



Research review paper

## Dye removal by immobilised fungi

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### ABSTRACT

Dyes are widely used within the food, pharmaceutical, cosmetic, printing, textile and leather industries. This has resulted in the discharge of highly coloured effluents that affect water transparency and gas solubility in water bodies. Furthermore, they pose a problem because of their carcinogenicity and toxicity. Therefore, removal of such dyes before discharging them into natural water streams is essential. For this, appropriate treatment technologies are required. The treatment of recalcitrant and toxic dyes with traditional technologies is not always effective or may not be environmentally friendly. This has impelled the search for alternative technologies such as biodegradation with fungi. In particular, ligninolytic fungi and their non-specific oxidative enzymes have been reported to be responsible for the decolouration of different synthetic dyes. Thus, the use of such fungi is becoming a promising alternative to replace or complement the current technologies for dye removal. Processes using immobilised growing cells seem to be more promising than those with free cells, since the immobilisation allows using the microbial cells repeatedly and continuously. This paper reviews the application of fungal immobilisation to dye removal.

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### 1. Introduction

Synthetic dyes have increasingly been used in the textile and dyeing industries because of their ease and cost-effectiveness in synthesis, firmness, high stability to light, temperature, detergent and microbial attack and variety in colour compared with natural dyes. This has resulted in the discharge of highly polluted effluents. Normally colour is noticeable at a dye concentration higher than 1 mg/L and an average concentration of 300 mg/L has been reported in effluents from textile-

manufacturing processes (Gonçalves et al., 2000; O'Neill et al., 1999). Over  $7 \times 10^5$  ton and approximately 10,000 different dyes and pigments are produced annually world-wide, about 10% of which may be found in wastewater (Deveci et al., 2004). Colour interferes with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota and interferes with gas solubility in water bodies (Banat et al., 1996). In addition, many dyes are believed to be toxic carcinogenic or to be prepared from known carcinogens such as benzidine or other aromatic compounds that might be formed as a result of microbial metabolism (Novotny et al., 2006; Karimniaae-Hamedani et al., 2007). Hence, removal of these dyes from the effluents is necessary. The structural diversity of dyes comes from the use of different chromophoric groups (e.g. azo, anthraquinone, triarylmethane and phthalocyanine groups) and different application technologies (e.g. reactive, direct, disperse and vat dyeing) (Heinfling et al., 1998). Common classes of dyes, based on the chromophore present, are shown in Table 1.

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**Table 1**

Dye structures according to their chromophores (<http://stainsfile.info/StainsFile/dyes/class/dyceclass.htm>)

Class	General formula
Acridine	
Antraquinone	
Azo	
Diazonium	
Nitro	
Oxazin	
Phthalocyanine	
Thiazin	
Triarylmethane	

The current existing techniques for the removal of dyes from dye-containing wastewater have serious restrictions such as high cost, formation of hazardous by-products or intensive energy requirements (Stolz, 2001). Table 2 summarises the advantages and drawbacks of different non-biological processes applied to textile wastewater decolouration. The use of bacteria in the biological treatment of dye effluents may result in the generation of colourless dead-end aromatic amines, which are generally more toxic than the parent compounds (Kulla et al., 1983; Banat et al., 1996) and, therefore, may have poor adaptability and limited application to a wide range of dye wastewater (Kulla et al., 1983). Hence, the development of efficient and environmentally friendly

**Table 2**

Advantages and drawbacks of some non-biological decolouration processes applied to textile wastewater (after Robinson et al., 2001)

Physical/chemical methods	Method description	Advantages	Disadvantages
Fenton reagents	Oxidation reaction using mainly H <sub>2</sub> O <sub>2</sub> -Fe (II)	Effective decolouration of both soluble and insoluble dyes	Sludge generation
Ozonation	Oxidation reaction using ozone gas	Application in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical oxidation	Reaction using mainly H <sub>2</sub> O <sub>2</sub> -UV	No sludge production	Formation of by-products
NaOCl Oxidation	Reaction using Cl <sup>+</sup> to attack the amino group	Initiation and acceleration of azo-bond cleavage	Release of aromatic amines
Electrochemical destruction	Oxidation reaction using electricity	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Dye removal by adsorption	Good removal of a wide variety of dyes	Very expensive
Membrane filtration	Physical separation	Removal of all dye types	Concentrated sludge production
Ion exchange	Ion exchange resin	Regeneration: no adsorbent loss	Not effective for all dyes
Electrokinetic coagulation	Addition of ferrous sulphate and ferric chloride	Economically feasible	High sludge production

technologies to reduce dye content in wastewater to acceptable levels at affordable cost is of utmost importance.

By far the single class of micro-organisms most efficient in breaking down synthetic dyes is the white-rot fungi. These fungi constitute a diverse eco-physiological group comprising mostly basidiomycetous and to a lesser extent litter-decomposing fungi capable of extensive aerobic lignin depolymerisation and

**Table 3**

Ligninolytic enzymes and their main reactions (after Hatakka, 2001)

Enzyme and abbreviation	Cofactor	Substrate, mediator	Reaction
Lignin peroxidase, LiP	H <sub>2</sub> O <sub>2</sub>	Veratryl alcohol	Aromatic ring oxidised to cation radical
Manganese peroxidase, MnP	H <sub>2</sub> O <sub>2</sub>	Mn, organic acids as chelators, thiols, unsaturated fatty acids	Mn(II) oxidised to Mn(III); chelated Mn(III) oxidises phenolic compounds to phenoxyl radicals; other reactions in the presence of additional compounds
Versatile peroxidase, VP	H <sub>2</sub> O <sub>2</sub>	Mn, veratryl alcohol, compounds similar to LiP and MnP	Mn(II) oxidised to Mn(III), oxidation of phenolic and non-phenolic compounds, and dyes
Laccase	O <sub>2</sub>	Phenols, mediators, e.g., hydroxybenzotriazole or ABTS	Phenols are oxidised to phenoxyl radicals; other reactions in the presence of mediators
Glyoxal oxidase, GLOX		Glyoxal, methyl glyoxal	Glyoxal oxidised to glyoxal acid; H <sub>2</sub> O <sub>2</sub> production
Aryl alcohol oxidase, AAO		Aromatic alcohols (anisyl, veratryl alcohol)	Aromatic alcohols oxidised to aldehydes; H <sub>2</sub> O <sub>2</sub> production
Other H <sub>2</sub> O <sub>2</sub> -producing enzymes		Many organic compounds	O <sub>2</sub> reduced to H <sub>2</sub> O <sub>2</sub>

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