

# Circular Economy: Recovery, Reuse & Valorization

## Metals

**KEYWORDS:** Recovery / Valorisation / Gold / Palladium / WEEE

The recovery of critical and precious metals from waste electrical and electronic equipment (WEEE) is an environmental and economic imperative. Biosorption has been considered a key technology for the selective extraction of gold from hydrometallurgical liquors obtained in the chemical leaching of e-waste. The potential of tannin resins prepared from *Pinus pinaster* bark to sequester and recover gold(III) from hydrochloric acid and aqua regia solutions was assessed. The adsorbent presented high selectivity towards gold. Future research is needed to examine more closely the elution of gold from the exhausted adsorbents and to extend the studies to Palladium recovery. Obtained results show good perspectives as regards the application of pine bark tannin resins for the selective extraction of Au from electronic waste leach liquors.

### Introduction

Gold (Au) is a precious metal commonly used in jewellery and electronics, but also in medicine and as a catalyst in various chemical processes. Waste electrical and electronic equipment (WEEE), or e-waste, is known to present high levels of gold, among other precious metals as Palladium (Pd), which could be recovered and reused. The recovery of gold and palladium from wastes is crucial for the construction of a sustainable circular economy.

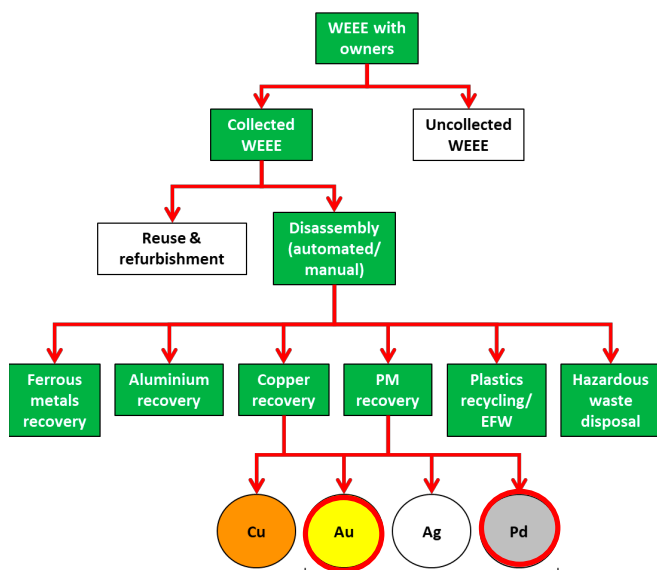


Fig 1. The recycling process chain with special focus on recovery of precious metals (adapted from R. G. Charles, PhD Thesis, Swansea University, 2018).

The use of bio-derived adsorbents has been regarded as a key technology, offering advantages related to the ready availability of the biomass, to the simple synthesis and chemical functionality, which usually make them good sequestrants for metals. Important criteria to be met by biosorbents for gold recovery include: (i) high uptake capacity of the metal from actual matrices; (ii) selectivity, i.e., adsorbents should be able to uptake gold to the detriment of other base metals and noble metals coexisting in solution; (iii) fast adsorption kinetics; and (iv) feasible subsequent recovery of the adsorbed metal.

Chloride, aqua regia, thiourea and thiosulfate are leaching reagents proposed to dissolve Au from WEEE and adsorption has been reported to be an effective process for recovery of gold from aqueous solutions. In the last years, our research group has been testing the use of tannin resins as adsorbents to sequester and recover Au(III) from hydrochloric acid and aqua regia solutions, simulating e-waste hydrometallurgical liquors.

### Current Development

Tannins are natural polyphenolic macromolecules present in leaves, wood, bark, seeds and fruits of various plants. Their abundance in nature, easy extraction with water, richness in hydroxyl groups and easy tailoring have made tannin materials interesting biosorbents for the removal of contaminants from water and for the uptake and recovery of precious metals. Tannin resins may be prepared through a crosslinking reaction (gelification) with aldehydes.

A tannin resin prepared from bark of maritime pine (*Pinus pinaster*) has been studied. The bark of this native Mediterranean tree is a forest residue and a by-product of wood conversion industry, which can give a contribute to bioeconomy.

Pine bark tannin resins were evaluated for the uptake and recovery of gold from simulated e-waste hydrometallurgical liquors. Higher extraction efficiencies of gold were obtained from HCl solutions, in comparison to aqua regia, but excessive levels of HCl caused a severe impact in the metal uptake from both aqueous systems.

Even though, at strong acidic levels and in both acidic systems, the pine bark tannin resin presented a good performance, with maximum adsorption capacities ranging from  $200 \text{ mg g}^{-1}$  ( $2.0 \text{ mol L}^{-1} \text{ H}^+$ ) to  $343 \text{ mg g}^{-1}$  ( $1.0 \text{ mol L}^{-1} \text{ H}^+$ ).

The selectivity of the adsorbent towards gold was evaluated using simulated hydrometallurgical liquors. The amount of gold extracted by the tannin resin from multi-metal solutions was similar to the values registered in the single-metal solutions and the co-adsorption of Pd(II), Cu(II), Fe(II), Ni(II) and Zn(II) was in general low.

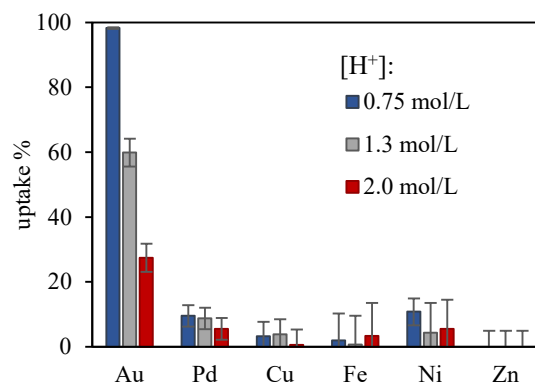


Fig 2. Uptake of metals by pine bark tannin resin from a multi-metal solution.

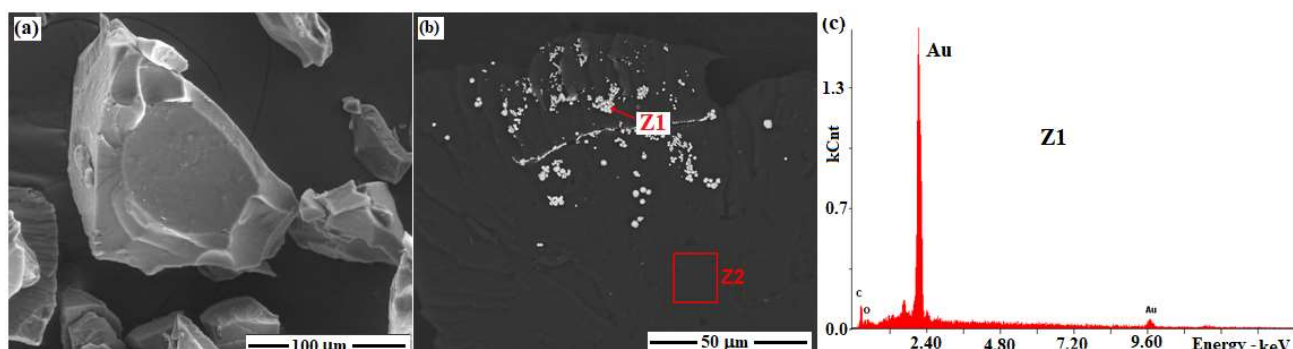


Fig 3. SEM images obtained for the pine bark tannin resin (a) before contact with gold, and after adsorption of gold (b) from 1.0 mol L<sup>-1</sup> HCl. EDS spectra obtained in the area denoted as Z1 (c).

Desorption and regeneration studies conducted in through three adsorption-desorption cycles, using a solution of 0.5 mol L<sup>-1</sup> thiourea and 0.5 mol L<sup>-1</sup> HCl as eluent, indicate desorption percentages of 38-57 %, although with only a mild loss of the adsorption capacity of the regenerated adsorbent. Considering the harsher conditions at which the pine bark tannin resin was evaluated, it can be said that it presents analogous or even better performance when compared to other biosorbents or synthetic resins.

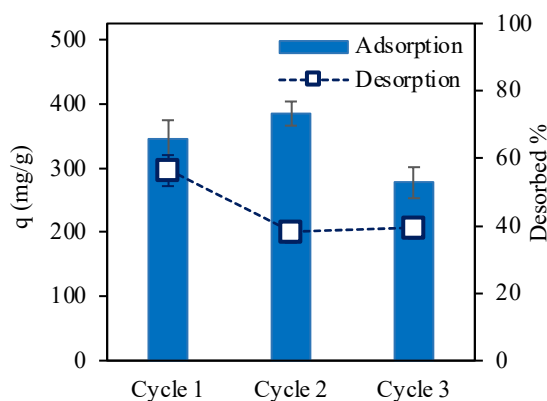


Fig 4. Results obtained in the adsorption and desorption cycles of Au on and from tannin resin.

#### Future Perspectives

Future research will extend the studies to Palladium (Pd) recovery. Adsorption experiments will be conducted in batch and continuous mode (fixed-bed column) and the effect of different operational variables, such as the type and concentration of the leaching reagent, temperature, pH, metal concentration, solid/liquid ratio and flowrate will be studied. Au and Pd's final recovery from the metal-loaded adsorbents will be studied by desorption, studying biosorbent's regeneration, and incineration. The purity of Au and Pd recovered in the resulting liquid or solid products will be assessed. A multiple columns system (sequential fixed-bed adsorbents) will be designed to recover Au and Pd sequentially. Different solid fractions of waste PCB will be collected and subjected to physical, chemical (removal of bulky metals) and hydrometallurgical processing. The adsorptive multiple column system's performance will be evaluated for the actual hydrometallurgical liquors generated from waste PCB. The recovery efficiencies of Au

#### Related Sustainable Development Goals



#### Outputs

##### PhD Thesis

Hugo Bacelo, Tannin resins from maritime pine bark as adsorbents for water treatment and recovery of substances, PDEQB, FEUP, 2021.

##### Master Dissertations

Maria Beatriz Torrinha, Adsorption of Gold from Leach Liquors using Tannin Adsorbents – Towards a Benign Au Recovery from E-waste, MIB, FEUP, 2020.

##### Selected Publications

M.B.Q.L.F. Torrinha et al., Water, 12(12), 1, 3456 (2020).

##### Team

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