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Physicochemical investigation of ultrasound effects on some steps of mink fur processing. A suggestion for improving the worker health and reducing the environmental impact

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ABSTRACT

The tanning industry is considered a source of major environmental pollution and hazard to the health of workers. The greasing stage is mainly performed to improve the softness of leather while the degreasing one serves to optimize the distribution in fatliquoring leather and eliminate its excess.

To produce mink fur commercially attractive the tanning-oil-greasing method is used, which requires a large excess of both grease and solvents. Tanning-alum-water greasing method which greatly simplifies machining cycles using less solvent in the degreasing stage could be harnessed. However, the fur absorbs only small tanning-greasing quantities resulting a poor quality product. Laboratory tests were carried out on mink fur to understand how to extend on a large scale the tanning-alum-water greasing method.

Experimental results, obtained irradiating the soaking bath with ultrasound at different powers, show that the cavitation is triggered in the range of 20–30 W and develops for larger powers. Results provides the basis for changing the tanning-alum-water greasing method to produce mink fur in a *single stage*. Particularly, enhanced optical microscopy indicates that fat globule diameters are reduced by 50% whilst skin absorption improves by 25%. How to rearrange the method on large-scale is also discussed. The method, considered as a whole must be considered "best available technology"

1. Introduction

The tanning industry employs many different processing cycles, which make use of large amounts of chemical compounds. The transformations of raw skins into leather are performed in particular reactors termed drums. In these reactors vegetable tannins, oils, aldheydes synthetic tannins, zirconium, alum, titanium and chromium salts are used to prevent putrefaction of skins and obtain leathers (Covington, 2001). Tanneries represent a industry segment with high environmental impact both for handling large amounts of conventional pollutants and for using biocides, surfactants and solvents which contaminate workplaces risking health and safety of workers (Dixit et al., 2015). Tanneries face the problem only occasionally, considering it an additional cost, not always sustainable.

In order to produce mink fur, tanneries can prepare two machining mode. A first process treats the skins with an unsaturated fish oil (rarely vegetable oil) solution in a kicking machine to force the oil into skin, referred as tanning-oil-greasing. The resulting fur are very soft and water resistant through operations complex and long lasting. A second process exploits the ability of aluminum salts in tanning hides and can be applied in one or in two-step mode. Two-step means that the skins are firstly tanned in alum aqueous solution, dried and then greasing with grease emulsified in water. One-step mode is realized in a single leather-paddle containing aluminum salts and grease, referred as tanning-alum-water-greasing method. It consists of short and simple operations, however the quality of the final product is poor. For any mink fur processing, regardless of whether it uses fish-oil or alum tanning, a degreasing step is provided to uniformly distribute

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the grease and remove its excess. Such operation is performed by processing the leather in a drum containing either solvent-soaked sawdust or water-solvent emulsion. A degreasing by solvents, in closed-circuit machines, was also suggested, although its large-scale use turns out to be very expensive (Pabst et al., 2004). It should be noted that the solvent excess is emulsified with water and discharged, therefore it is a pollutant load of wastewater. An issue that plagues all tanneries is the solvent evaporation that makes unhealthy workplaces. Currently solvents are removed by a set of recycling and incineration, although some studies suggested to use supercritical CO^2 (Marsal et al., 2000) for the degreasing step. The method is able to achieved degreasing efficiency levels of 94%, however the high installation costs and poor quality of fur have made this method unworkable.

From the above, it is clear that producing mink fur, according to industrial specifications, with tanning-alum-water-greasing method, means to simplify enormously the industrial process with significant reduction of costs. Furthermore washing-degreasing step through solvents is replaced by one with aqueous solutions of surfactants. Herein, on the basis of laboratory tests, we suggest a novel approach where the production of good quality fur may be attained with a single stage of tanning-alum-water-greasing bath ultrasound assisted. Since today tanneries seem to be so mature to willingly accept innovative change in the production-cycle we are very confident that our suggestions will be helpful to tanneries. It is noteworthy that, in the literature is well-documented how to exploit ultrasounds at the greasing or tanning stage (Sivakumar et al., 2009), but separately and, in all cases, it is never treated the production of mink fur.

2. Materials and methods

2.1. Chemicals

Chemicals purchased from Carlo Erba (Milan, Italy) were poduct of purity RE and used without further purification. Mixtures were prepared using tap water, according to industrial practice.

2.2. Fur

Skins of male Danish mink was kindly provided by Manifattura Italiana del Brembo (MIB), Pontirolo Nuovo Bergamo, Italy. Before being used the skins were subjected to physical tests and chemical analysis according to methods recommended by International Union of Leather Technologists and Chemists Societies. All measurements were performed in triplicate and results collected in Table 1.

2.3. Soaking bath

The soaking bath consisted of a 5 L tank containing a solution of 20 g L^{-1} NaCl and 2 g L^{-1} nonylphenol ethoxylate. The tank was thermostated at 25 °C.

Table 1
Physical test and chemical analysis of furs.

Analysis parameter	mean ± σ
Volatile compounds(%)	12.2 ± 0.2
Sulphated Ash(%)	5.8 ± 0.9
Substances soluble in Dichlromethane(%)	4.2 ± 0.2
Load at break(kg)	42 ± 5
Load bursting(kg)	23 ± 5
Elongation at break(%)	36 ± 2
Distension at grain cracking (mm)	15.6 ± 0.9

2.4. Tanning-alum-water greasing bath

The oil tanning bath was mimicked by filling the 5 L tank with a mixture containing 40 g L^{-1} of NaCl, 40 g L^{-1} of alum and 5 g L^{-1} of sodium acetate and 20 g L^{-1} of partially sulfonate grease.

2.5. Experimental set-up

The skins kept in stock lose their softness and flexibility and cannot be processed to obtain the finished fur. They have to be hydrated to become processable. This object is achieved by immersing the dry skin in a soaking bath. When a liquid is irradiated with ultrasound, the effects produced do not arise from the interaction matter-acoustic waves on molecular scale, but rather by the formation and breakage of micro-bubbles (*cavitation*). A pair 24 kHz center frequency transducers were mounted on outer bottom in the water tank. The temperature of water was maintained at 25 °C. The transducers were 6.0 cm in diameter and were focused to a depth of about 4 cm. The vibrations and shock waves developed by cavitation in the liquid media were monitored capturing, by means of a hydrophone needle, the sound generated by the breakage of the bubbles. The hydrophone was mounted on an assembly that allowed vertical manipulation of the needle axes relative to transducers. The sound in the liquid medium was transmitted to the piezoelectric sensor at the needle tip and converted into an electric signal proportional to the mechanical stress. A suitable labVIEW based application was developed for data acquisition, analysis and signal processing.

2.6. Adsorption measurements

The adsorption measurements were performed on samples of shaved skin, using a one-arm-balance. Sample was attached to the arm and suspended in the tanning-bath by ballast, as schematically illustrated in Fig. 1. Ultrasonic transducers placed under the tank guarantee an uniform irradiation of the dispersion and fur sample. The adsorbate amount, per gram of dry sample, was calculated from the relationship

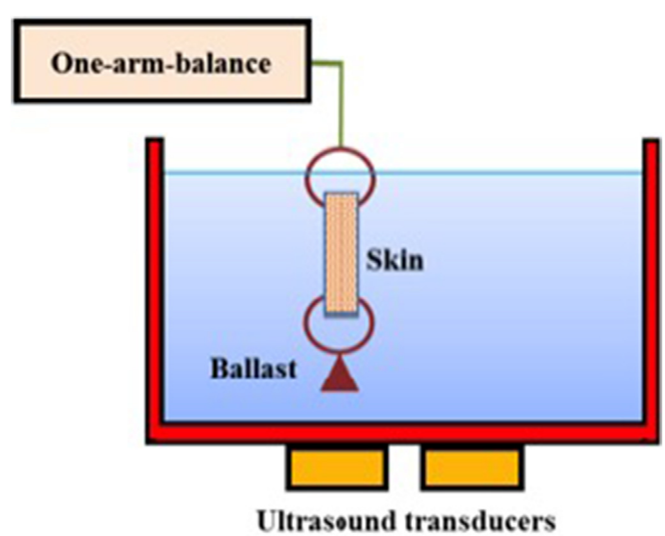

Fig. 1. Schematic representation of adsorption measurements by means of one-arm-balance in a tannin-alum-water greasing bath, thermostated at 25 °C.