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Review

Tannin-based biosorbents for environmental applications – A review

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HIGHLIGHTS

- Literature review on the synthesis of tannin-based biosorbents.
- Discussion about the factors affecting the performance of tannin-based biosorbents.
- Overview of the use of tannin-based biosorbents for water decontamination.
- Overview on the use of tannin-based biosorbents for critical metals recovery.

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ABSTRACT

Adsorption has been proved as an efficient process to remove a multiplicity of solutes from aqueous solution. Various biosorbents have found promising applications in wastewater treatment and in the recovery of critical metals that is, nowadays, the spotlight due to the promotion of environmental and economic sustainability. Tannins are excellent candidates to produce biosorbents. These ubiquitous and inexpensive natural biopolymers are of easy extraction and conversion into insoluble (tannin gels and tannin foams) or immobilized matrices. Tannin-based adsorbents (TBAs) have a natural affinity to uptake heavy metals, dyes, surfactants and pharmaceutical compounds from contaminated waters, and to accumulate selectively precious and critical metals from aqueous streams. Furthermore, chemically modified forms, such as iron-loaded and amine-modified tannin gels can be produced with relative ease and enhance the adsorption ability of many substances. In this paper, the literature about the production of different types of TBAs (resins, foams, immobilized tannins on support matrices, iron and amine treatments) is revised. The actual state of knowledge, in respect to TBAs application for water remediation and recovery of substances is presented.

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1. Introduction

Adsorption processes are viewed as relatively simple methods, effective on the removal of various contaminants from aqueous solution, in water or industrial wastewater treatment, usually at a post-treatment level (polishing) [1,2].

Adsorption phenomenon results from the existence of a force field at the surface of a solid, which reduces the potential energy of the adsorbed specie below that in the fluid phase [3]. Two broad classes of adsorption can be distinguished: physical adsorption and chemisorption. Physical adsorption results from van der Waals forces (dipole-dipole interactions, dispersion forces, induction forces). The chemisorption is based on chemical reactions between adsorbate and adsorbent surface, and then involves much stronger forces and higher adsorption enthalpy [4].

In general, adsorbents for application in aqueous phase include natural materials, such as clay minerals, zeolites, oxides and biopolymers, and engineered materials, such as carbonaceous adsorbents, polymers, oxidic adsorbents and zeolite molecular sieves [4]. In the last years, an increasing research interest has been recorded on low-cost adsorbents (biosorbents, agricultural by-products, industrial waste) as alternative options to the manufactured adsorbents. These materials can found suitable applications in wastewater treatment. Considering safety reasons, drinking-water treatment applications have been basically restricted to activated carbon and oxidic adsorbents [4], in spite of the high energy costs involved in their manufacture and the implications for the acquisition price and for the environment. In fact, to reduce the environmental impact of adsorption processes, adsorbents should be ideally effective, renewable materials, abundant and should require minimal processing before use. Biosorption gives a key contribution to reach these goals. It is defined as the property of certain biomolecules or types of biomass (biosorbents), to bind and concentrate selected ions or molecules from aqueous solutions by a metabolically-passive process [5]. The mechanisms of biosorption are generally based on physico-chemical interactions between adsorbates and the functional groups present on the biomass surface, such as electrostatic interactions, ion exchange, metal ion chelation or complexation [6]. In the last years, biosorption on marine seaweeds, agricultural wastes, forest residues and industrial byproducts, in native or modified forms, have been indicated as promising technologies for the uptake of heavy metals and organic contaminants from waters [7–11]. In addition to the water remediation, biosorption technology has also recognized applications in the recovery of metals from effluents and hydrometallurgy processes [6,12,13]. Adsorbents derived from lignocellulosic and tannin materials, seaweeds and chitosan, have shown great potential to selectively uptake precious and critical metals, and to be used in added value applications, such as catalysis [6].

Among the considerable variety of biosorbents, the present article is focused on tannin-based materials (TBAs). Tannins are inexpensive and ubiquitous natural polymers [14], polyphenolic secondary metabolites of higher plants, mainly present in soft tissues (sheets, needles or bark) [15,16]. After cellulose, hemicellulose, and lignin, tannins are the most abundant compounds extracted from biomass [16], leaves, roots, bark, seeds, wood and fruits [17].

The most common tannin feedstocks are mimosa bark (*Acacia mearnsii*, or *mollissima*), quebracho wood (*Schinopsis balansae* and *Schinopsis lorentzii*), pine bark (*Pinus radiata*) and Gambier shoot and leaf (*Uncaria gambir*). However, multiple trees and shrubs contain significant amounts of tannins [18]. Tannin contents reported in literature for some vegetable sources are presented in Table 1.

Tannins are important commercial substances, traditionally used as tanning agents in the leather industry, allowing the transformation of hide into leather. Other uses include adhesives (as phenol substitutes in the formulations), medical, cosmetic, pharmaceutical and food industrial applications [17,25]. Regarding the woodland conservation, particularly to avoid the fell of trees such as quebracho, mimosa and chestnut, alternative tannin sources, such as locally available residues or byproducts, should be selected. Possible sources include wine wastes (grapeseed), chestnut peels (from chestnut industry processing), forest exploitation wastes, timber, pulp and paper mills residues. Some of these biomass residues are incinerated, landfilled, used in horticulture or as energy source. It is however known that their use for heat/power generation have operational, economic and environmental limitations [26]; in addition, these options despise the valuable chemical content of the biomaterials. The extraction of tannins from vegetable residues constitutes then an important contribute for their reuse and valorization, and for tannins sustainable production.

Tannins are historically classified into two groups: hydrolysable or non-hydrolysable (condensed). On the basis of their structural characteristics, however, a classification into four major groups is preferable: gallotannins, ellagitannins, complex tannins, and condensed tannins [16,17]. Hydrolysable tannins can be fractionated into simple components, by treatment with hot water or by enzymes [17]. Condensed tannins have a higher activity towards aldehyde, being chemically and economically more interesting for the preparation of resins, adhesives and other applications apart from the leather [18]. Fig. 1 presents the structures of a catechin unit and a condensed tannin [18].

The presence of phenolic groups in tannins clearly indicates its anionic nature [27]. Phenolic groups act as weak acids, easily deprotonate, being good hydrogen donors, to form phenoxide ion which is resonance-stabilized.

Table 1
Tannin contents reported for some vegetable materials.

Plant material	%
Quebracho heartwood [19,20]	20–30
Wattle (acacia bark) [19]	15–50
Black oak [19]	8–12
Pinus pinaster bark [20]	22.5
Eucalyptus bark [21,22]	16–40
Mangrove bark [19]	15–42
Chestnut (endodermics/hull)[23]	2.50/0.94
Chestnut wood [19]	4–15
Grey and black Alder [24]	12