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Review

Enzymatic decolorization and degradation of azo dyes – A review

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ABSTRACT

Azo dyes are aromatic compounds with one or more –N=N– groups. These dyes are the most important and largest class of synthetic dyes used in commercial applications. Several methods have already been used to treat textile effluents including physico-chemical methods such as filtration, carbon activated, coagulation and chemical flocculation. Although these methods are effective, but they are expensive and involve formation of concentrated sludge that creates a secondary disposal problem. In recent years, use of bioremediation based technologies for treating textile wastewater containing dyes has attracted much interest. The ability of microorganisms and their dye degrading enzymes to decolorize and metabolize the dyes has long been known and has proved to be the best option for bioremediation. As far as decolorization and degradation of textile dyes are concerned, azoreductases, laccases, peroxidases and many other important enzymes seem to have shown great potential to decolorize the textile dyes and these enzymes are considered as effective molecular weapon for bioremediation of azo dyes.

Contents

1. Introduction

Azo dyes make up about one-half of all dyes synthesized and are predominantly used synthetic dyes in the textile, food, paper, printing, leather and cosmetic industries (Chang and Lin, 2001). About 50,000 tons of textile dyes are discharged in the environment annually from dyeing processes globally (Lewis, 1999). They are the most visible indicator of water pollution as some dyes are visible at concentrations as low as 0.005 mg l^{-1} (O'Neill et al., 1999). It has been estimated that approximately 10–15% of the dyes used in dyeing process do not bind with the textile fibers and are found freely into the environment (Asad et al., 2007). These dyes are recalcitrant in nature. According to Jin et al. (2007) an estimated 2.8×10^5 tons of textile dyes are discharged in textile industrial effluent each year worldwide. The release of these dyes into ecosystem is harmful, not only because of its color, but also due to the fact that many azo dyes (Fig. 1) and their breakdown products (colorless amines) are toxic and/or mutagenic to living organisms (Weisburger, 2002; Xu et al., 2007). Azo dyes are believed to be electron deficient xenobiotic compounds because they possess electron withdrawing groups, generating electron deficiency in the molecule (dyes) making them resistant to degradation (Singh et al., 2014). About 80% of azo dyes are used in the dyeing process of

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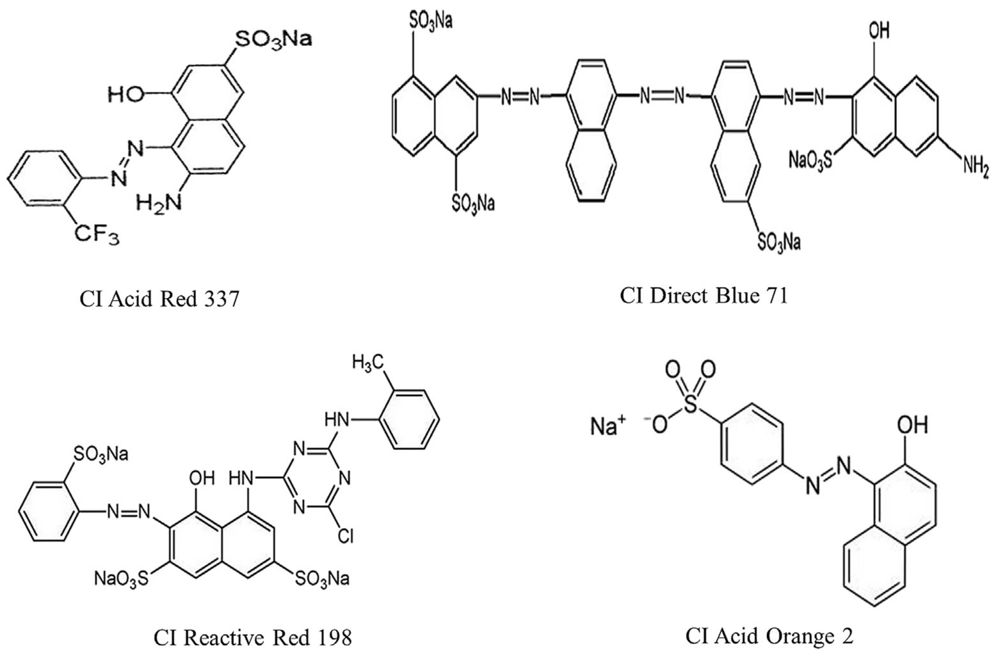

Fig. 1. Structure of some azo dyes.

textile industries. The presence of these dyes in the water ecosystem is the cause of serious environmental and health problems (Fang et al., 2004; Asad et al., 2007). Metanil yellow, an azo dye, has been proved to be hepatotoxic in albino rats (Singh et al., 1987, 1988). The metabolic disposition of metanil yellow and orange II has also been studied using rat and guinea pig as model systems (Singh, 1989, 1991a, 1991b). Metanilic acid and p-amino diphenyl amine were identified as metabolite of metanil yellow where as orange II was degraded into sulfanilic acid and 1-amino-2-nepthol. Azo dyes possess one or more azo group and are widely used in many industries because of their chemical stability and its comparatively easier synthetic processes (Raffi et al., 1997).

Several physico-chemical methods such as adsorption, chemical treatment and ion pair extractions have been used for azo dye decolorization, but these methods are expensive and produce large amounts of sludge after treatment. Extensively used coagulation or flocculation techniques create or generate large amounts of sludge, which requires safe disposal. Adsorption and, to a certain extent, membrane filtration techniques lead to secondary waste streams which need further treatment. There are many reports on the use of physico-chemical methods for color removal from dye containing effluents (Churchley, 1994; Vandevivere et al., 1998; Swaminathan et al., 2003; Behnajady et al., 2004; Wang et al., 2004; Golab et al., 2005; Lopez-Grimau and Gutierrez, 2006) but in present scenario biological treatment methods are most suitable and widely used due to their cost effectiveness, ability to produce less sludge, and eco-friendly nature (Song et al., 2003; Chen, 2006). Different taxonomic groups of microorganisms such as bacteria, fungi, yeast, and algae are capable of degrading azo dyes under anaerobic and aerobic conditions (Talarposhti et al., 2001). Most azo dyes are not cleaved in the presence of oxygen in conventional sewage treatment plants, but are reduced by various microorganisms under anaerobic conditions to their corresponding aromatic amines, which are further degraded in presence of oxygen (Stolz, 2001; Dos Santos et al., 2007). Azo bonds (–N=N–) in these dyes are resistant to cleavage and therefore dyes ultimately increase in the environment upto very high extent. In presence of oxygen, treatment of azo dyes with bacteria usually shows low efficiencies since oxygen is a strong electron acceptor than azo dyes. It is observed that efficient color removal of azo dyes is obtained under anaerobic and static condition with a bacterial culture. Anaerobic processes are usually not specific with regard to microorganisms involved in the reduction of dyes (Stolz, 2001). Therefore, the biological degradation of these dyes by microorganisms has potential advantages in developing decolorizing bio-treatment method of wastewater (Suzuki et al., 2001; Ooi et al., 2007; Gou et al., 2009).

Biological treatment of azo dyes is based on the enzymes synthesized by microorganism. Although these enzymes reduced certain types of azo dyes, some dyes are not degraded efficiently. To establish a biological wastewater treatment system for azo dye removal, it is necessary to screen out microorganisms that express enzymes with wide substrate (dyes) specificities.

In this review, different enzymatic mechanisms by which diverse categories of microorganism produced enzymes bring about the degradation of dyestuffs have been elucidated. This review compiles different enzymatic mechanisms in the decolorization and degradation of recalcitrant azo dyes.

2. Enzymatic decolorization and degradation of azo dyes

The primary step in bacterial decolorization of azo dyes, in either anaerobic or aerobic conditions, is the reduction of the azo bond (–N=N–) chromophore group. This reduction may involve various mechanisms, such as enzymes, low molecular weight redox mediators, chemical reduction by biogenic reductants like sulfide, or a combination of these and the location of the these reactions may be either intracellular or extracellular sites (Fig. 2).

In case of enzymatic decolorization and degradation of azo dyes, two enzymes families i.e. Azoreductases and Laccases seem to have shown great potential. Laccases have great potential to decolorize an extensive range of known industrial dyes (Rodriguez et al., 1999; Reyes et al., 1999). There are certain enzymes like Manganese peroxidase (MnP), Lignin peroxidase (LiP), Polyphenol oxidase