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Article

Antifungal Activity of Vanillic Acid Grafted Chitosan Derivatives against Plant Pathogenic Fungi, *Fusarium* sp.

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ABSTRACT: The present work aimed to obtain chitosan derivatives with greater solubility in water, good physicochemical properties, and potent antifungal activity against plant pathogens. In this study, the modification of chitosan (CS) with vanillic acid (VA) was achieved via free radical grafting by optimizing the VA to CS ratio. The grafted CS (VA-*g*-CS) samples were characterized, and their antifungal activity toward *Fusarium solani* and *Fusarium proliferatum* was evaluated. All VA-*g*-CS samples demonstrated successful conjugation between CS and VA, with different grafting degrees, altered surface morphology, and improved water solubility. The results indicated that VA-*g*-CS with a mass ratio of 0.5:1 exhibited the highest content of VA (74.6 ± 1.42 mg of VAE/g) with an amino substitution percentage of 50.3 ± 0.54%. Increasing the concentration of VA-*g*-CS from 1.0 to 5.0 mg/mL enhanced their antifungal activity. Furthermore, VA-*g*-CS (0.5:1) at 5.0 mg/mL showed better antifungal activity than other grafted CS, with more than 80 and 76% inhibition against *F. solani* and *F. proliferatum*, respectively. The modification of CS with VA offers a new strategy for controlling plant pathogenic fungi.

KEYWORDS: *chitosan, Fusarium sp., grafting, material synthesis, fungicide, vanillic acid*

1. INTRODUCTION

Fungi, responsible for more than 80% of plant infections, pose a significant challenge to global food security.[1] Approximately 6000 fungal species have been identified for causing diseases in cultivated plants. Annually, rice blast disease leads to a 12.5% loss in global rice crops,[2] while in Malaysia, the main production site of black pepper is impacted by yellowing disease, with 90.4% attributed to *Fusarium solani*.[3] Relying on chemical pesticides is not a viable long-term solution, as this approach negatively impacts human health and the environment, leading to the development of more resistant strains. Besides, fungi are resilient, well-adapted, and quickly develop resistance to the available fungicides. Thus, an alternative method is needed to combat plant infections. In this case, chitosan (CS) can be a promising and eco-friendly agent to retard fungal infection in plants due to its low toxicity and biodegradability. CS is widely utilized as a polymeric backbone for synthesizing various functional biomaterials due to its high compatibility and the presence of amino and hydroxyl groups, facilitating easy grafting with suitable reagents. Nevertheless, CS's limited solubility at pH exceeding 6.5 restricts its use in aqueous formulations due to the formation of aggregates. Thus, modification of this biopolymer with phenolic acids may significantly improve the water solubility and enhance its functional properties, as reported in other studies related to food packaging applications.[4−6]

Phenolic acids, characterized by aromatic ring structures, offer promising bioactive benefits but are hindered by drawbacks such as light instability, susceptibility to elevated temperatures, and oxidation in the presence of oxygen.[7] Phenolic acids have been demonstrated as potent antioxidants and possess antibacterial activities by researchers.[8] Incorporation of phenolic acids, either hydroxybenzoic acids[5] or hydroxycinnamic acids,[8] onto the CS backbone not only enhances the stability of the free phenolic acid but also provides better biological activities than the native CS due to the presence of phenolic hydroxyl groups.[9] This grafting reaction can be achieved through three distinct methods:[6] 1. Activated ester-mediated reaction; 2. enzyme-mediated reaction; and 3. free radical grafting. In the activated ester-mediated modification, a cross-linker like 1-ethyl-3-(3-dimethyl aminopropyl)carbodiimide (EDC) creates a covalent linkage between CS and phenolic acids, resulting in higher grafting efficiency.[10] However, this method involves expensive chemicals and generates toxic residues. The enzyme-mediated method, using enzymes like laccase, tyrosinase and peroxidase, offers a more environmentally friendly option with a less harmful byproduct, but expensive.[11] The most cost-effective method is free radical grafting, as it requires inexpensive chemical cross-linkers, operates at room temperature, and employs commonly available chemicals (such as hydrogen peroxide and ascorbic acid). Compared to other grafting reactions, modification of CS with phenolic acids via free radical-mediated grafting emerges as a rapid, cheap, and environmentally friendly method.[12] In free radical grafting,

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