

FTIR Spectroscopy Applied in Remazol Blue Dye Oxidation by Laccases

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ABSTRACT

We have used FTIR with attenuated total reflectance (ATR) technique to analyze the decolourization process of Remazol Blue dye (RB19) caused by the oxidative activity of laccase enzyme. It is known that laccases catalyze the oxidation of a large range of phenolic compounds and aromatic amines carrying out one-electron oxidations, although also radicals could be formed which undergo subsequent nonenzymatic reactions. The enzyme laccase is a copper-containing polyphenol oxidase (EC 1.10.3.2) which has been tested as a potential alternative in detoxification of environmental pollutants such as dyes present in wastewaters generated for the textile industry. In order to ensure degradation or avoid formation of toxic compounds it is important to establish the mechanism by which laccase oxidizes dyes. In this research individual ATR-FTIR spectra have been recorded for several reaction times between 0 to 236 hours, and the temporal dependence of the reaction was analyzed through the relative diminution of the intensity of the infrared band at 1127 cm⁻¹ (associated to C–N vibration), with respect to the intensity of the band at 1104 cm⁻¹ (associated to S=O) from sulfoxide group. Decolourization process of this dye by laccase could be attributed to its accessibility on the secondary amino group, which is a potential point of attack of laccases, abstracting the hydrogen atom. This decolourization process of remazol blue dye by laccase enzyme might in a future replace the traditionally high chemical, energy and water consuming textile operations.

1. INTRODUCTION

Around 10⁶ tons and more than 10,000 different synthetic dyes and pigments are produced annually worldwide and used extensively in textile and printing industries. It is estimated that about 10% are lost in industrial effluents [1]. The discharge of wastewater that contains high concentrations of dyes is a well known problem associated with dyestuff activities causing a high environmental impact when released into the environment without correct treatment. Reactive dyes are extensively used in dyeing activities mainly due to their capacity to bind on textile fibers by covalent bonds. By reason of these attributes, the reactive dyes represent approximately over 12% of the worldwide production [2]. Anthraquinone dyes belong to that group of most durable dyes, so they are often used in products that must satisfy strict requirements concerning resistance to solar radiation and ambient conditions. This useful feature of dyes is naturally a problem in their neutralization [3].

Laccase (EC 1.10.3.2) is a multicopper oxidase, which reduces oxygen to water and simultaneously performs one-electron oxidation of many aromatic substrates such as phenols and aromatic amines [4, 5]. They catalyze the removal of a hydrogen atom from the hydroxyl group or ortho- and para-substituted mono- and polyphenolic substrates and from aromatic amines by one-electron abstraction to form free radicals capable of undergoing further depolymerization, repolymerization, demethylation, or quinone formation [6, 7]. Laccase also has been shown to decolorize anthraquinone, azo and triarylmethane dyes [8, 9, 10, 11]. Initial discolouration velocities depended on the substituents of the phenolic rings in the dye. However, the mechanism(s) by which the laccase oxidise those compounds are not completely determined and this knowledge could be helpful for the process design and optimization. There are some reports on detection of azo type dyes degradation products ([12, 13, 14]. This enzyme decolorizes some azo dyes without direct cleavage of the azo bond through a highly non-specific free radical mechanism, thereby avoiding the formation of toxic aromatic amines [15]. Over long periods of time, there can be a coupling between the reaction products, and even polymerization. Liquid chromatography-mass spectrometry analysis of azo dyes showed the formation of phenolic compounds during the dye oxidation process as well as a large amount of polymerized products that retain azo group integrity [14].

Knowing that oxidation of dyes is a complex process leading to different reactions and products and that those events depend mainly on the type and structure of the dye it is necessary first to detect and identified the foremost