PODEBA: AN INDUSTRIAL SYMBIOSIS CASE

Extended abstract

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Background

Leather processing involves a series of unit operations that can be classified into three groups: i) pre-tanning, to clean the hides or skins; ii) tanning, to permanently stabilize the skin or hide matrix; iii) the post-tanning and finishing operations, in which aesthetic value is added (Palanisamy et al., 2004). At each stage, various chemicals are used. The bating process takes place in the pre-tanning phase. It is the process of removing proteins other than collagen using proteolytic enzymes. The bating enzymes cause physical-chemical changes in the skin (Palanisamy et al., 2004) and remove its coagulable proteins. This process prepares the hide or skin for the tanning phase, which completely stabilizes them, to obtain finished leather products. In the bating stage, proteolytic enzymes or mixtures of enzymes with acid ammonium salts are normally used, to neutralize the fleshed and alkaline hides and to allow enzymes to act. This process has a high environmental impact, because of water consumption and N charge (for wastewater) (Zengin et al., 2002).

Poultry Dejections (PoDe) are the major waste/animal by-product in poultry intensive farming, and their disposal is often a relevant problem. They are composed of organic carbon, nutrients (nitrogen and phosphorus compounds), microorganisms and extracellular enzymes. Their main use is for soil manuring, often after storage or treatment. And their distribution is based on N dose per hectare, according to Agronomic Use Plan (Water Framework directive 2000/60/EC). Poultry farms are very often intensive and concentrated in restricted areas. Because of farm concentration, often the soil surface needed for their correct distribution becomes a problem. It is therefore important to pursue different PoDe uses in a bioeconomy strategy to overcome this limitation.

The use of PoDe has an historical background thanks to their proteolytic enzyme content which can weaken the three-dimensional structure of derma, breaking elastin and collagen, swelling and preparing de-limed pelts for the tanning phase. This PoDe utilization was abandoned because of its high environmental impact (odour and health aspects). Through a LIFE project, its use as a bating agent has been reintroduced, in a modern and controlled way, overcoming the limitations described above.

LIFE project PODEBA (LIFE10 ENV/IT/365, Use of poultry dejections for the bating phase in the tanning cycle) is demonstrative of an industrial symbiosis case. In fact, the byproducts of agro-industrial production (output) are used, after proper treatment and transformation into Deodorized and sanitized Poultry Manure (DPM), as technical products (input) for the tanning industry (Fig. 1). This results in an increase in the efficiency of the agrifood industry while reducing the environmental impact of the tanning industry. PoDe bio-treatment is aimed both at deodorizing and sanitation and it is performed according to a European patent (AMEK, CTI, 2002).

The development of the project is consistent with European policy and strategies:

- Roadmap to a Resource Efficient Europe (2011)

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• DG Enterprise Sustainable Industry-Going for Growth & Resource Efficiency (2011)
• European Climate Knowledge and Innovation Community (2012)
• European Resource Efficiency Platform (2012)
• Directive 96/61/EC, on Integrated Pollution Prevention and Control (IPPC)
• Water Framework Directive 2000/60/EC
• REACH Regulation, EC 1907/2006 (Registration, Evaluation, Authorization and Restriction of Chemical substances; European Community Regulation on chemicals and their safe use)

Fig. 1. PODEBA as an industrial symbiosis: transformation of waste from intensive poultry farming into a resource (Poultry manure as bathing agent) for tanning industry

Objectives

The activities were focused on the following 4 issues:
• Suitable PoDe to be transformed into bathing agents, based on chemical-physical properties required by bathing process conditions.
• Suitable PoDe drying management system, chosen among recognized Best Available Technique (BAT).
• PoDe treatment (Manure preparation), already identified in PODEBA project.
• Application of DPM in the bathing phase, taking into account odour aspects and final leather characteristics.

Outline of the work

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Methods

The bathing process inside rotating drums needs water soluble/dispersible reagents, without the presence of material such as straw pieces which could inflict mechanical damage to pelts during rotation. Therefore, PoDe from laying hens without litter were chosen. PoDe were taken from intensive poultry farms in order to have available amount that are large enough for industrial application and to obtain a standardized final product quality.

The most common PoDe drying systems were investigated in order to obtain a final product for leather processing. In particular, the Manure Drying System (MDS) and the ventilated belt system were tested in PODEBA activities. Both systems are classified as BAT according to BREF (EC, 2003) and they are representative of large (>100,000 animals) and medium size (30-50,000 animals) intensive poultry farms in Europe. MDS allows drying up to 85% DM, in a tunnel outside poultry housing in 72 hours. A ventilated belt system allows drying up to 60-65% DM, in 6 days time.

As provided for in the project, Bio-Treatment was performed according to the European patented process “A process for maturing and stabilizing biomasses under reduction of smelling emissions” (AMEK, CTI, 2002). It describes a complex product, a natural enzymatic cocktail named Vegetable Active Principles (VAP), prepared from selected plants, picked up in their balsamic period. VAPs were developed in order to speed up biooxidation processes, reduce biomasses turning and to maintain N in slow release form. Treatment consists in adding VAPs to dried manure directly inside bioreactors (big bags (1m³ of size) as they are being filled by conveyor belt, in doses up to 1 kg/m³. In bioreactors, manure matures at least for 120 days by means of static batch processes in; at the end the big
bags are ready for marketing. Two generations of DPM were produced with a slightly modified VAP recipe, which ensures sanitary conditions (Golfari et al., 2010).

Laboratory tests for the use of DPM as bating agent were carried out in order to check its efficiency in comparison with SF and define the appropriate use condition Biozym MC/N is the most commonly used formulation (SF); it is composed of proteolytic enzymes (0.5-5 % w/w), Ammonium Sulphate (about 60% w/w), Ammonium Chloride, saw dust and other inerts. Another aim of the test was to verify the effect of the bating agent on odour impact both as far as the bating floats and the leather products. Bating trials were carried out on cow hides which were then treated in order to obtain tight items (for shoes and leather goods) and soft items (upholstery, garments). The bating process variables under investigation were:

- Qx, the quantity (%) of bating agent, depending on bating agent activity; DPM quantity, to use in comparison with SF, was calculated on the basis of DPM enzyme activity, which was assessed by means of the Lohlein-Volhard method (Lohlein-Volhard method, 2001).
- tx: bating process time (min), depending on bating agent efficiency.

Different bating agents were used for this study, in order to investigate olfactory impact as well, as reported in Fig. 2. Also used a bating treatment without agent as reference for odour emissions (to recognize leather emissions) in order to understand the usefulness and the efficiency of the bating agent.

![Fig. 2. The different bating agent samples tested. First and second generations differ for VAP recipe.](image)

The effects of the different bating agents were observed by means of selected indicators for final leathers (leather structure and cleaning surface of final product) and odour aspects both for bating phase and final products (Dall’Ara et al., 2012). Technicians and tanning process developers assessed odour impact modifications in bating process conditions and in finished leather. Also measurements were made of the volatile fraction in process wastewater samples and volatile fraction in wet blue leather (leather right after bating and chromium tanning).

Furthermore, leather samples were subjected to different quality control processes according to international standards (EN-ISO) to verify their suitability for use in the manufacture of footwear (breaking strength, tensile strength and breaking elongation).

**Results and discussion**

The results of laboratory tests are reported in Table 1, where results are related to standard conditions with SF (Biozym MC/N), as shown in Fig. 2.

<table>
<thead>
<tr>
<th>Trial code</th>
<th>Smell during process</th>
<th>Smell on wet blue leather</th>
<th>Smell on finished leather</th>
<th>Leather's structure</th>
<th>Cleaning surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without</td>
<td>bad</td>
<td>bad</td>
<td>No</td>
<td>quite harder</td>
<td>less</td>
</tr>
<tr>
<td>A</td>
<td>bad</td>
<td>bad</td>
<td>No</td>
<td>similar</td>
<td>similar</td>
</tr>
<tr>
<td>V</td>
<td>quite bad</td>
<td>notable</td>
<td>No</td>
<td>similar</td>
<td>similar</td>
</tr>
<tr>
<td>P</td>
<td>quite similar</td>
<td>weak</td>
<td>No</td>
<td>very similar</td>
<td>similar</td>
</tr>
</tbody>
</table>

The patented PoDe bio-treatment ensures sanitary conditions (Golfari et al., 2010), but only the new VAP recipe (the one used for the second generation DPM) solved the odour issue and was suitable for the purpose of this project. In fact, the first generation DPM had a reduced odorigen impact in dry conditions but showed a significant odorigen impact under wet conditions (in bating phase with water and delimed pelts). In the second generation, the new bio-treatment recipe allowed to obtain a DPM that was suitable for bating, since the smell developed during the bating process was very weak and it was not a problem for workers. The smell of at the wet blue leather stage was
very weak and there was no effect on finished leather. Final leathers were characterized and properties measured: those obtained with DPM showed pleasant appearance, fine-grain and adequate smoothness, softness, flexibility, grain firmness, and fullness. The physical parameters measured in final leathers showed that the recommended values for the manufacture of footwear were achieved. Leather structure, surface cleaning, odours during process, and smell on finished leather were very close to the standard. It is important to emphasize that the use of big bag as bioreactor allows to perform PoDe treatment practically inside the sale packaging, and this makes both marketing and symbiosis easier from a practical point of view.

Nowadays poultry farms are often concentrated in a limited areas and poultry manure is delivered to farmers for free, just to get rid of the dejections. PoDe partial reuse as a resource for tanning industry can solve the problem of waste management and disposal in intensive poultry farming, in the areas where the farms are more concentrated. It also leads to profits and/or to the elimination of costs for poultry farm owners.

Pre-tanning and tanning processes contribute 80-90% of the total pollution in the industry and generate noxious gases, such as hydrogen sulfide and other wastes (Palanisamy et al., 2004). The use of DPM instead of chemical mixture allows to eliminate the need for sodium sulfide and other chemicals during the bating process, thus reducing toxic waste and water pollution.

Implementation of this symbiosis is also a strategy to prevent waste production, to save resources and to reduce environmental impact, consistently with the need of European leather producers to exploit more efficiently their raw materials in order to remain competitive in the global market place. It represents a waste prevention device because PoDe are directly treated and transformed into a technical product right on the farm. It saves resources since each ton of DPM used as bating agent prevents the use of 0.3-0.6 tons of ammonium sulphate. Also wastewater load is reduced during bating phase by using DPM: more than 40% for TKN and ammonia.

The tanning industry aims to achieve environmental protection objectives such as waste reduction, recycling and recuperation of secondary raw materials. Accordingly, EU tanners are adjusting their production towards higher quality output and high fashion content leathers.

Concluding remarks

This paper presents a process which is suitable to transform PoDe (animal by-product) into a technical product (DPM), a bating agent for tanning. This gives rise to a potential case of industrial symbiosis between agro-industry (egg production) and the tanning industry, as developed in a European project carried out in Italy and Spain, countries that represent 90% of the European leather sector. Technical viability was demonstrated for different types of leather (soft and tight items), for different raw materials (hides, skins) and for different articles (shoes, upholstery). Investigations of the economic aspects are in progress.

If this solution were applied it could require large amount of PoDe to be transformed into bating agent, (2-3% of Italian PoDe production). Furthermore, implementing this solution could reduce the environmental impact; by the end of PODEBA project an assessment of the overall impact reduction will be carried out through a LCA analysis.

Keywords: industrial symbiosis, leather, poultry dejections, tannery

Acknowledgements

The work has been performed within the framework of the project “Use of POultry DEjections in the BAting phase of the tanning cycle (PODEBA), LIFE10 ENV/IT/365, co-financed by EU, within the LIFE program

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