REDUCTION OF RESIDUAL TANNINS CONCENTRATION USING *Cerioporus squamosus* BIO-AUGMENTED POLYMERIC CARRIERS

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The oldest use of polyphenols in the leather industry is based on their ability to stabilize collagen in the skin against rotting. Leather tanning processes are among the most polluting industrial sources in terms of undesirable and toxic parameters (COD, BOD, content of tannic acids, fats, sulphureous residues, chloride, chromium, suspended solids etc.). Tannic acid is a naturally occurring phenolic compound and is widely used in the tanning processes, being one of the main pollutants in leather industry derived wastewaters. Current paper explored the ability of HDPE carrier, functionalized with *Cerioporus squamosus* microbial strain, to reduce the residual concentration of five natural tannins, widely used in the tanning processes in leather industry: Quebracho, Chestnut, Mimosa, Myrobalan and Gambier, in concentration of 1% in the tested solution. Bio-augmentation experiment of the HDPE structures were carried out in an experimental laboratory installation, and treatment of each aqueous solution, was carried out for 7 straight days, and percentage reduction of residual tannins was calculated at 3 and 7 days. Results highlighted varying degrees of reduction of the residual tannin concentration in the solutions, depending on the tannin tested, the best efficiency being achieved against Myrobalan tannin, with a maximum percentage reduction in residual concentration of 41% after 7 days, followed by Mimosa tannin (34%-7 days), Quebracho (28%-7 days), Chestnut (22%-7 days) and Gambier (9.30%-7 days).

Keywords: Wastewater, tannins, MBBR.

INTRODUCTION

Environmental protection issues have become an essential component of the last thirty years. Determining the origin and quality characteristics of wastewater requires knowledge of the industrial technological process for the proper design of treatment technologies, along with knowledge of the source of the main tributaries and their characteristics is necessary to define the treatment methods (Yusuf and Sonibare, 2004). As far as the leather industry is concerned, the leather tanning process consists of converting raw leather, into leather, a stable material that can be used to manufacture a wide range of products. The whole process involves a complex sequence of chemical and physical operations. Following these operations, the finished product will have excellent properties such as stability, appearance, water resistance, temperature resistance, elasticity, air permeability, etc. This process is a major producer of waste water, air and soil pollutants (Zao and Chen, 2019). Environmental impacts come from liquid, solid and gaseous waste streams and the consumption of raw materials such as raw hides and skins, energy, chemicals and water. The main pollutants in the wastewaters come from wet processing and post tanning operations.

The process of disposing of leather wastes or residues from the tanning process represents an important niche for the protection of both the human health and the environment. Tannins, or tanning substances, are a class of organic compounds with a heterogeneous polyphenolic structure. Compounds in this class are mainly used in the leather industry, having the property of transforming raw leather into tanned leather.

https://doi.org/10.24264/icams-2022.II.9

There are two subclasses of tannins, based on structural criteria and chemical properties: gallo tannins (hydrolysable tannins) and catechin tannins (condensed tannins) (Neamțu, 2011).

MATERIALS AND METHODS

Microbial Strain and Treatment Installation

For the reduction of tannins experiments, *Cerioporus squamosus* (a basidiomycete bracket fungus) strain was used, which was started as fresh culture, on Sabouraud-Dextrose-Agar media (SAB) (Fig. 1). *Cerioporus squamosus* is a bracket fungus species in the *Polyporaceae* family, and it is most commonly known by the names of "Dryad's Saddle" and "Pheasant's Back Mushroom".

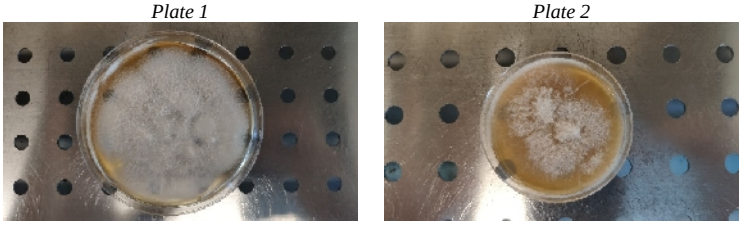

Figure 1. *Cerioporus squamosus* grown on SAB nutritive media

A laboratory treatment installation (Fig. 2-a) was used for the biofunctionalization of the high-density polyethylene (HDPE) structures (Fig. 2-b) with the *C. squamosus* strain. The installation allowed controlled aeration of the media, by infusions of filtered air, which served a dual purpose: providing oxygenation for microbial growth, and bubbling of the media, for a better dispersion of the strain inside the liquid volume.

Laboratory treatment installation | HDPE carriers in treatment installation | HDPE carriers

Figure 2. Bio-augmentation of HDPE structure

The polymeric structures, with composition of 5% talcum, 7% cellulose and 88% HDPE, were bio-augmented in the experimental treatment installation, in a total volume of 12L, with addition of Czapek-Dox nutrient media, for 14 days, at 28°C, and continuous aeration (in a Lovibond thermoreactor). The initial microbial inoculum volume was 100mL of fresh strain, obtained in Czapek-Dox liquid media. The process

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led to obtaining of polymeric structures covered with fungal biomass, which where the active part of the treatment process.

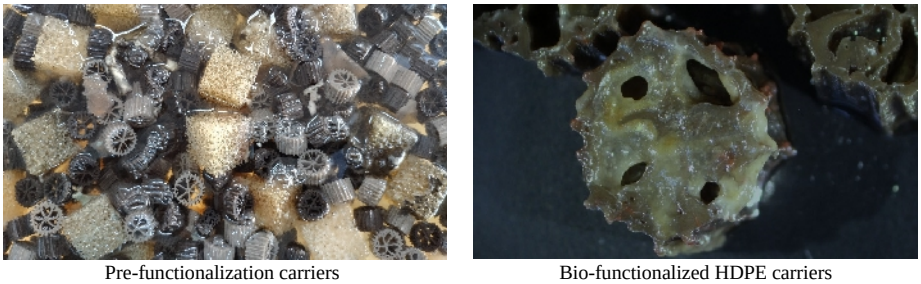
Selected Tannins

Five natural tannins were selected for experiments to reduce the residual concentration in synthetic solutions: Quebracho, Chestnut, Mimosa, Myrobalan and Gambier. The reduction of the residual tannin concentration in the analyzed samples was performed on a UV-VIS T70 spectrophotometer (Oasis Scientific) with 5-point calibration curves for each tested tannin. The ability of the phenolic ring to absorb UV light is exploited to quantify these compounds (Aleixandre-Tudo *et al.*, 2017). The visible UV spectra of a tannin are thus attributed to electronic transitions occurring in the hydroxyl groups of phenolic molecules, with different transitions corresponding to different phenolic subclasses (Sanna *et al*., 2014). Different classes of tannins from different sources show characteristic UV absorption bands (Nakagawa and Sugita, 1999).

After the bio-augmentation period, the entire medium was evacuated from the installation, leaving only the polymeric supports in the reaction vessel. The installation was again charged with 12L of solution of each tannin, at 1% concentration (Quebracho solution=1%; Chestnut solution=1%/; Mimosa solution=1%; Myrobalan solution=1%; Gambier solution=1%), with the process run in five distinct batches for each tannin.

RESULTS AND DISCUSSION

The HDPE carrier's specific composition allowed for both growth and fixation of the microbial strain, especially in the chambers of the carriers. Constituent cellulose was used as C source by the strain, while talcum allowed a better fixation of the biofilm inside the chambers (Fig. 3).



Pre-functionalization carriers Bio-functionalized HDPE carriers

Figure 3. Percentage reduction grades of Quebracho tannin residual concentration

The treatment process was carried out for 7 days, for each tannin, with incubation at 28°C (Lovibond thermoreactor) with continuous aeration. Samples were taken at T3 (3 days of process) and T7 (7 days of process) and the degree of percentage reduction compared to T0 (considered 0% percentage reduction of residual tannin concentration at the beginning of the process) was calculated (Fig. 4-8).

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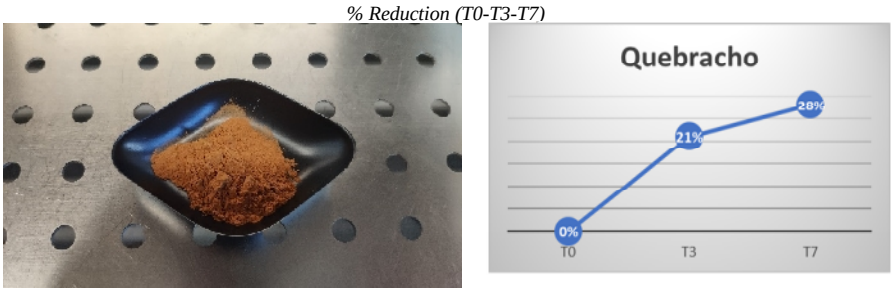

Figure 4. Percentage reduction grades of Quebracho tannin residual concentration

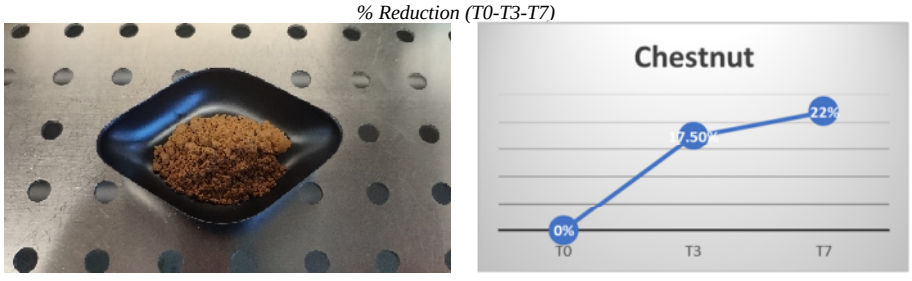

Figure 5. Percentage reduction grades of Chestnut tannin residual concentration

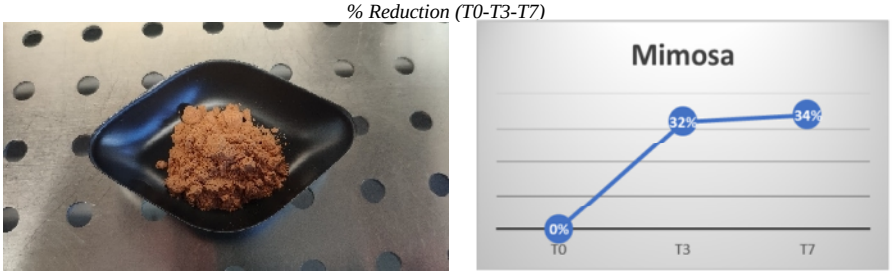

Figure 6. Percentage reduction grades of Mimosa tannin residual concentration

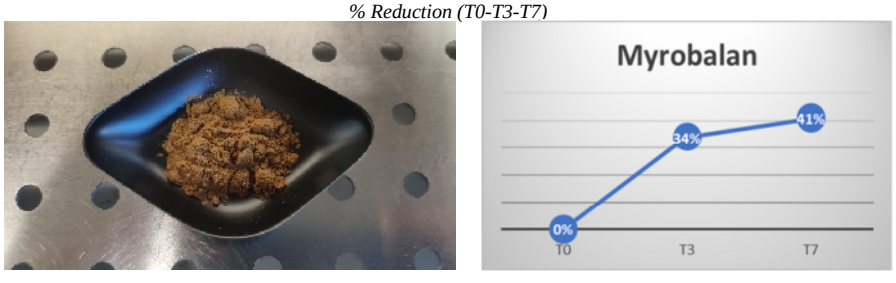

Figure 7. Percentage reduction grades of Myrobalan tannin residual concentration

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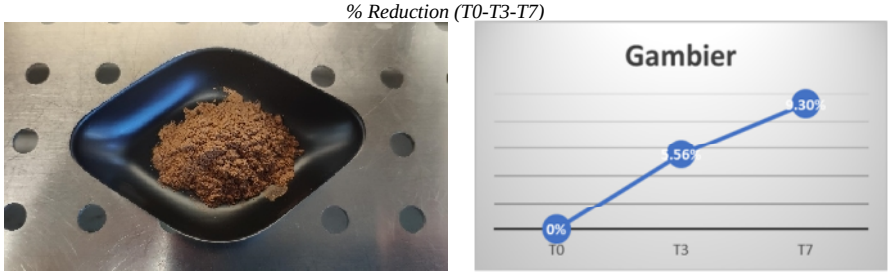

Figure 8. Percentage reduction grades of Gambier tannin residual concentration

The results of the analyses show varying degrees of reduction of the residual tannin concentration in the solutions, depending on the tannin tested. Thus, the best efficiency was shown for the tannin Myrobalan, with a maximum percentage reduction in residual concentration of 41% after 7 days, followed by Mimosa tannin (34%), Quebracho (28%), Chestnut (22%) and Gambier (9.30%). An upward trend could be observed on all samples, with the reduction rates increasing from T3 to T7. Gambier tannin showed the lowest percentage reduction rates of residual concentration in solution, which may be due to a pronounced antimicrobial character that this tannin has, due to the (+) catechin content, thus inhibiting the enzymatic activity of the microbial strain.

The use of MBBR specific technology is not currently emerging as a novel treatment technology, as the treatment efficiency of this technology is already settled throughout the years. However, new demands regarding treatment of industrial wastewater, which also includes leather industry specific wastewaters, dictates the necessity of novelty within the MBBR treatment systems, along with intelligent approaches for the efficient treatment of complex wastewater matrices.

CONCLUSIONS

A large amount of waste, especially organic waste, is inherent in leather manufacturing industry. Both organic waste fractions and other residues can be prevented and reduced to a large extent in process units, by use of non-conventional treatment technologies. Tanning agents such as plant tannins, synthases and aldehydes mainly affect surface water, leading to problems which arise because of their low biodegradability and toxicity to aquatic life. Tannins residual concentration reduction experiments, carried out on *Cerioporus squamosus* bio-functionalized HDPE carriers (specific to MBBR systems), showed promising efficiency for leather industry originated wastewaters, with efficiencies ranging from 5.56% (Gambier tannin) to 34% (Myrobalan tannin), after 3 days of treatment, and between 9.30% (Gambier tannin) to 41% (Myrobalan tannin), after 7 days of treatment. The proposed treatment technology proved more efficient against Myrobalan tannin, which was the most susceptible to microbial degradation, compared to Gambier tannin, which was the most resistant, with catechin constituent, which is proven to have antimicrobial activity.

https://doi.org/10.24264/icams-2022.II.9

Acknowledgment

The publication of the scientific paper is funded by the Ministry of Research, Innovation and Digitization within Program 1 – Development of the national R&D system, Subprogram 1.2 – Institutional Performance – RDI excellence funding projects, Contract no. 4 PFE/2021.

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