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Review

Fungal decolouration and degradation of azo dyes: A review

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ABSTRACT

The textile industry is a substantial consumer of water and produces enormous volumes of contaminated water; the most important contaminants are azo dyes. Fungal processes for the treatment of textile wastewater have the advantage of being cost-effective and environmentally friendly and producing less sludge. Unlike bacteria, fungi possessed strong ability of degrading complex organic compounds by producing extracellular ligninolytic enzymes including laccase, manganese peroxidase and lignin peroxidase, hence, researchers paid more attention on fungi in recent years. The mechanism of fungal decolouration occurs from adsorption, enzymatic degradation or a combination of both. The goal of fungal treatment is to decolorize and detoxify the dye contaminated effluents. In this review, we summarize the methodologies used to evaluate the toxicity of azo dyes and their degradation products. Recent studies on the decolouration or degradation of azo dyes with Advanced Oxidation Processes (AOPs) and Microbial Fuel Cells (MFCs) are discussed in this review.

1. Introduction

In recent years, greater attention has been paid to the discharge of effluents containing synthetic dyes (Miranda *et al.*, 2013). Worldwide, 280,000 tons of textile dyes are discharged in industrial effluents every year (Jin *et al.*, 2007). To dye 1 kg of cotton with reactive dyes, 0.6–0.8 kg NaCl, 30–60 g dyestuff and 70–150 L water are necessary; the wastewater produced has 20–30 % of the applied unfixed reactive dyes, with an average concentration of 2000 ppm, high salt content and dyeing auxiliaries (Babu *et al.*, 2007). The release of these effluents into the environment is undesirable due to the serious environmental problems linked with the dyes and their breakdown products (Ozdemir *et al.*, 2013). Among commercial synthetic dyes, azo dyes are the largest class with a broad range of colours and structures and represents up to 70 % of the total textile dyestuffs used (Lang *et al.*, 2013). Azo dyes are regularly used in various applications in food, pharmaceutical, paper, cosmetic, textile and leather industries (Saratale *et al.*, 2013). These dyes belong to the class of aromatic and heterocyclic compounds having the azo bond (–N=N–) which are recalcitrant and

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even possess carcinogenic properties (Saratale *et al.*, 2011). As they are introduced into the environment due to the inefficiency during the dyeing process and subsequent discharge, they accumulate mainly in water bodies and have adverse effects in terms of dissolved oxygen (DO), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), colour, etc., (Saratale *et al.*, 2013; Solís *et al.*, 2012). Therefore, their removal from wastewater is of utmost importance before discharge of the wastewater into the environment (Ayed *et al.*, 2011).

Extensive research and development has focussed on biological methods as an eco-friendly alternative for remediation of dyes (Kaushik and Malik, 2009). Most studies on azo dye biodegradation have focused on bacteria and fungi, in which bacteria were widely used for azo dyes decolorization due to their high activity, extensive distribution and strong adaptability (Pearce *et al.*, 2003; Dos Santos *et al.*, 2007). However, decolorization of products such as aromatic amines can inhibit the activity of bacteria (Qu *et al.*, 2010). By contrast, fungi can degrade complex organic compounds through catalysis with extracellular ligninolytic enzymes including laccase, manganese peroxidase and lignin peroxidase (Gomi *et al.*, 2011). Many fungal species such as *Pleurotus ostreatus*, *Pichia* sp., *Penicillium* sp., and *Candida tropicalis*, have been confirmed to decolorize azo dyes through adsorption and/or degradation (Kalmis *et al.*, 2008; Qu *et al.*, 2010; Gou *et al.*, 2009; Tan *et al.*, 2013). Moreover, some fungi can partially or even completely mineralize azo dyes (Miranda *et al.*, 2013; Qu *et al.*, 2012; Tan *et al.*, 2013). Compared with the dyes themselves, some decolorization intermediates such as aromatic amines and phenolics can be highly toxicity and lower biodegradability. Fungi have shown strong adaptability and efficiency in the removal of these aromatic compounds. For instance, the fungal strains belonging to *Thamnidium elegans*, *Zygorhynchus moelleri* and *Yarrowia lipolytica* were confirmed to efficiently degrade aromatic phenolics (Papanikolaou *et al.*, 2008; Bellou *et al.*, 2014). In this context, fungi offer an efficient system due to large surface area and easy solid–liquid separation (Mishra and Malik, 2013). Fungi also possess multiple mechanisms for degradation of organic and inorganic contaminants (Awasthi *et al.*, 2014). However, pollutant removal has been largely studied under single pollutant exposures and often using pure cultures (Singh and Singh, 2014; Mishra and Malik, 2012). These studies demonstrate the utility of a certain fungal strain for removing a particular pollutant. Moreover, there are wide variations in the dye uptake capacity among various strains. Industrial effluents are a cocktail of various metals and organic contaminants (Ruta *et al.*, 2010; Yadav *et al.*, 2010). For example, textile industry effluents contain both residual dyes (from dyeing operations) and metals (used as mordant). Likewise pulp and paper industries, tannery industries and dyeing industries are also generate effluents rich in metals as well as dyes. Therefore, in order to develop a biological system capable of remediating such wastewater, diverse types of microbial strains need to be used to form of a consortia (Mahapatra *et al.*, 2014). The use of a microbial consortia has a clear advantage for bioremediation applications as a richer metabolic network can be preserved and exploited for the bioremediation of co-contaminated matrices. Therefore, in a mixed waste stream, each of the consortium partners can specialize in the uptake of a particular contaminant. As a result, simultaneous removal of several contaminants can be successfully accomplished.

Therefore, exploitation and study of new fungal strains capable of degrading azo dyes efficiently are still necessary for field application. Though the use of specific contaminant-degrading fungi in the wastewater treatment system can provide an effective way to enhance the degradation of toxic organic pollutants, high degradation rate of pollutants would not persist for a long time in wastewater treatment systems due to the loss of degrading microorganisms through being washed out from the system (Li *et al.*, 2013). Immobilization of fungi has been suggested as a strategy for maintaining efficient degradation biomass in the systems, and different methods of immobilization have been developed which lead to improved effectiveness in wastewater treatment (Moreno-Garrido, 2008). Entrapment is one of the most commonly used methods for immobilizing single-celled microorganisms such as yeast, which can effectively avoid the loss of microorganisms from treatment systems. In this way, the microbial cells are immobilized in alginate beads or polyvinyl alcohol (PVA) gel pellets (Samuel *et al.*, 2013; Martínez *et al.*, 2013). Unlike the bacteria in conventional wastewater treatment systems, aerobic white-rot fungi (WRF) can degrade wide varieties of resistant compounds including textile dyes by non-specific extracellular enzymes (Yang *et al.*, 2013). Several white rot fungi like *Phanerochaete chrysosporium* and *Trametes versicolor*, due to their efficient ligninolytic enzymatic systems, have been reported to degrade or sequester azo, heterocyclic, reactive or polymeric dyes (Solís *et al.*, 2012). This review summarizes the recent achievements in the fungal technologies developed for the removal of azo dyes using simulated effluents and real textile industry effluents. The principal factors that affect dye removal are analysed, and the fungal decolouration systems based on the use of yeast, filamentous fungi, genetically modified strains, fungal consortia, and fungal processes in combination with AOPs and MFCs are discussed with particular reference to the analysis of the toxicity of the metabolic products of azo dye decolouration and the methodologies used to evaluate this toxicity.

2. Generalities in the fungal decolouration of azo dyes

A wide variety of fungal organisms are capable of decolorizing a wide range of azo dyes (Fu and Viraraghavan, 2001). Many genera of fungi have been employed either in living or inactivated form. The use of white-rot fungi such as *P. chrysosporium* in decolorizing textile wastewater has been widely reported in literature (Bilgic *et al.*, 1997; Cammarota and Sant Anna, 1992; Lankinen *et al.*, 1991; Tatarko and Bumpus, 1998; Young and Yu, 1997; Gomaa *et al.*, 2008; Sharma *et al.*, 2009; Faraco *et al.*, 2009). Apart from white-rot fungi, other fungi such as *Aspergillus niger* (Fu and Viraraghavan, 2000, 2001, 2002), *Rhizopus arrhizus* (Zhou and Banks, 1991), *Rhizopus oryzae* (Gallagher *et al.*, 1997) can also decolorize and/or biosorb diverse dyes.