | Froth Test[13] | ++ | ++ | + | - | + | - |
| 3 | Phenols | Ferric Chloride test[14] | ++ | ++ | + | ++ | ++ | ++ |
| 4 | Tanins | Ferric chloride test[13] | ++ | ++ | + | + | ++ | ++ |
| 5 | Alkaloids | Mayer's and Wagner's test[13] | ++ | + | + | + | + | - |
| 6 | Starch | Iodine test[15] | ++ | + | + | ++ | - | ++ |
| 7 | Protein | Biuret test[16] | ++ | + | + | + | + | - |

Key: (-): Not detected, (+): Weak positive test and (++): Strong positive test

**Flavonoids Detection:** The current study found strong positive (++) flavonoids in both distilled water and ethanol extracts of the stems part and weak positive (+) flavonoids in distilled water and acetone extracts of the plant leaves (Table III). Similarly, Jayanthi and Lalitha[17] reported that flavonoids were detected in water hyacinth plant collected from both Singanallur boat house, and Tondano Lake in India.

**Saponins Detection:** Froth test approach revealed the existence of strong positive (++) saponins in both distilled water extracts of stems and leaves. As well as weak positive (+) saponins were detected in both ethanol and acetone extracts of the plant leaves (Table III). Similar results were found by Aravind et al.[18] who reported the presence of saponins in water hyacinth plant collected from various marshy lands in Kayamkulam, Mavelikkara, Allepy, and Kerala.

**Phenols detection:** In ferric chloride test, strong positive (++) phenols were detected in both distilled water and ethanol extracts of the stems and leaves parts, as well as strong positive (++) phenols detected in the acetone extracts of the stems part, and weak positive (+) phenols in detected in the acetone extract of the leaves part (Table III). Similar findings were found by Rorong et al.[19] who reported the presence of phenols in water hyacinth plant collected from Singanallur boat house, Tamil Nadu, and Tondano Lake in the district of Minahasa, india.

**Tannin detection:** In tannin detection using ferric chloride test, strong positive (++) tannins were detected in both distilled water and acetone extracts of stems and leaves parts, and weak positive (+) tannins were detected in both ethanol extracts of leaves and stems (Table III). Similar Rorong et al.[19] reported the presence of tannin in water hyacinth collected from Tondano Lake in the district of Minahasa, and Warangal district.

**Alkaloids detection:** In Mayer's and Wagner's test, the presence of strong positive (++) alkaloids detected in leaves distilled water extract and weak positive (+) alkaloids in both leaves and stems acetone and ethanol extracts was detected (Table III). Related findings by Lalitha et al.[20] showed the existence of alkaloids in Eichhornia crassipes (WH) collected from lakes near Kurichi in Coimbatore, India and Bilaspur district of Chhattisgarh, India.

**Starch detection:** Iodine test approach[40] detected the presence of strong positive (++) starch in the acetone and ethanol extracts of the stems part and in distilled water extract of leaves part. Likewise, a weak positive (+) starch was detected in both ethanol extracts of the leaves and stem parts, and in distilled extracts of leaves part and acetone extracts of the stem part (Table III).

**Protein detection:** Biuret test revealed the presence of strong positive (++) protein in the distilled water extract of leaves part (Table I). Correspondingly, weak positive (+) protein is detected in both distilled water and ethanol extracts of stems part and in both ethanol and acetone extracts of leaves part (Table III). Similarly, Jayanthi[17] reported the presence of protein in water hyacinth collected from lakes near Kurichi in Coimbatore, India.

**Tannin and tannin content determination by Hide powder method**

Tannins are amorphous, astringent compounds found in a broad range of plant materials, including bark, wood, leaves, and resinous exudations.[21] Tannins are non-crystalline, colorless compounds that form colloidal solutions in water and have an astringent flavor. Tannins are polymeric phenolic compounds with various hydroxyl groups and chemical structures that are very complex. The tannin content of water hyacinth leaves and stems was determined by means of the Hide powder method[21] and the tannin content of water hyacinth leaves and stems parts were determined at the Central Leather Research Institute (CSIR) Laboratory in India.

As shown in Table IV, the tannin content of water hyacinth leaves was higher (4.1%) than that of the plant stems part (2.7%). The tannin content of water hyacinth leaves is close to that of Salix folium (4.0%) and Kepok banana bunch (4.1%),[22] but higher than that of acacia Senegal barks (3.49%).[21] However, the tannin content in the *water hyacinth leaves is* lower than that of Acacia seyal bark, 28.9%.[22] Similarly, the tannin content in this study is higher than that of water hyacinth leaves (0.98%), as investigated by Sangbrita,[41] but lower than that of water hyacinth roots (5.4%) and leaves (6.9%), as investigated by Lara-Serrano.[2]

**FT-IR Analysis**

Fourier transform infrared (FTIR) spectroscopy is an important technique used for chemical analysis of biological substances.[23] Based on this, the leaves and stems parts of water hyacinth plants were analyzed using FTIR to determine the plant's relative functional group.

**Table IV**

**Tannins content found in the Water Hyacinth plant's leaves and stems**

| Water Hyacinth Plant part | Tannin (%) | Total Ash (%) | PH water soluble | Test Method |
|---|---|---|---|---|
| Leaves | 4.1 | 14.8 | 6.3 | IS 5466: 2013 |
| Stems | 2.7 | 15.6 | 5.8 | IS 5466: 2013 |

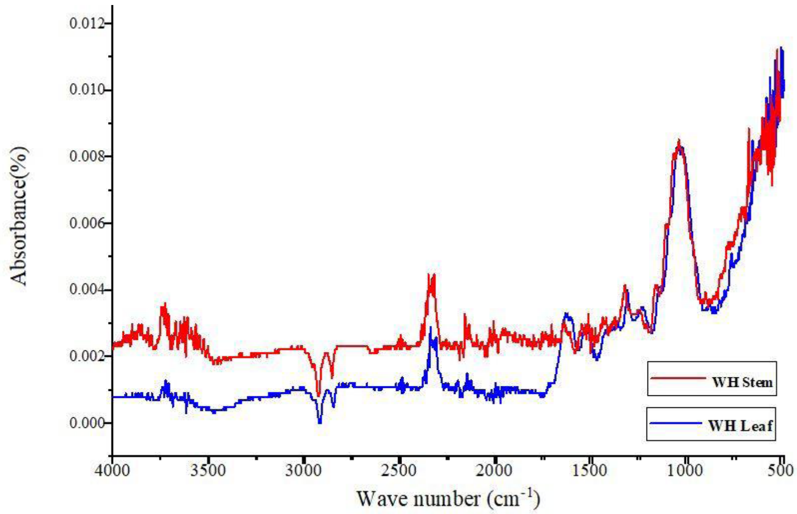


**Figure 4.** FT-IR spectra of Water Hyacinth plant leaves and stem part

The FTIR spectra of water hyacinth plant leaves and stem parts are shown in Figure 4.

As shown in Figure 4, the FTIR data was recorded with a scan speed of 2 mm/s and the plant samples were added as a powder with a wavelength resolution of 4000 $cm^{-1}$ - 500 $cm^{-1}$.[24] FTIR analysis, revealed the presence of amines (N-H stretching) by the peak between 3340 - 3400 $cm^{-1}$,[25] and the presence of alkanes/lipids (C–H stretch) were revealed by the peak between 2890 $cm^{-1}$ and 2889 $cm^{-1}$.[26] The alkynes have a plateau at 2346 $cm^{-1}$ and 2347 $cm^{-1}$ (C-C Stretch).[27] The peak at 1640 $cm^{-1}$ revealed carboxyl group absorption (C=O stretch)[28] and the presence of lignin content at 1609 $cm^{-1}$ (C-C stretch).[29] The O–C=O asymmetrical stretching caused the peak at 1318 $cm^{-1}$, and a peak at 1063 $cm^{-1}$ showed the presence of hemicellulose (C–C stretch). The absorption bands of lignin, cellulose, and hemicelluloses are well known to be in the wavelength range of 1800 - 800 $cm^{-1}$ (stretching and bending vibrations within the molecules, also known as the fingerprint region).[30] A peak of 1035 $cm^{-1}$ revealed C–O stretching of primary alcohol in cellulose and hemicelluloses.[28] As shown in Figure 4 the recorded values of FTIR spectra nearly identical for both the leaves and stems part of the water hyacinth plant.

Due to OH stretching vibration,[42-43] all tanning compounds, including quebracho,[44] have a strong band between $3600^{-1}$ and 3400$cm^{-1}$, however FTIR analysis of water hyacinth leaves indicated a very small peak between $3400^{-1}$ and 3600 $cm^{-1}$ in the study. Because of this, the water hyacinth lacks key O-H stretching functional groups required for maximum tanning effect.

**Physical characteristics of vegetable tanned leather**

Each batch of tanned leather was labelled, and physical property characterization carried out using standard instruments available at Leather Industry Development Institute Laboratory, Addis Ababa. Shrinkage temperature, tearing strength, tensile strength, percent elongation at break, distention at grain crack, distension at burst, and thickness were assessed for leathers tanned with water hyacinth (WH) leaves, combination (i.e., water hyacinth and quebracho) and quebracho tanning material (control). Physical/mechanical strength tests, moisture-related tests, and chemical analysis are the three major categories of leather tests. These properties have variations depending on the various factors but most importantly the type of tanning agent. Since leather is an inconsistent material by nature, independent leather testing and analysis is necessary prior to usage especially when a new tanning material is proposed.[31]

The tanned leathers were taken for final testing after the vegetable tanning was completed. As shown in Table V, the experiments were assessed for both hide tanned with water hyacinth lives and quebracho (control) experiments.

**Tearing strength:** This refers to the consistency level relating to tearing load indicates the strength of the leather goods in use, and the minimum tearing strength required for leather product making should be at least 35N.[33] This study found the tearing strength of all tanned leathers with water hyacinth leaves were higher than 35 N. The tanned leather with 10 wt% and 20 wt% water hyacinth leaves had a tearing strength of 37 N and 45 N respectively. Similarly, the tanned leather with 5 wt% quebracho and 5 wt% water hyacinth leaves (combination) had a tearing strength of 106.2 N and 10 wt% quebracho (control) had 115 N. As shown in Table V, the study finding revealed that the tanned leather with water hyacinth fulfilled the minimum tearing strength (35 N) requirement for leather product making.[32]

**Shrinkage temperature:** Shrinkage temperature is a very important parameter in characterizing the thermal stability of leather and it is the temperature at which the leather sample starts to shrink in water or over a heating medium.[34] The shrinkage temperature provides

**Table V**

**Physical test results of vegetable tanned leather**

| S/n | Physical Properties | Physical test result 10 wt% WH Leaves | 20 wt% WH Leaves | 5 wt% WH Leaves and 5 wt% Quebracho (Combination) | 10 wt% Qubracho (Control) | Minimum recommended value for leather products making[32] |
|---|---|---|---|---|---|---|
| 1 | Shrinkage Temperature ($T_S$ °C) | 55 | 52 | 58 | 76 | Min > 75°C |
| 2 | Tear Strength (N) | 37 | 45 | 106.2 | 115 | Min > 35 N |
| 3 | Tensile strength ($N/mm^2$) | 6 | 7.2 | 8.9 | 22 | Min > 20 $N/mm^2$ |
| 4 | Percent Elongation at break (%) | 47 | 42 | 60.5 | 62 | Min > 40% |
| 5 | Distention at grain crack (mm) | 7 | 6.5 | 9.4 | 10 | 6.5 mm |
| 6 | Distension at burst (mm) | 7.8 | 9 | 12.5 | 11.4 | 7 mm |
| 7 | Thickness (mm) | 2 | 2.5 | 3.3 | 2.2 | > 0.5 mm |

information about the degree of tanning because better crosslinking reaction between collagen fibers and tannins increases the shrinkage temperature.[1] In the current study, the hide tanned with 10 wt% quebracho (control) had the maximum shrinkage temperature of 76°C whereas the hides tanned with 10 wt% and 20 wt% water hyacinth leaves had 55°C and 52°C, respectively and combination tanning (5 wt% quebracho and 5 wt% water hyacinth leaves) had 58°C. This indicates that the tanned hide with 10% and 20% water hyacinth leaves resulted in a shrinkage temperature of between 52 - 58°C, which is below the acceptable shrinkage temperature (75°C) for leather product making.

**Grain crack and Grain burst:** Other physical tests used to assess the leather quality are the grain crack and grain burst tests. They indicate how resistant the grain is to cracking during the top lasting of the shoe uppers. All the tanned hides exceeded the minimum recommended values of grain crack (7 mm) and grain burst (6.5 mm). The WH leaves had a maximum grain crack of 7 mm (10 wt% WH leaves) and a grain burst of 9 mm (20 wt% WH leaves). Different studies on vegetable tanning materials have found different values for grain crack and grain burst.[35]

**Tensile Strength:** In the present study, hide tanned with 10 wt% quebracho (control) had the highest Tensile strength of 22 $N/mm^2$. However, the hide tanned with 10 wt% and 20 wt% of water hyacinth leaves had a tensile strength of 6 $N/mm^2$ and 7.2 $N/mm^2$, respectively, and a combination (5 wt% quebracho and 5 wt% water hyacinth leaves) had a tensile strength of 8.9 $N/mm^2$.

This shows that the tensile strength of hide tanned with 10 wt% and 20 wt% water hyacinth leaves and a combination (5 wt% water hyacinth and 5 wt% quebracho) were less than the expected minimum requirement of tensile strength of (20 N/mm) leather product making. Therefore, the hide tanned with water hyacinth leaves has inadequate tensile strength and it cannot be used to produce leather products with good strength requirement.

**Elongation Analysis:** The percentage elongation of leather is another physical property measured when assessing the leather quality and this has a relationship with the tensile strength. Elongation refers to the ability of a leather product to lengthen/stretch when stress is applied to it and represents the maximum extent leather can stretch without breaking.[36]

From Table V, hide tanned with 10% and 20% water hyacinth leaves, as well as a combination (5 wt% water hyacinth and 5 wt% quebracho), had 47%, 42%, and 60.5% elongation, respectively, which were lower than commercial quebracho 62% elongation. However, all tanned hides had ≥ 40% percentage elongation, and are comparable to those reported from other studies.[37] Likewise, Nasr et al.[35] reported vegetable tanned leather with quebracho and Mimosa had percent elongation 59.06% and 55.32% respectively.

**Thickness (mm):** In the present study, the thickness of all tanned hide found between 2 mm to 3.3 mm, which were greater than the minimum recommended thickness (0.5 mm) for leather products making.

## Conclusion

Leather is a durable and flexible material made from raw hide and skin by tanning process, which prevents the collagen fibrous protein in animal skins or hides from putrefaction. The most commonly used tanning methods are chrome and vegetable tanning. The tannin content of water hyacinth plant leaves was 4.1%, which is less than that of conventional quebracho (>40%) vegetable tanning material. Most of the recommended parameters for leather product manufacturing, such as tear strength, elongation at break, grain crack, grain burst and thickness, were realized in the hide tanned with water hyacinth leaves. However, the leather had a tensile strength of 7.2 N/mm$^2$ and a shrinkage temperature of 52°C, which are both below the minimum standards for leather product manufacturing. Thus, water hyacinth leaves extract has limited potential as a vegetable tanning agent, and the tanned leather will not be appropriate to produce leather products which requires good tensile and thermal properties. However, the water hyacinth leaves tanned leather will be used to produce leather products that requires minimal tensile strength and thermal properties such as leather photo frames, bound leather sketchbook etc. Since water hyacinth leaves tannin is less than ideal as a tanning agent due the minimum shrinkage temperature and tensile strength of the tanned leather, the potential of the plant leaves as a retanning agent will be studied in the future.

## Recommendation

This study mainly focused to determine potential of water hyacinth leaves extract as a leather tanning agent. The study revealed that water hyacinth leaves extract has limited potential as a vegetable tanning agent. The water hyacinth-tanned leather had low tensile strength and thermal property, failing to meet the minimum requirements for leather product manufacture. Since water hyacinth tannin is less than ideal as a tanning agent owing to the tanned leather's minimum shrinkage temperature and tensile strength, the plant's potential as a retanning agent should be investigated in the future.

## Competing Interests

The authors declare that they have no competing interests.

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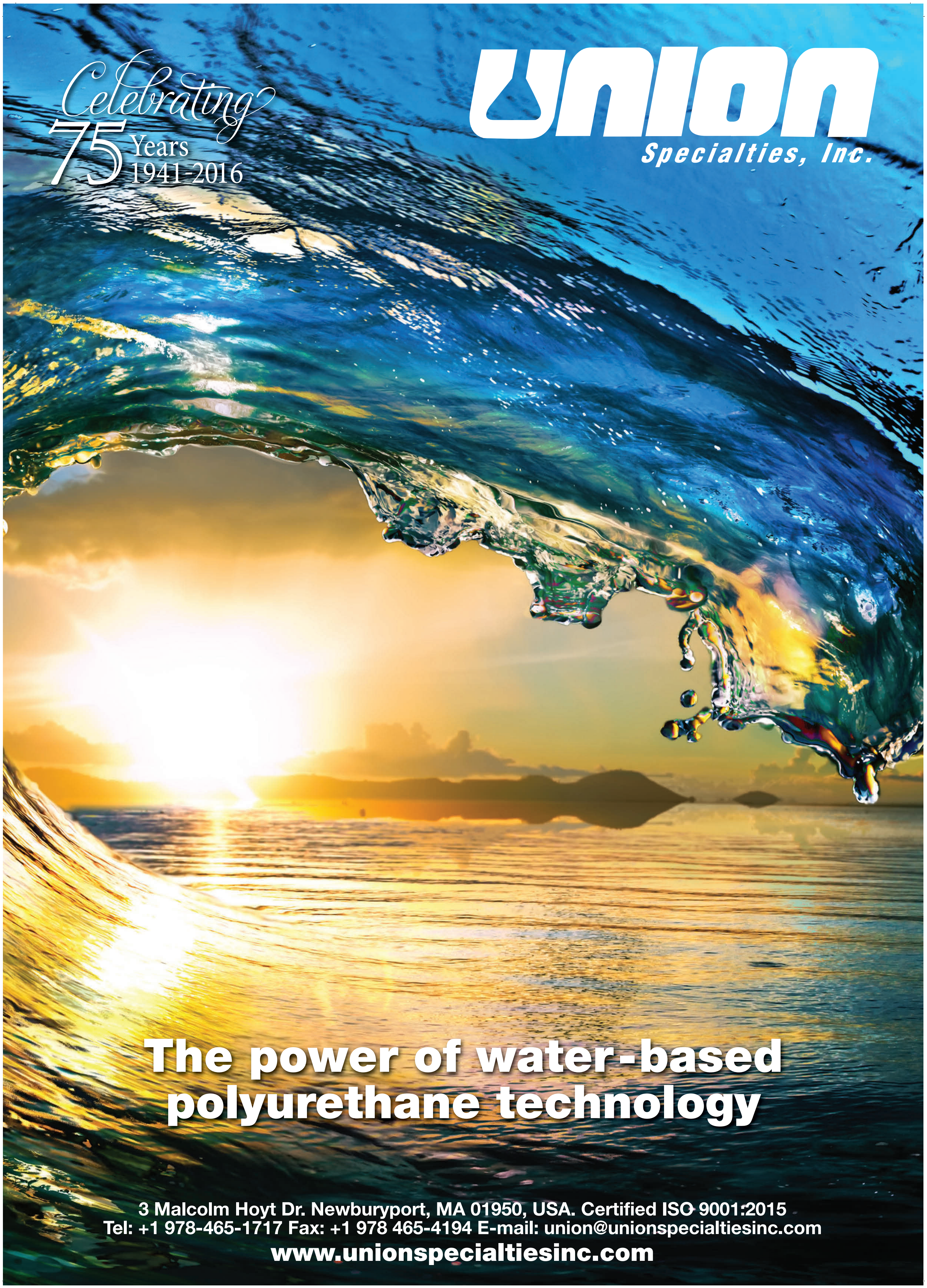
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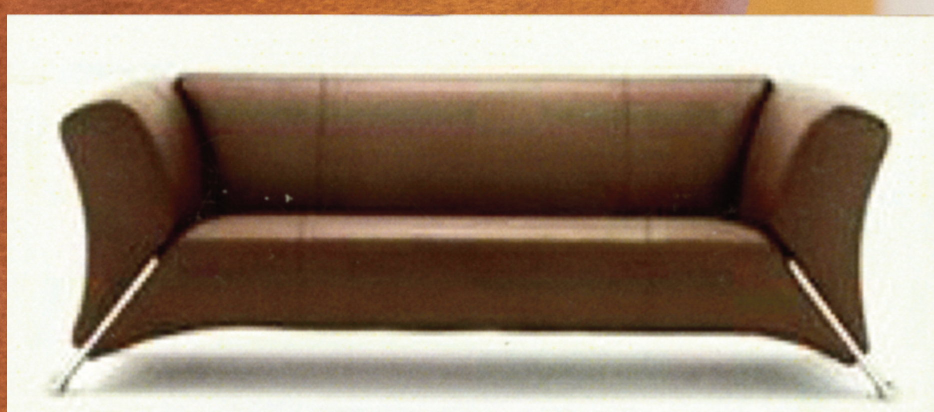

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# Lifelines

**Hailemichael O. Yosief** received his BSc degree in Pharmacy from the University of Asmara, Eritrea and he worked as a teaching assistant at the Orotta School of Medicine, Eritrea. He received his PhD in Chemistry from the University of Cincinnati, OH. His graduate research work was focused on the synthesis of carbohydrates and their application for pathogen and toxins detection. After earning his doctoral degree, he was NIH sponsored postdoc at the University of Massachusetts, Boston where he worked on the design and synthesis of imidazo-pyridine- and dihydropteridinone-based bromodomain inhibitors. Before joining USDA-ARS in November 2018, he worked as an adjunct chemistry faculty at the Cincinnati State Technical Community College. As a USDA-Postdoc, he is engaged in modifying biomass and byproducts into value-added products also in designing environmentally friendly formulations for hide preservation. His graduate and postdoctoral research works have led to several publications and patents.

**Majher I. Sarker** see *JALCA* **113**, 34, 2018

**Syed A. Hussain** earned his PhD degree under the Chinese Government Scholarship Program. His Ph.D. research was focused on the Medium-chain fatty acids (MCFAs) producing cell factories via metabolic engineering approaches and fermentation optimization technologies. He has worked as a visiting scholar in University of Texas at San Antonio. He is currently working as a Postdoctoral Research Fellow at Sustainable Biofuels and Co-Products Research Unit, Eastern Regional Research Centre (ERRC) of Agriculture Research Service, US Department of Agriculture (USDA), where, he has the privilege to work on different projects which principally include 1) identification and decontamination of food borne pathogens, 2) Use of different inducers to enhance the microbial biomass, 3) Use of NGS approach for pathogen identification, 4) Use of different new chemical compound to control the growth of Salmonella and Listeria, 5) conversion of agriculture feedstock into useful products.

**Zerlina Muir** see *JALCA* **106**, 218, 2011

**Resmi Mohan** see *JALCA* **110**(12), 2015. She has now published 10 papers in peer-reviewed journals of repute.

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**S. Shrividhya** has done her B. Tech (Chemical Engineering) from Sri Ram Engineering College, Chennai in the year 2007.

**Venkatasubramanian Sivakumar** see *JALCA* **113**(2), 72, 2018. He has currently published 63 Papers in Peer-reviewed Journals of repute as well as Filed – 5 Patents and Granted 5 Patents.

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**Fitsum Etefa Ahmed** has been a Senior Lecturer at the Ethiopian Institute of Textile and Fashion Technology (EiTEX) at Bahir Dar University since 2015. He graduated from Bahir Dar University-EiTEX in Ethiopia with a Bachelor's degree in Textile Engineering in 2015 and a Master's degree in Leather Product Design and Engineering in 2018. He served as the Head of Leather Engineering Program at Bahir Dar University, EiTEX, from September 8, 2017 to March 18, 2020 and now serving as the Director of the Leather Processing & Product Engineering Research and Innovation Center since March 2020. He has mentored and supervised 20 undergraduate students in data collection and analysis for their BSc Degree Thesis work, as well as preparation and presentation of research findings, since 2015. His research interests include Leather product design, leather supply chains, leather waste management and composite materials.

**Gemeda Gebino Gelebo** has been a Senior Lecturer at the Ethiopian Institute of Textile and Fashion Technology (EiTEX) at Bahir Dar University since 2015. He graduated from Bahir Dar University-EiTEX in Ethiopia with a Bachelor's degree in Textile Engineering in 2015 and a Master's degree in Textile Chemistry in 2018. He served as a Polymer and Fiber science course chair at Bahir Dar University, EiTEX, from April, 2019 up to now. He has mentored and supervised more than 16 undergraduate students in data collection and analysis for their BSc Thesis, as well as preparation and presentation of research findings, since 2015. His research interests include polymers, fiber science, industrial waste management and composite materials.

**Belay Meles Gebre** has been a Senior Technologist at Ethiopian Leather Industry Development Institute since 2011. He graduated from Addis Ababa University in Ethiopia with a Bachelor's degree in Applied Chemistry in 2007 and a Master's degree in Chemical Engineering - Leather Stream in 2015. He served as a Research and development team leader at Ethiopian Leather Industry Development Institute, from March 2017 up to now. His research interests include Leather Processing, industrial waste management and composite materials.

# Industry News

## IULTCS Welcomes New Korean Members

The IULTCS is pleased to announce that two organisations from the Republic of Korea have joined the IULTCS family. Representing leather industry companies 'Korea Tanners' Association' has joined as an Associate Member and also leather producer Whanam Leather Ind Co Ltd has joined as a Supporting Member.

IULTCS President, Jean-Pierre Gualino, welcomed the new member organisations saying "On behalf of the Executive Committee I am pleased to welcome South Korea to IULTCS thorough the memberships of Korea Tanners' Association and Whanam Leather Ind Co Ltd the scientific community becomes stronger with their participation and we look forward to their active involvement in IULTCS activities".

## Registration for AICLST Conference in New Zealand Underway

The 12th Asia International Conference on Leather Science and Technology (AICLST) will be taking place in a hybrid format from 18 – 20 October at Massey University's Sport and Rugby Institute, situated in Palmerston North on the North Island of New Zealand.

Conference organiser and Director of New Zealand Leather and Shoe Research Association, Mr Geoff Holmes, welcomes abstracts from potential presenters and registration for delegates wishing to attend in person or virtually. He highlighted some of the key benefits of attending the conference saying "The 12th AICLST Conference will provide a 3-day programme that seeks to stimulate discussion and bring together the wider leather community of scientists, leather manufacturing companies and chemical and equipment suppliers. It will showcase the latest advances in leather science and technology, promoting science excellence and impact in support of the drive towards more sustainable leather production.

The Gala Dinner for AICLST will be held at Massey University's Refectory. The 3-day event costs $250 NZD per person or just $75 NZD for those joining remotely."

Full details can be found on the conference website:
https://www.aiclst.org

There will be 7 main themes covering a wide range of topics to appeal to anyone involved in leather science or manufacturing:

1. Advances in Basic Leather Science
2. Raw stock improvement
3. Cleaner leather production and closed-loop processing
4. Value-added uses for waste streams and by-products
5. Environmental protection and impact assessment
6. Industry 4.0. Detection and traceability
7. Advances in machinery used in the leather processing Industry
8. The AICLST conference also offers the opportunity for sponsorship.

Mr Holmes ends by saying "While celebrating our 75th year of incorporation we invite scientists and industry chemists from across the globe to join us for this joyous occasion, to foster international communication and collaboration across the leather community and to boost advancement in leather science and related manufacturing technology."

## INDEX TO ADVERTISERS


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