New Challenges in Oxidative Beamhouse: Latest Innovations on Process Sustainability

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Abstract

XXI Century is bringing new challenges to Leather Industry. Each day more tanneries request a cleaner process, not only from the effluent point of view but for the production of splits and trimmings into collagen for food or pharmaceutical use gelatines. This paper shows our latest developments to achieve these targets, combining engineering and biotechnology to convert state of art beamhouse process into clean, low waste waters, odourless food grade production.

This paper includes our latest experiences on scaling up oxidative beamhouse process, protein recovery and its use in fertilisers production, considering new techniques in waste water treatment, aimed to sludge and sulphate reduction.

Introduction

XXI century tannery is facing new challenges from the environmental point of view. Low water consumption and by-products management are the clues of the success in sustainability issues. As early in the process as we are able to manage organic waste such as flesh and trimmings, better possibilities we have to achieve the fully sustainability target of our industry. We should assume that water is not an endless resource being in the centre of this puzzle where the importance of each single tile is vital.

Fig.1 – Leather raw material: natural and biodegradable.

The growing demand for pharmaceutical and food grade collagen, is an example of how the boundary food industry / leather industry is moving from the end of the slaughterhouse operations to that of the Beamhouse. All these new requirements which our industries are facing should be accomplished in an everyday higher quality demanding market. These new challenges can only be achieved towards the meticulous analysis of each process step, and by the co-operation of multi discipline specialists working together for this target. In this project we put together a renown turn-key tanneries and waste treatment plants builder,

Italprogetti Engineering, a company specialised in biotechnologies applied to leather industry and waste treatment, Biodermol, and a laboratory dedicated to the study of environmental leather processing and chemicals analytics, Ars Tinctoria.

View of the process

In Leather industry our starting raw material is natural and biodegradable. State of art processes mostly generates from it a non-biodegradable product with plenty of non-

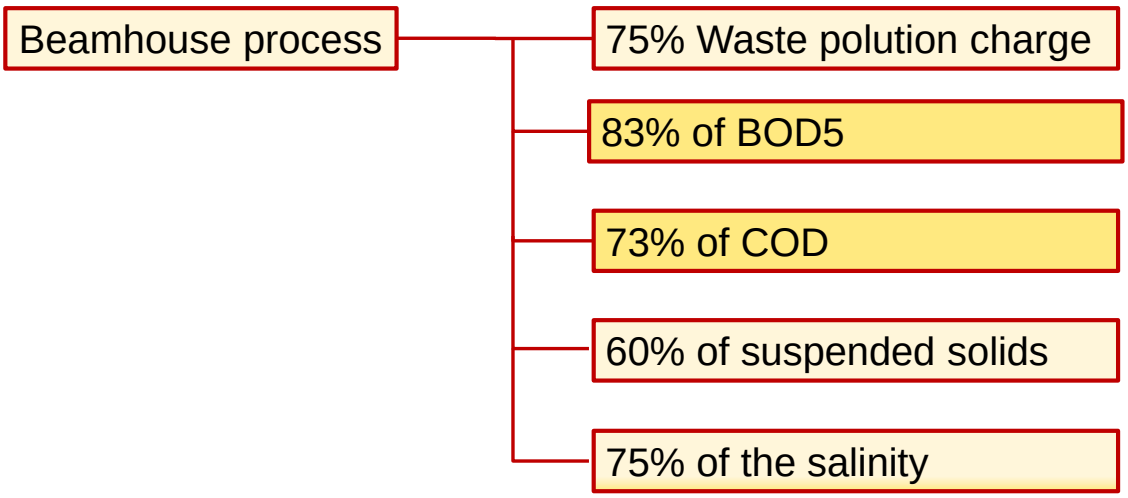


Fig.2 – Beamhouse contribution to environmental treatment considering the whole leather process.

biodegradable wastes, by means of chemicals which may affect environment or which implies costly treatments to be removed or neutralised. Sulfide containing waters should be carefully treated by oxidation before any pH reduction or environmental treatment to avoid poisonous SH_2 generation. Even after oxidation, chemical and biological treatment should be done with enough air diffusion to avoid anaerobic sulfide generation.

It is well known beamhouse contribution to environmental treatment is very high considering the whole leather process figures (fig. 2). Several proposals for sulfide elimination by means of oxidative beamhouse processes were presented in the past years, showing the advantages of this technology in terms of Leather quality and environmental management. In several papers it was demonstrated that depilation can be performed safely with less damage respect to traditional processes, however, some disadvantages were also present such as temperature increase and excessive swelling and more open bellies than usual.

In our personal experience, oxidative beamhouse showed the following advantages from the application point of view:

- Pale, even colour, total elimination of scuds and pigmentation.
- More intense and even dyes.
- Does not induce metals oxidation on metal free tannages.
- Compatible with any tannage.

From the environmental and safety point of view:

- Deliming and Pickle process does not generate any dangerous gas.
- Less personal and environmental protection devices.
- Drastic reduction of dangerous emissions in atmosphere.
- Effective cleaner working environment.
- Easy to treat / reuse waste waters

Process' logic:

Skins should be pre-soaked and green fleshed, so as to avoid excessive H_2O_2 consumption. The scope of the main soaking should be removing globular proteins, and achieving the necessary liquids diffusion in the skin. Depilation process is carried on with H_2O_2 at a stable 12,6 pH adjusted with NaOH. Considering NaOH's dissolution is exothermic, it is advisable to use liquid NaOH 30% concentration. Once hair is pulped, and epidermis is easily removed, a small portion of Calcium hydroxide is added running automatic overnight.

Pelts are eventually fleshed and lime splitted and trimmed, and return to deliming and bating process. Sulfide free trimmings and splits can be easily used in industrial gelatine production. Less advisable from the sustainability point of view, but technically possible, is to carry on the process in full substance splitting after selection as usual. H_2S generation is possible, so it is safe to reduce pH in Leather and effluent.

Hair-save vs hair-destroy systems:

Although hair-save systems were experimented, from the protein recovery point of view, hair-destroy systems are more advantageous. Hair save systems moves the problem of hair's BOD and COD contribution to a low biodegradability solid waste which should be somehow disposed. Hair's high nitrogen content may be used, if destroyed and recovered as protein, as a base raw material for good quality fertilizers.

Technical developments for oxidative beamhouse:

Scaling up oxidative beamhouse processing implies, apart of rethinking the whole process, finding technical solutions for its safe application. H_2O_2 is highly corrosive to wood and metal. In this context modern developed PPE vessels are the best available solution in terms of durability. Scaling up the process is easier by constantly monitoring and adjusting depilation parameters. For this purpose a prototype PPE drum was built (fig. 3). This vessel has a float circulation system thru a lab box, predisposed with pH / redox potential meters which may interact with a central control system. Two membrane pumps were installed respectively to automatically dose NaOH and H_2O_2, which can be operated automatically in function of pH measurement towards a central control system or manually. The engine is

Fig.3 – Prototype PPE drum by Italprogetti engineering.

Fig. 4 – pH – redox potential measuring device.

commanded towards an electronic inverter allowing a wide range of speeds. Four different running speeds can be pre-set. We have installed in this prototype vessel a liquid circulation conditioning system able to work in heating or cooling mode, with the purpose of controlling eventual temperature variations, or setting particular working conditions such programming heating curves for tannage, etc. A pH – redox measuring device was also installed (fig. 4), allowing us to record all vital parameters throughout the entire process so as to evaluate the right tactic to follow on scaling up.

Oxidative beamhouse and chemical auxiliaries:

Most traditional auxiliaries such as bactericides, surfactants, soaking enzymes, soda ash, etc., may act in detriment of the expected results rather than showing the known benefits in traditional processes. In most cases these auxiliaries will just consume H_2O_2 sometimes producing unwanted products, or generating unwanted exothermic reactions. Oxidative beamhouse processing shows different challenges to solve. For this purpose tailor-made auxiliaries were developed face the peculiar necessities of this process. Wrinkles are not a problem in oxidative processing, but swelling and temperature increment must be controlled. Certain traditional soaking enzymes may have a strong action on dermis in detriment of grain quality, and this fact is more evident on oxidative processing. New specific enzymes based auxiliaries allowed us to produce excellent soaking performances keeping grain quality intact.

Fig. 5 – Oxidative beahouse scale up on fresh hides.

The correct auxiliaries' selection allowed us to reduce running times without compromising lime penetration.

Carbonates in main soaking are not the best choice to regulate pH (even in traditional processing). Its interaction with calcium and magnesium will always play against achieving good quality dyes. Same situation regards the choice of the soaking auxiliaries: too lipophilic soaking agents may bring fats in emulsion, which will be later precipitated with lime addition, disturbing the correct hair bulb cleanness.

These factors were vital when we needed to scale up from few skins to real production.

Deliming and bating operation should be done with care. We suggest avoiding the use of ammonium salts and keeping low temperature till the end of deliming process, increasing temperature for bating.

Fig.6 – Scale up trial on French Frisian hides.

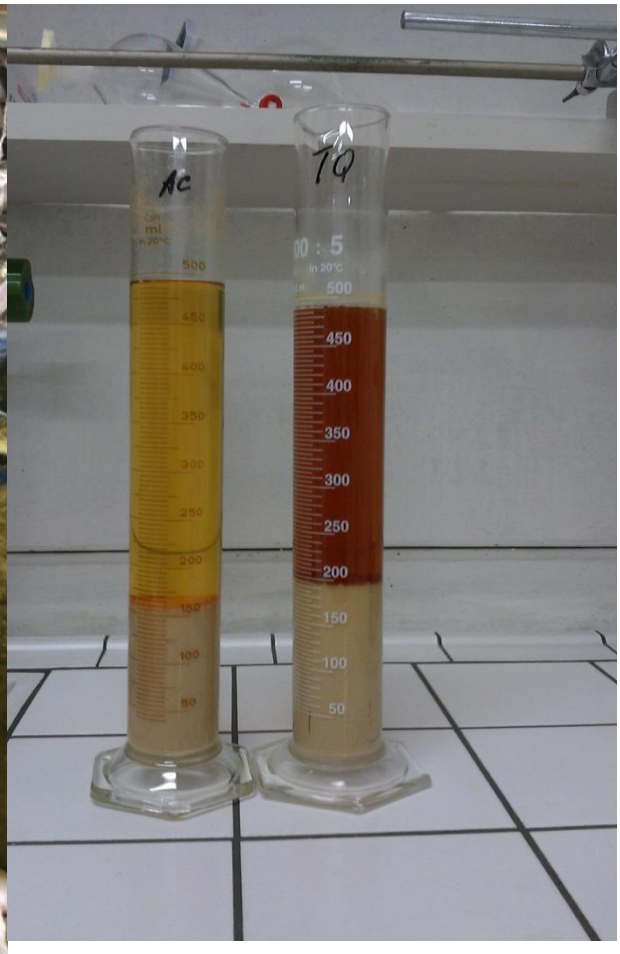


Fig. 7 – Depilation floats with/without acidification.

We noted that skins processed with this system are more reactive to tannage than usual, and thus it is advisable not to mix the skins from oxidative and traditional processing in tannage. In wet blue processing, for example, is a good practise to begin tannage with a small chrome portion (1%), increasing concentration with other two additions. This precaution ensures a very fine grain. Same care should be taken in case of wet white and veg tannage.

Environmental waste treatment

The greatest advantage of an oxidative beamhouse process is the generation of a sulfide free high concentrated protein float. Effluent from oxidative depilation system may be streamed and treated with sulphuric or phosphoric acid. In this condition proteins can be collapsed with a reduction of over 90% of BOD_5 and COD values (fig. 7). Spontaneous flocculation is also possible, but COD reduction not so effective. The precipitated proteins can be filter-pressed and after pH conditioning and sterilization as requested by the European regulations, can be used as a base for fertilizers. The rest of the effluent can be streamed and treated together with the remaining of the waters in an MBR (Membrane Bio Reactor) where filtrate can be pH conditioned and reused. MBR technology allows a filtration at microorganism level.

In our experimental tests COD on the untreated depilation float was in the same order respect to the state of art technology. Traditional beamhouse depilation floats led to a COD in the order of 90.000 – 100.000 mg/l, while oxidative beamhouse 75.000 – 90.000 mg/l. The advantages lay on a safe protein flocculation in oxidative beamhouse. By means of acids, is easy to achieve a COD reduction to 5.000 – 7.000 mg/l without using flocculants.

Oxidative beamhouse under the microscope

Our latest production trials were monitored by means of microscopical analysis. Soaking auxiliaries were evaluated with special sensible to aminoglycans stains, allowing us to choose the best conditions for processing different hides origins.

In figure 8 and 9 we can observe respectively the leather cut with and without stain.

Fig. 8 – Soaking process without stain

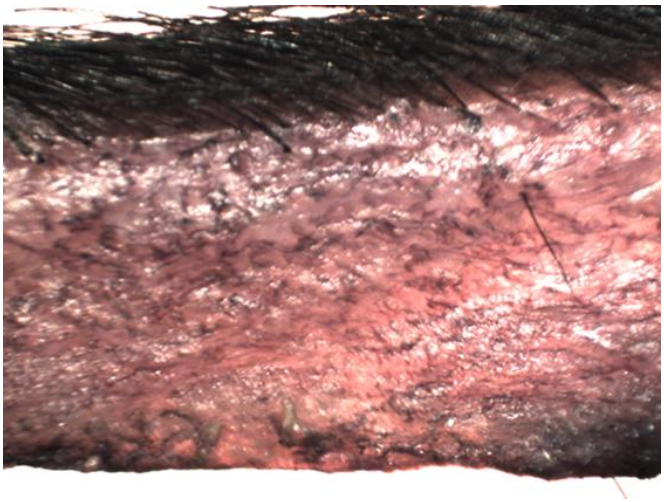


Fig. 9 – Soaking process with stain.

After 2 hours depilation hair bulb is still intact but there is evident gelatinisation of superficial hair (figure 10). We can observe the first signs on hair degradation, while black pigmentation

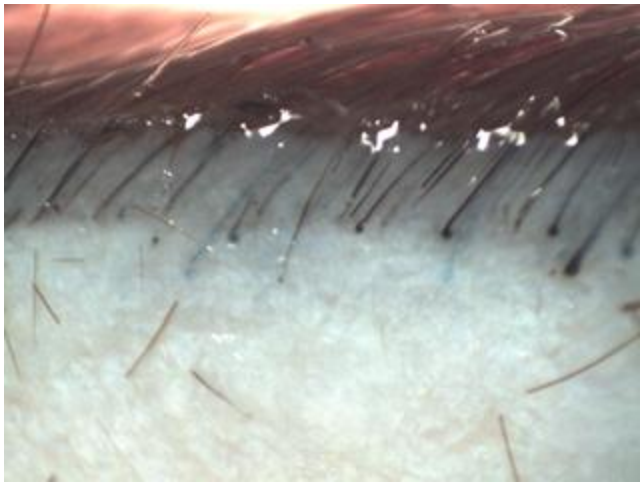


Fig. 10 – Depilation after two hours peroxide addition.

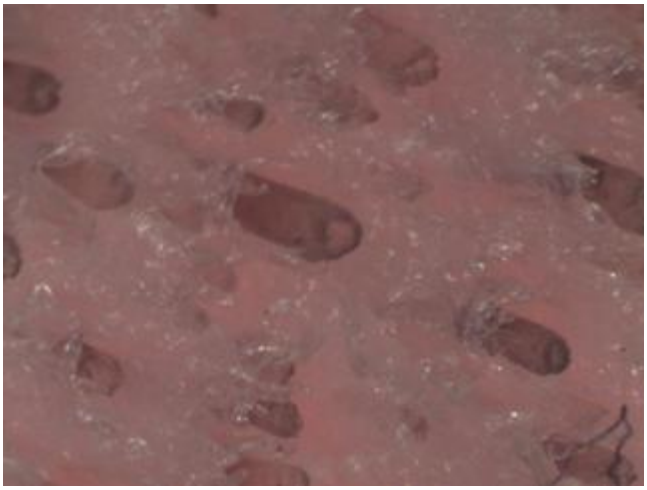


Fig. 11 –Intact hair roots after two hours depilation.

becomes red.

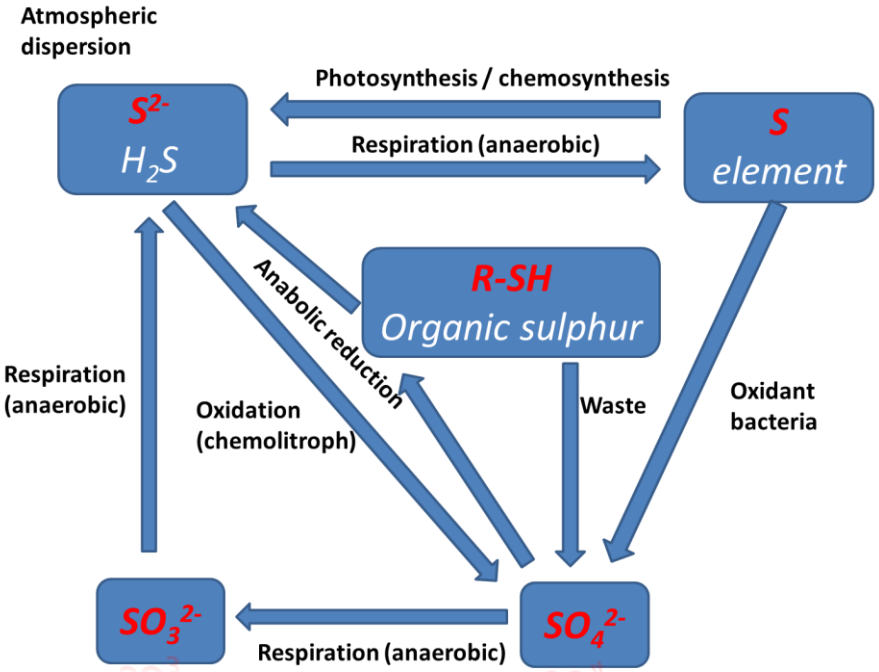
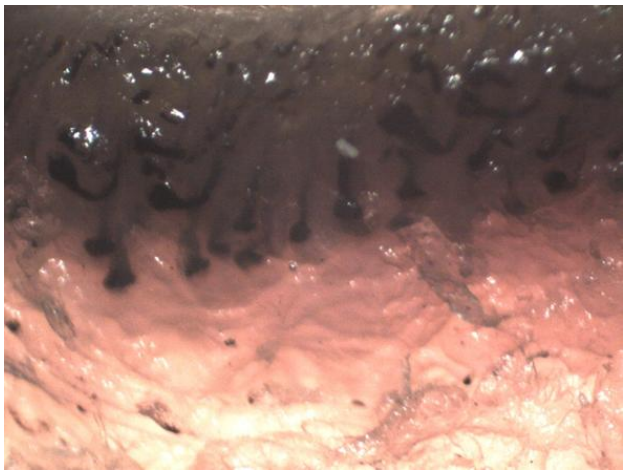

Atmospheric dispersion
Photosynthesis / chemosynthesis
S^{2-}
H_2S
Respiration (anaerobic)
S
element
R-SH
Organic sulphur
Anabolic reduction
Respiration (anaerobic)
Oxidation (chemolitroph)
Waste
Oxidant bacteria
SO_3^{2-}
Respiration (anaerobic)
SO_4^{2-}

Fig. 14 – Sulphur cycle.

Figure 11 shows the surface after cleaning it mechanically. Hair bulb is still intact and epidermis with evident gelatinisation signs. Figure 12 shows hair roots with evident sign of degradation after 4 hours



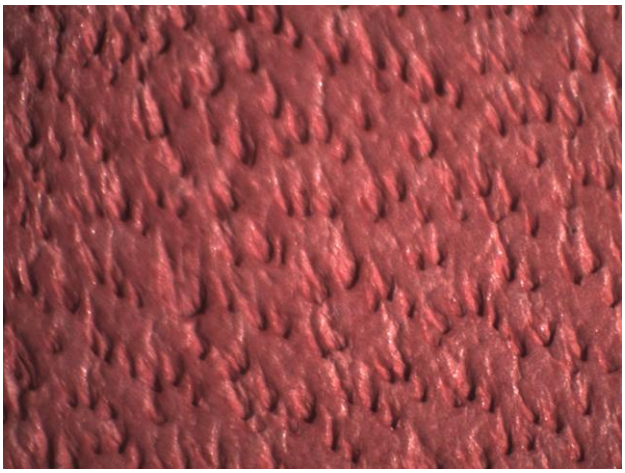


Fig. 12 – Hair roots after four hours depilation.

Fig. 13 – Grain aspect after retannage.

depilation. Figure 13 shows an intact fine grain in a shoeupper retanning.

Biological sulphates remediation in effluent treatment

Oxidative beamhouse generates near no sulphates from depilation, but following processes (mostly retannage) are based on organic sulphates, containing relatively high amounts of neutralisation and standardisation salts. Salts management in water treatment is nowadays one of the most critical parameters to consider.

This new technology developed aims to the enzymatic digestion of inorganic sulphates. SO_4^{2-} can be used by selected micro-organisms to incorporate sulphur for metabolic functions. This technique is actually applied in water treatment plants obtaining a media ca. 30% sulphates reduction after biological treatment.

Conclusions

Respecting the biological nature of leather's raw material is the clue for the sustainable future of our industry. When thinking on producing a good piece of Leather we must consider that from now on that should be done without harming the delicate natural equilibrium of our environment. Our first scope was producing a saleable piece of Leather and our present results demonstrate that this technique may be applied achieving excellent quality standards. First scales up experiences of oxidative beamhouse processing were performed with similar to better results than traditional process in terms of tensile properties and fullness. Dyeability of the leather obtained was always superior, mostly when producing pastel shades and brilliant colours. Trials were made on various types of hides and skins, of all weight ranges. The most interesting results were achieved on fresh hides, where wrinkles were perfectly extended, veins eliminated, and bellies fuller than usual with

fine and uniform grain. Latest developed wet white processes technologies showed improved results on oxidative processing, with quicker and better penetration, improved shaving, and paper-white colour. Processing costs are comparable to those of a traditional process, and may be lower considering the advantages of waste converted into by-products, and the improved image we can give to our industry.

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