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Chitosan–halloysite hybrid-nanotubes: Horseradish peroxidase immobilization and applications in phenol removal

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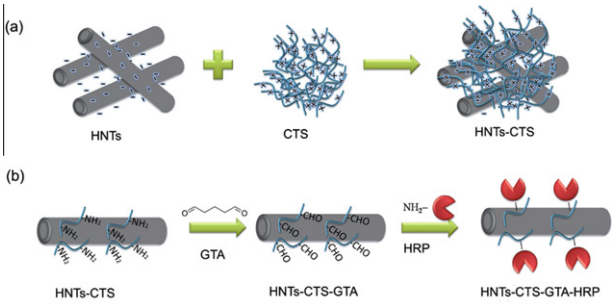
HIGHLIGHTS

- Assembling chitosan onto the halloysite to form hybrid-nanotubes.
- High enzyme loading through covalent binding method.
- About 100% retention rate of original activity for immobilized horseradish peroxidase.
- High removal efficiency for phenol by immobilized enzyme.

GRAPHICAL ABSTRACT



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ABSTRACT

Chitosan–halloysite hybrid-nanotubes were synthesized through the assembly of chitosan onto halloysite, a natural nanotubular aluminosilicate. Nitrogen adsorption–desorption measurement, Fourier-transform infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy analysis were employed to elucidate the structure of the hybrid-nanotubes. The results indicated that the hybrid-nanotubes could form three-dimensional (3D) nanocomposites with hierarchically porous structure. As-prepared structure showed excellent capacity for horseradish peroxidase (HRP) immobilization through cross-linking by glutaraldehyde. The maximum enzyme loading reached as large as 21.5 mg/g, higher than 3.1 mg/g of raw halloysite. After 35 days storage, the immobilized HRP did not undergo any activity loss while the free HRP only retained 27% of its original activity. Phenol removal efficiency by the immobilized HRP was also explored. The result showed the immobilized HRP exhibited overall high removal efficiency for phenol from wastewater.

1. Introduction

Enzymes are versatile biocatalysts that control specific chemical reactions effectively. To make enzymes cost-effective, long-lived, and highly active, various supports have been utilized to immobilize enzymes [1–3]. Nanometer scale materials have potential to serve as reliable enzyme supports due to their large surface-to-volume ratios in comparison with traditional macroscale materials resulting in the reduction of substrate size, which induces the deactivation and the desorption of enzymes during catalysis reactions [4–6]. So far, nanotube is one of the most efficient supports for enzyme immobilization due to its hollow and porous structure as well as large surface area [7]. For example, carbon nanotubes (CNTs) could enhance the catalytic activity and the thermal stability of enzymes; peptide nanotubes could maintain the enzymatic function and the binding inside the nanotube did not hinder the catalytic reaction [8–10]. However, large-scale implementation of the nanotube supports are limited by the price, which is too high to make nanotube immobilized enzyme commercially favorable.

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