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Review

The controlled release of bioactive compounds from lignin and lignin-based biopolymer matrices

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ABSTRACT

This article presents the perspectives on the lignin-based controlled release (CR) of bioactive materials which are based on the researches that took place over the last three decades. It encompasses three broad spectra of observations: CR formulations with mixed-matrix of lignin; CR formulations with modified lignin; and the lignin-based CR formulation modelling. The article covers a range of bioactive materials aimed for agricultural utilisations viz. herbicides, pesticides, insecticides and fertilisers for their controlled release studies, which were formulated either with lignin or lignin-based biopolymers. The inherent complexities, structural heterogeneities, and the presence of myriad range of functionalities in the lignin structure make it difficult to understand and explaining the underlying CR behaviour and process. In conjunction to this issue, the fundamental aspects of the synthetic and biocompatible polymer-based drug controlled release process are presented, and correlated with the lignin-based CR research. The articulation of this correlation and the overview presented in this article may be complemented of the future lignin-based CR research gaining better insights, reflections, and understanding. A recommended approach on the lignin depolymerisation is suggested to fragmenting the lignin, which may be tailored further using the re-polymerisation or other synthetic approaches. Thus it may allow more control with flexibilities and improved properties of the modified lignin materials, and help achieve the desired CR outcomes.

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1. Introduction

Lignocellulosic materials are abundant in nature. The cellulose is the major constituents of all plant materials forming about half to one-third of plant tissues [2]. Lignocellulosic materials are renewable and expected to be utilised as alternatives to fossil resources. A particular example of a lignocellulosic bagasse material may reflect on the state of its abundance. According to statistics, 54 million tons of dry sugar-cane bagasse was produced annually throughout the world [40]. The bagasse is fibrous by-product, and generally remains after sugar is extracted from the sugar-cane. The lignocellulosic materials are widely used either as a fuel source in the sugar factory or raw materials for the pulp and paper industry or various applications of lower values. Lignocellulosic materials contain about 40–50% glucose-based polymeric cellulose as the

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dry residue, and are mostly crystalline; whereas about 25–35% is hemicellulose which are amorphous polymer, and are composed of xylose, arabinose, galactose, glucose and mannose [28]. The remainder of the lignocellulose composition are mostly lignin; where other types of residuals exist as minerals, waxes, and chemical compounds. Lignin is a ramified polymer made up of phenylpropane molecular units [20,30]. Lignins are found in an amorphous state. The cellulosic and hemicellulosic fractions are encrusted in an amorphous layer of lignin [51].

The natural abundance of lignin is second to cellulose; in a global scale, around 5×10^6 metric tons of lignin is produced annually [29]. Lignins are generally obtained as a by-product from the black liquor of chemical pulping process [17]. Lignins are also recovered as a residue from lignocellulosic biomass-based ethanol production [51]. A range of processes are involved where lignins are obtained from various plants or biomass. Among them, the most notable processes are: alkaline pulping process, sulphite pulping process, process of milling in ball mill, enzymatic release process, extraction with organic solvents, and steam explosion process [31]. Lignins are readily available plant-derived biocompatible materials, which are relatively cheap. Currently lignins are under-utilised resource.

It is apparent from the past undertaken researches that, a range of strategies have been implemented so far towards adding more commercial values to lignin, and finding the proper ways of the lignin biomass utilisation. Few examples of such utilisations include: (i) converting lignin to fuels or other value added products; (ii) utilising lignin as a carrier for the CR of bioactive compounds especially in the agricultural areas where the bioactive materials are used as pesticides, herbicides, insecticides and fertilisers; (iii) depolymerising the lignin to simple monomeric and oligomeric O-containing aromatic units that can be considered as useful intermediate for upgrading to higher value products such as polymers; and, (iv) biodegradation or biotransformation of lignin to its unit compounds that can be tailored further to more useful materials with high commercial values. The focus of this article is on the lignin-based CR of bioactive formulations, and their researches in this particular area.

Prior to formulating any lignin-based CR materials the pertinent aspects that require careful considerations, are: (i) consideration about the ultimate fate of lignin substrate or carrier and, understanding the realistic condition of the materials which will be left behind in the environment after all bioactive compounds are diminished from the formulated CR matrix, (ii) the degradation profiles of the lignin carrier materials that may progress in various possible ways such as hydrolysis, structural collapse, microbial degradation, effect of water, effect of pH of the soil on the materials, effect of salinity of soils, and, (iii) an understanding about the degraded residual components that requires to be adequately responsive to the environment for sustenance. Owing to the variable properties of bioactive materials, their losses between application and uptake by the target organism can be considerable. The bioactive materials which are more volatile or have short persistence and, is dependent on first order release kinetics could be intrinsically inefficient because of rapid environmental losses. Some persistent bioactive compounds may have undesirable side-effects. The dilemma of these two properties can partially be offset by the use of effective controlled release formulation which can release the bioactive compounds from lignin matrices at a rate appropriate to their application [49].

In this article, a brief overview is presented on the CR of bioactive materials from the lignin-based formulations. It is based on the researches that took place over the last three decades. A range of bioactive materials (total of 13) which were used in the previously undertaken researches (e.g. herbicides, pesticides, insecticides and fertilisers) are discussed. The presented overview is encompassed with three broad areas of observations: (i) CR formulations with mixed-matrix of lignin, (ii) CR formulations with modified lignin, and, (iii) modelling of lignin-based CR formulations. In this article, all presented bioactive materials are used with their commercial names for the purpose of simplicity. However, the types, corresponding chemical structures, and physico-chemical properties of all involved bioactive materials are presented in Table 1. A brief discussion is presented on the fundamental aspects of synthetic and biocompatible polymer-based drug CR research and, is correlated to the lignin-based CR research. Such correlation may render better insights, reflections, and well understanding and, in turn, may be helpful in translating into lignin-based CR research for improved outcomes in the future. For future prospects, a recommended approach on the lignin depolymerisation is suggested to fragmenting the lignin, which may be tailored further using the re-polymerisation or other synthetic approaches. This way it may allow more control with flexibilities and improved properties of the modified lignin materials, and help achieve the desired CR outcomes.

2. Characteristics of lignin biopolymer

Lignin is a macromolecule which is built up from "polyphenyl propane" units with β-*O*-4-aryl ether linkages; and, is found to be the most abundant inter-ether unit linkage in all lignin. Lignin consist of a single inter monomeric linkage; and thus connects their monomers which are covalently bonded as alkyl-aryl ether and C—C bonds. The lignin copolymer structure has three defined phenylpropane monomer units as mono-lignols, such as para-cumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Apart from β-*O*-4-aryl ether linkages, the other major linkages present in the ligninstructures of various sources are: α-*O*-4-aryl ether, 4-*O*-5-diaryl ether, β-5-phenylcoumaran, 5-5-biphenyl, β-1-(1,2-diarylpropane) and β-β-(resinol) [33]. The chemical structural unit of poly(phenylpropane) present in lignin biopolymer [30] is presented in Fig. 1.

Lignins are non-amphiphilic in nature; and, have three dimensional (3D) networked aromatic amorphous polymer structures. Lignin has high degree of chemical stability and, consists of aromatic rings with side chains. The major functional groups present in Lignin are hydroxyl, methoxyl, carbonyl, and carboxyl. The presence of number of functional groups and their relative amounts depends on the origin and the extraction process employed [46]. The main reactive groups of lignin are present in their side chains as *p*-substituted phenolic hydroxyl groups. Lignin lacks stereoregularity or structural integrity as the repeating units in the lignin molecule is too heterogeneous and complex, and thus makes it difficult to determine its correct structure [21]. Lignin is partly soluble in neutral organic solvents[52]. Some of the methoxyl groups of native lignin can be hydrolysed due to the influence of variable conditions

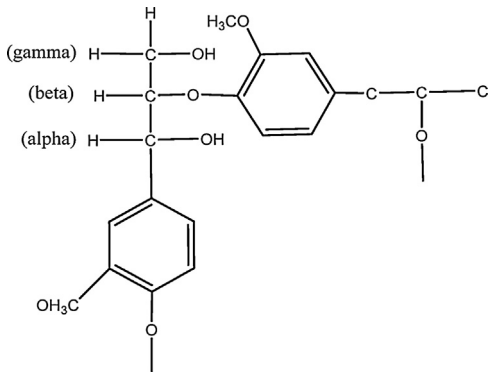

Fig. 1. The chemical structure of phenylpropane unit present in lignin biopolymer [30].