



# Clean Laccase immobilized nanobiocatalysts (graphene oxide - zeolite nanocomposites): From production to detailed biocatalytic degradation of organic pollutant

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## ABSTRACT

In this paper, the Laccase enzyme was covalently immobilized onto nanoparticle of zeolite (NZ)-graphene oxide (GO) composites to prepare the novel nanobiocatalysts for degrading Direct Red 23 as an organic pollutant. Graphene oxide-zeolite (GZ) nanocomposites with 0.03, 0.05, and 0.07 g amounts of GO (denoted as GZ3, GZ5, and GZ7, respectively) were synthesized. The materials were silanized for synthesizing SNZ, SGZ3, SGZ5, and SGZ7. The glutaraldehyde as a cross-linking agent was used to prepare GSNZ, GSGZ3, GSGZ5, and GSGZ7. Laccase was immobilized on them for synthesizing Laccase immobilized nanobiocatalysts including LIGSNZ, LIGSGZ3, LIGSGZ5, and LIGSGZ7. The SEM, FESEM, XRD, FTIR, TEM, HPLC, and UV-vis were used for characterizing materials and dye degradation. The effects of GO ratio, catalyst dosage, dye concentration and pH on pollutant biodegradation were evaluated and optimized. The nanobiocatalysts indicated well reusability over five cycles, high storage stability, and thermal stability.

## 1. Introduction

Several processes use various dyes for lots of applications [1,2]. Different industries applied dyes and their wastewaters have large amounts of materials. Over 700,000 tons of dyes are annually prepared [3]. Therefore, the development of novel materials for improving colored wastewater treatment processes is imperative [4]. Some dyes produce toxic intermediates during their degradation [5]. If not properly treated, the disposal of dye will cause these effluents to release large amounts of dyes into waterways. In this regard, different techniques such as adsorption, biodegradation, and advanced oxidation have been proposed [6–8]. The biodegradation through enzyme has been regarded as a promising manner to others due to its environmentally friendly, excellent performance at harsh situations and high recycling potential.

Laccase has attracted much attention for removing dye because of

its nontoxicity and high efficiency [9,10]. It is one of the multi-copper enzymes with copper atoms as a catalytic center [11,12]. One of the limitations of the use of free Laccase is its poor operational stability and low recyclability. The immobilization of enzymes showed various preferences including high stability, reusability, and easy separation from the water and wastewater. The suitable enzyme carriers should be available, cheap, non-toxic and considerably increased the biocatalytic efficiency [13–16]. Table 1 presented that several enzymes were immobilized on different supports [17–21]. The data indicated that the dye removal rate by some biocatalysts was acceptable but it did not reach 100 %. However, the biocatalysts are green and eco-friendly alternatives for the treatment of polluted water.

Graphene oxide (GO)-based materials can increase the electron transfer between the enzyme and support. They can accomplish good bio-compatibility, the perfect ability for functionalization, and well water dispersibility due to hosting an oxygen functional group [22–24].

**Abbreviations:** FTIR, fourier transform infrared; FESEM, field emission scanning electron microscopy; GO, graphene oxide; GSGZ3, the glutaraldehyde cross-linked silanized SGZ3; GSGZ5, the glutaraldehyde cross-linked silanized SGZ5; GSGZ7, the glutaraldehyde cross-linked silanized SGZ7; GSNZ, the glutaraldehyde cross-linked silanized SNZ; GZ, graphene oxide – zeolite nanocomposite; GZ3, graphene oxide – zeolite nanocomposite (0.03 g of GO); GZ5, graphene oxide – zeolite nanocomposite (0.05 g of GO); GZ7, graphene oxide – zeolite nanocomposite (0.07 g of GO); HPLC, high performance liquid chromatography; LIGSGZ3, the Laccase immobilized GSGZ3; LIGSGZ5, the Laccase immobilized GSGZ5; LIGSGZ7, the Laccase immobilized GSGZ7; LIGSNZ, the Laccase immobilized GSNZ; NZ, nanoparticle of zeolite; SEM, scanning electron microscopy; SGZ3, the silanized GZ3; SGZ5, the silanized GZ5; SGZ7, the silanized GZ7; SNZ, the silanized NZ; TEM, transmission electron microscopy; XRD, X-ray diffraction

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