Science of the Total Environment 576 (2017) 646–659

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Immobilized ligninolytic enzymes: An innovative and environmental responsive technology to tackle dye-based industrial pollutants – A review

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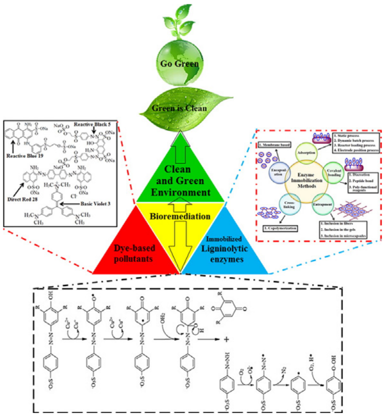
HIGHLIGHTS

- Immobilization strategies and trends in enzyme engineering are reviewed.
- The recent achievements of immobilized LMEs for the degradation of dye-based pollutants are summarized.
- The present review illustrates valorization of LMEs by biotechnology.
- Economic and environmental net benefits of the immobilized enzymes are positive.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 August 2016
Received in revised form 15 October 2016
Accepted 18 October 2016
Available online xxxx

Editor: Jay Gan

Keywords:
Biocatalysis
Green biotechnology
Lignin modifying enzymes
Immobilization
Stabilization
Dye degradation

ABSTRACT

In the twenty-first century, chemical and associated industries quest a transition prototype from traditional chemical-based concepts to a greener, sustainable and environmentally-friendlier catalytic alternative, both at the laboratory and industrial scale. In this context, bio-based catalysis offers numerous benefits along with potential biotechnological and environmental applications. The bio-based catalytic processes are energy efficient than conventional methodologies under moderate processing, generating no and negligible secondary waste pollution. Thanks to key scientific advances, now, solid-phase biocatalysts can be economically tailored on a large scale. Nevertheless, it is mandatory to recover and reprocess the enzyme for their commercial feasibility, and immobilization engineering can efficiently accomplish this challenge. The first part of the present review work briefly outlines the immobilization of lignin-modifying enzymes (LMEs) including lignin peroxidase (LiP), manganese peroxidase (MnP) and laccase of white-rot fungi (WRF). Whereas, in the second part, a particular emphasis has been given on the recent achievements of carrier-immobilized LMEs for the degradation, decolorization, or detoxification of industrial dyes and dye-based industrial wastewater effluents.

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http://dx.doi.org/10.1016/j.scitotenv.2016.10.137
0048-9697/

Contents

1. Statement of problem and potential opportunities

Undoubtedly, the industrial establishment is necessary for the economic growth. However, it is always associated with a cost paid regarding environmental pollution (Daâssi et al., 2014; Bilal and Asgher, 2015a, 2015b; Lade et al., 2015; Dai et al., 2016). Furthermore, the release of numerous pollutants with or without partial treatments, which are toxic in nature, especially industrial-based original dyes and/or dyes-based toxic wastewater effluents (Verlicchi et al., 2012; Ba et al., 2014; Hayat et al., 2015; Zucca et al., 2016; Bilal et al., 2016a–d), is a major environmental concern. The scientific literature has shown that annually >7 × 10^5 tons of dyes are produced, and nearly 10–15% of the total dyes get discharged in surrounding environment due to the low yields of textile processes (Robinson et al., 2001; Keharia and Madamwar, 2003). In addition to the textile industry, dyes are also being used in many industries including paper and pulp, food, cosmetic, pharmaceutical, tannery, photographic and plastic industries. (Ramírez-Montoya et al., 2015), though in different proportion with mix combinations. Moreover, owing to their carcinogenic, genotoxic and/or mutagenic nature, the discharge of these chemical agents into the main water streams seriously endangered the equilibrium of natural ecosystem (Leme and Marin-Morales, 2009; Salleh et al., 2011; Sathishkumar et al., 2014; Vakili et al., 2014; Punzi et al., 2015), thus posing serious health-related issues. Therefore, the effective treatment of dye-based effluents without producing any secondary pollution is indispensable to impede ecosystem deterioration.

During the past several years, the environmental engineers are continuously struggling to develop a new or improve the existing innovative technologies. Evidently, various treatment approaches have been attempted for the treatment of dyes or effluents (dos Santos et al., 2007; Arulkumar et al., 2011; Kabra et al., 2013; Sathishkumar et al., 2014). Much sadly, none of them has been implemented, at large scale, due to the following reasons among others i.e. (1) high treatment costs, (2) labor-intensive, (3) extreme operational conditions, (4) toxic by-products, and (5) less adaptability to wide-ranging structurally different dyes, etc. (Fongsatitkul et al., 2004; Fersi and Dhahbi, 2008; Srinivasan and Viraraghavan, 2010; Hayat et al., 2015). Hence, additional effort and broader validation for industrial applications are mandatory to alleviate this problematic issue.

Though the remediation science is not a new, however, the industrial exploitation of enzymes, as a green catalyst, for remediation purposes has received lots of interest recently, since they function in a wider pH and temperature ranges, contaminant and saline concentrations (Rao et al., 2014). The strong oxidative capabilities, low substrate specificity, and no steric selectivity render the WRF-based LMEs, particularly fascinating for environmental exploitability (Asgher et al., 2014). Though, the natural catalysts are efficient, vigorous and sustainable. However, they are often not perfectly adapted for industrial exploitability (Krajewska, 2004). In this context, enzyme immobilization engineering offered an effective and remarkable approach to avoid instability problems and obtain industrially desirable biocatalyst (Krajewska, 2004; Kunamneni et al., 2008; Spahn and Minteer, 2008; Wang et al., 2012; Liese and Hilterhaus, 2013). Besides heat inactivation issues, the immobilized catalyst also offers greater stability against heavy metals, salinity, organic solvents, denaturants and autolysis issues (Gardossi et al., 2010). Table 1 exemplifies a comparative evaluation of merits and demerits of various immobilization strategies.

2. White-rot fungi and their lignin-modifying enzymes

WRF are a physiological group of basidiomycetes that possess a remarkable capability to degrade lignin and lignin-like substances by giving a bleached white appearance to the wood, they attack (Hestbjerg et al., 2003). The LMEs mainly comprised on lignin peroxidase (LiP, E.C. 1.11.1.14), manganese peroxidase (MnP, E.C. 1.11.1.13) and laccase (Lac, EC 1.10.3.2) along with other supporting enzymes such as versatile peroxidase (VP, E.C. 1.11.1.16), glyoxal oxidase (GO, E.C. 1.2.3.5), aryl alcohol oxidase (AAO, E.C. 1.1.3.7), oxalate decarboxylase (OD, E.C. 4.1.1.2) and cytochrome P-450 monooxygenase (E.C. 1.14.14.1) (Asgher et al., 2008; Iqbal et al., 2011). Different WRF strains secrete individual and multiple ligninolytic enzymes complexes in various proportions under suitable fermentation environment. Therefore, WRF has been divided into four groups based on their ligninolytic enzymes composition and secretion in various categories as mentioned below:

a. LiP, MnP and laccase producing: *Pleurotus ostreatus* and *Pleurotus eryngii*, *Trametes versicolor*, *Ganoderma lucidum* and *Schyzophylum commune* (Périé et al., 1998; Asgher et al., 2010; Iqbal et al., 2011; Asgher et al., 2014).
b. MnP and laccase producing: *Pycnoporus cinnabarinus* and *Phlebia radiata* (Stewart and Cullen, 1999; Asgher et al., 2014).
c. LiP and MnP producing: *Phanerochaete chrysosporium* (Veronica et al., 2010; Asgher et al., 2014).
d. LiP and laccase producing: *Dichomitus squalens* (Garmaroody et al., 2011; Asgher et al., 2014).

LiP has the discrepancy of being able to oxidize methoxylated aromatics deprived of a free phenolic group by generating cationic free radicals which react further through multiple pathways, such as ring