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Review

Lignin in storage and renewable energy applications: A review

Q1 José Luis Espinoza-Acosta[a,*], Patricia I. Torres-Chávez[b], Jorge L. Olmedo-Martínez[a], Alejandro Vega-Rios[a], Sergio Flores-Gallardo[a], E. Armando Zaragoza-Contreras[a]

[a] Department of Engineering and Materials Chemistry, Centro de Investigación en Materiales Avanzados, Miguel de Cervantes #120, Complejo Industrial Chihuahua, Chihuahua, México
[b] Departamento de Investigación y Posgrado en Alimentos (DIPA), Universidad de Sonora, Hermosillo, Sonora, México

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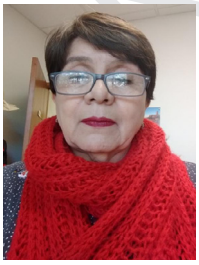
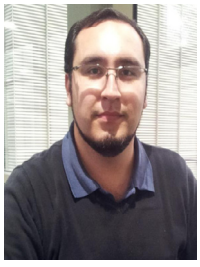
ABSTRACT

Lignin is a cheap, abundant and non-toxic group of complex phenolic polymers obtained in large amounts from the papermaking and cellulosic biofuel industries. Although the application of lignin has been explored in these and several more industries, there are limited applications of lignin in the energy industry. However, numerous research revealed a great interest in the exploration of this renewable biopolymer in storage energy devices. Some of these applications include the use of lignin as an expander for lead–acid batteries, electrodes for primary and rechargeable batteries, electrodes for electronic double layer capacitors and electrochemical pseudocapacitors, and to feed different types of fuel cells. The use of lignin in energy storage devices improves not only the performance of these devices but also decreases the price and toxicity, contributing to obtaining greener energy devices. Based on the above, this review provides an overview of the main research work related to the use of lignin as a renewable component, suitable to replace some synthetic and toxic compounds used in the fabrication of energy storage devices with particular emphasis on batteries, advanced supercapacitors, and solar and fuel cells.

José Luis Espinoza-Acosta received his Ph.D. degree in Food Science and Technology at Department of Food Research & Graduate Program (DIPA), University of Sonora, Mexico, in 2015. Currently, he is conducting a research as a postdoctoral fellow at Research Center for Advanced Materials (CIMAV-CONACYT). His research interests focuses in the extraction, characterization, and application of lignins isolated from different sources, the development of lignin-starch composites, and the synthesis of conducting polymers-lignin composites for application in high-performance supercapacitors.



Patricia I. Torres-Chávez is a Senior Researcher and full-time professor in Food Science and Technology at the Department of Food Research & Graduate Program, University of Sonora (DIPA-UNISON), Mexico. Dr. Torres received her Ph.D. degree in Food Science at Research Center for Food Development (CIAD-CONACYT), Mexico, in 2000. Her research interests mainly focuses on the study of carbohydrates functionality and proteins in cereals and the application of lignin extracted from agricultural wastes.



Jorge L. Olmedo-Martínez received his M.Sc. degree in Materials Science at Research Center for Advanced Materials (CIMAV-CONACYT), Mexico, in 2016. He is currently a Ph.D. student at the University of the Basque Country, Spain. His subjects of interest include the study of solid polymer electrolytes for lithium batteries, and the development of advanced dye-sensitized solar cells.

Alejandro Vega-Rios received his D.Sc. degree in Chemistry at Technological Institute of Tijuana (Graduate Center & Chemistry Research), Mexico, in 2011. He made a postdoctoral stay at Research Center for Advanced Materials, (CIMAV-CONACYT), Mexico in 2012. In 2013, he began working at CIMAV as a Senior Researcher and full-time professor. His research interests included synthesis, characterization and modification of polymeric materials, design and synthesis of conjugated polymers, and synthesis of modified cellulose nanocrystals with RAFT agents.

* Corresponding author.
E-mail address: jose.espinoza@cimav.edu.mx (J.L. Espinoza-Acosta).

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Sergio G. Flores-Gallardo received his D.Sc. degree in Polymers at Research Center in Applied Chemistry (CIQA-CONACYT), Mexico, in 2003. He is the head of Engineering and Chemistry of Materials Department at Research Center for Advanced Materials, (CIMAV-CONACYT). His research focuses on the polymers processing and, in particular, on additive manufacturing such as nanocomposites, multifunctional polymers as chain extenders, 3D printing.

E. Armando Zaragoza-Contreras received his D.Sc. degree in Polymers at Research Center in Applied Chemistry (CIQA-CONACYT), Mexico, in 1999. He is currently a Senior Researcher at Research Center for Advanced Materials (CIMAV-CONACYT), Mexico. His subjects of interest include conducting polymers, chemical sensors, polymers in dispersed media, and nanocomposites.

1. Introduction

Nowadays, the environmental problems, the reduction of fossil fuel sources, and the severe environmental safety policies are forcing the industry to be sustainable. In the energy industry, there is a great interest in developing more efficient energy storage devices using renewable raw materials [1]. Over the past decade, important research directed to improve the field of energy storage devices and renewable energy devices using alternative materials was performed. *Iota*-carrageenan [2], cellulose [3], and lignin [4] are considered suitable natural polymers for the development and improvement of energy devices because they are inexpensive and highly abundant. Particularly lignin has gained interest because it is a non-toxic aromatic polymer obtained in large amounts (up to 50 million tons per year) as a by-product from the industrial processing of cellulose pulp and the production of cellulosic fuels [5]. This lignin acquires both a name and chemical properties based on their extraction method. Over three decades, the applications of several types of lignin have been explored outside the pulp and paper industry, for example, as an additive for concrete [6], feed additives [7], and phenolic resins [8,9]. In the last two decades, the design and fabrication of lignin advanced composites, in combination with other organic and inorganic polymers, have been the focus of much research [10,11]. More recently, the biological activity of lignins (e.g., antioxidant and biological activity) from different sources has been studied [12–15], which, under certain circumstances, were more efficient than some synthetic antioxidants [16].

In spite of a large number of possible applications reported in the literature for lignin, in the energy storage field, its application is still limited [17]. However, over the last few years, considerable research has reported the exploration of several lignins as an interesting component for applications in storage energy devices. The first research reported the use of lignosulfonate (LS) as an expander of lead–acid batteries for increasing their useful life [18]. The incorporation of LS retards the reactions of charge and discharge but increases the capacity of the negative plates. In lithium batteries, some lignins have been used in the preparation of organic cathodes with promising results [19]. Besides, the application of lignin as a natural binder for lithium-ion batteries (LIBs), with the aim of replacing conventional binders which are toxic to animals and humans, has been explored [20]. Many composites based on conductive polymers doped with LS or alkali lignin have been investigated for application in electrochemical capacitors [21]. The use of some lignins in the development of organic solar cells [22] and fuel cells [23] have been also explored. Furthermore, lignin is considered as one of the most viable "green" carbon precursors [24]. For this reason, several lignins are being transformed into carbonaceous materials with well-defined porous structure, such as activated carbon nanofibers and hierarchical porous carbons (HPCs) [25], which have been used in the preparation of electrodes for LIBs and supercapacitors [26].

A large number of reviews about lignin, with different approaches, have been published, for example, the use of lignin and its derivates with beneficial effects on the human health [27], the antioxidant and antimutagenic activity of different lignins [28], the elaboration and design of lignin-based biodegradable composites [29], and the preparation of nanoparticle based-lignin and other nanostructures with different applications [30]. The conversion and depolymerization of lignin using thermochemical methods for obtaining valuable chemicals have also been reviewed [31–33]. In the energy storage energy field, the role of lignin as electrode and binder for batteries has been brefly reviewed [34,35]. However, although there is considerable research related to the use of lignin in the development of energy devices, a review devoted to this specific topic has not been published yet. For the reasons as aforementioned, this review provides an overview of most relevant advances concerning the use of lignin in the fields of energy storage devices and solar cells.

2. Background of lignin

Plants are composed of cellulose, hemicellulose, lignin, and minority compounds. Lignin comprises 20–30% of the plants solid weight, where the remaining 70–80% are cellulose and hemicelluloses. In plant tissues, lignin is not available as an independent polymer. Instead, it is covalently bound to the polysaccharides cell wall such as cellulose and hemicellulose. The separation of lignin from the rest of the cell wall components includes the rupture of natural lignin using different separation methods. The literature reports that lignin is an amorphous and highly branched polyphenolic polymer, composed of three main units, *p*-coumaryl, coniferyl, and sinapyl alcohol, jointly called monolignols [36]. The lignin polymer network is obtained by the radical random coupling of the monolignols. In the lignin molecule, the aromatic constituents of the three main monolignols are *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, which have a different methoxylation degree on the aromatic ring (Fig. 1). The proportion of H, G, and S units is highly variable according to the plant type [37]. For example, G units are abundant in gymnosperms, GS units constitute hardwood, while the grasses contain the three monolignols HGS-units [38]. The main interunit linkages in the lignin structure are condensed bonds (β–O–4, α–O–4, β–β) and uncondensed bonds (β–5, β–1, 5–5) [39].

2.1. Lignins isolation processes

There are many isolation processes reported to separate lignin from the other polymers contained in the biomass [41]. The sulfate and the sulfite processes are the dominant isolation, producing more than 90% of the industrial lignin. In these processes, kraft lignin and lignosulfonates are obtained as a by-product of the wood processing. In the sulfate process, kraft lignin is separated from the rest of the components under strongly alkaline conditions [42] breaking the lignin into smaller chains, making it soluble in water and alkali solutions. The use of sulfur compounds, such as sodium sulfide, produces lignin with hydrophobic aliphatic thiol groups (Table 1). In the sulfite pulping process, lignosulfonate is obtained in a similar way to the kraft lignin but the alkaline medium is replaced with an acidic one. LS contains sulfur but in the form of sulfonate groups (SO_3^-). A simplified chemical structure of various lignin is shown in Fig. 2.

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