Chapter 58
Microbial Ligninolysis: Avenue for Natural Ecosystem Management

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ABSTRACT
Lignin is the second most abundant natural polymeric carbon source on earth after cellulose. It is a plant-originated polymer with three-dimensional network of dimethoxylated (syringyl), monomethoxylated (guaiacyl), and non-methoxylated (phydroxyphenyl) phenylpropanoid and acetylated units. The structural complexity and insolubility of lignin make it highly recalcitrant for degradation. Its biological degradation is critical to the global carbon cycle. Bioligninolysis involves application of microorganisms and their enzymes in degradation of lignin which provide environmental friendly technology for various industrial applications. As a major repository of aromatic chemical structures, lignin bears paramount significance for its removal from woody plants/lignocellulosic material, owing to potential application of bioligninolytic systems on commercial scale. This chapter provides an overview of microbial ligninolysis and its role in carbon cycling, various industrial process and pollution abatement for natural ecosystem management.

INTRODUCTION
Lignin is the most important renewable source of organic carbon on earth and represents nearly 30% of the carbon sequestered in plant materials annually (Boerjan et al., 2003). About 438–425 million years ago (even before the appearance of vascular water-conducting cells), lignin like moieties were present in the earliest terrestrial life (Rogers & Campbell, 2004). Lignin as a major repository of aromatic chemi-
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cal structure has a central point for its removal owing to potential applications of ligninolytic systems in industries, such as bioethanol production and manufacture of cellulose-based chemicals and materials, pulping, bleaching, and treating the wastes (Mester & Tien, 2000). Pulp and paper industries are the primary user of wood and non-wood products for production of paper. In paper making industries lignin as a coloured material must be removed from pulp as it makes mechanical pulp fibers stiff and turn newsprints yellow. During the chemical and mechanical pulping process almost 90-95% dissolved lignin generated as wastewater, which is also known as black liquor. Whereas, in bioethanol production from lignocellulosic biomass, the lignin barrier limits the accessibility to fermentable sugars (derived from cellulose and hemicelluloses). Conventionally disruption of this barrier is achieved through mechanical and chemical methods, including high-temperature and strong chemical reagents. During which, chemicals react with lignin and other components of the pulp, results in formation of chlorinated organics that further contribute colour to wastewater (D’Souza et al., 2006).

A controlled biocatalytic breakdown process can represent lignin as a major renewable source of aromatic and phenolic bio-products, which would be valuable raw materials for the food and flavour industry, and for fine chemicals and materials synthesis such as \( \tau \)-cinnamic acid, ferulic acid, vanillic acid, vanillin acid and gallic acid (Raj et al., 2007). In the future, biorefinery processes will extract first high-value chemicals present in the biomass, such as fragrances, flavoring agents, food-related products, high-value nutraceuticals, and other fine chemicals. Later, plant polysaccharides and lignin will be processed into feedstocks for bio-derivate materials, bulk chemicals, and fuels (Ragauskas et al., 2006). Lignin content in plant biomass is major factor to determine the rate of litter decomposition in different ecosystems. Lignin degradation involves both biochemical and physical processes and regulated by various biotic and abiotic factors. Bioligninolysis involves multiple biochemical reactions, such as cleavage of internomeric linkages, demethylation, hydroxylations, side chain modifications and aromatic ring fission followed by dissimilation of aliphatic metabolites that have to take place simultaneously (Paliwal et al., 2012). Insolubility of lignin and lack of its steroiregularity contribute difficulty in its degradation. Although much work has been done to understand the process of biological lignin degradation, still many aspects of enzymatic degradation of lignin need to explore that could offer a solution to major problem of waste disposal and ecosystem impairment caused by industries.

BACKGROUND

Lignin plays a significant role in terms of protecting microbial access to labile carbon compounds in plants and provides structural integrity to the cell walls of woody plants. Wood and vascular tissues generally contain 20–30 g/kg of lignin, while on earth a proportion of lignin has been estimated equivalent to \( 3 \times 10^{11} \) metric tons (Kirk & Farrell, 1987; Whittaker & Likens, 1975; Rahman et al., 2013). In lignocellulosic material lignin contributes 10-20% by weight and 40% by energy. Because of high energy content lignin can be consider as potential renewable resource of chemicals and fuels (Wang et al., 2013). Bioethanol has been produced since 1970’s via extraction of sucrose. The second generation biofuels have attracted considerable attention over first generation (bioethanol) due to utilization of non-food part of plant crop for bioenergy production by conversion of plant lignocelluloses into bifuels. Therefore, lignin degradation is an important and crucial step not only in biomass conversion but also in nutrient cycling and carbon balance in terrestrial ecosystem. Degradation of lignin in nature can be achieved by two basic processes such as chemical (photolysis) and biological (bioligninolysis or micro-