VIETNAM NATIONAL UNIVERSITY - HCMC
HO CHI MINH CITY UNIVERSITY OF TECHNOLOGY

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DISSERTATION INFORMATION

Title: ***Synthesis of reduced graphene oxide-based TiO_2 nanocomposites doped with ZnO, $MgFe_2O_4$ for photodegradation of methylene blue in water.***

Major: **Chemical Engineering** Major code: **9520301**

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Advisors: **Assoc. Prof. Dr. Nguyen Huu Hieu**

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Major Contributions of This Dissertation:

In this thesis, selenium (Se) materials were greenly synthesized using plant extracts (*Pseuderanthemum palatiferum* leaves (HN), *Guava* leaves (OI), and *Muntigia calabura* leaves (TC)) as reducing and stabilizing agents. A suitable extract was selected to synthesize Se-based graphene oxide composite (SeGO) materials and chitosan-poly(vinyl alcohol)-SeGO (CTS-PVA-SeGO) membranes. The composite and membranes were characterized and tested for biological activities. The detailed contents of the thesis are summarized as follows:

Selenium materials: Synthesized with extracts of HN leaves, OI leaves, and TC leaves as reducing and stabilizing agents, the materials have the corresponding symbols HN-Se, OI-Se, and TC-Se. Herein, the effects of synthesis conditions such as temperature, time, and extract:precursor (Na_2SeO_3) volume ratio to the morphology of the material was investigated to detemine and characterize appropriate materials. Through FE-SEM results, it showed that suitable synthesis conditions for: HN-Se are 90°C, time 60 minutes, and extraction volume ratio HN:Na_2SeO_3 are 1:1 (HN-Se-12); OI-Se are 130°C for 90 min, and OI:Na_2SeO_3 are 1:2 (OI-Se-13); and TC-Se are 100°C, 120 min, TC:Na_2SeO_3 are 1:2 (TC-Se-14). Modern methods were used to analyze the characteristics of suitable materials such as field emission scanning electron microscope (FE-SEM), ultraviolet-visible absorption spectroscopy (UV-vis), infrared spectroscopy Fourier transform (FTIR), X-ray diffraction (XRD), X-ray energy dispersive spectroscopy (EDS), zeta potential, and inductively coupled plasma optical emission spectrometry (ICP-OES). The analysis results show that HN-Se-12 and OI-Se-13 possessed the spherical shape, while TC-Se-14 involved simultaneously both spherical and rod shapes; diameters of the three materials were in a range of 100 – 500 nm. In addition, the antibacterial ability of these three Se materials was investigated by the agar disk diffusion method with Gram-positive bacteria (*Staphylococcus aureus* (*S. aureus*)), Gram-negative bacteria (*Pseudomonas aeruginosa* (*P. aeruginosa*), and *Escherichia coli* (*E. coli*)) and method to poison cells (normal cells HEK-293) and liver

cancer cells (Hep-G2) using reagent 3–[4,5–dimethylthiazol–2–yl]–2,5–diphenyl–tetrazolium bromid (MTT). The results indicated that OI leaf extract is the most suitable to synthesize Se with the highest antibacterial ability with antibacterial zone diameters for *S. aureus*, *P. aeruginosa*, and *E. coli* of 28.66, respectively; 28.99; and 27.29 mm. In addition, Se could induce liver cell toxicity at a concentration of 32 μg/mL. Therefore, OI-Se-13 material was selected as a precursor to synthesize the SeGO material.

SeGO materials: Synthesized by the *ex-situ* method of the OI-Se-13 (Se) and GO, wherein, the effects of the Se:GO ratio on the morphology of the SeGO were investigated. It can be observed that, through FE–SEM images, with a Se:GO volume ratio of 1:2, the Se material with a diameter of 475 nm was evenly distributed on the GO substrate to produce suitable SeGO (SeGO-3). The characterization of the SeGO-3 was analyzed by FE–SEM, FTIR, XRD, Raman spectrum, High-resolution transmission electron microscopyzeta potential (HR–TEM), EDS, zeta potential, specific surface area by Brunauer–Emmett–Teller (BET) method, X-ray photoelectron spectroscopy (XPS), and ICP-OES. On the other hand, the biological activities of the SeGO-3, including antibacterial, cytotoxicity, antioxidant, and *α*–glucosidase enzyme inhibition, were examined by measuring optical density (OD), MTT, free radical scavenging, and albumin inhibition. Resultantly, it can be observed that the highest antibacterial activity for *S. aureus* was 83 % and the weakest was recorded 6 % in the case of *E. coli* at material concentration of 256 μg/mL; when the concentration increases from 0 to 250 μg/mL, the toxic effect on liver cancer cells (Hep–G2) and lung cancer cells (A549) gave an IC_{50} value of 1 μg/mL but did not cause any effect to healthy cells HEK–293. Besides, the percentages of free radicals 2–diphenyl–1–picrylhydrazyl (DPPH) and 2,2'–azino–bis(3–ethylbenzothiazoline–6–sulfonic) (ABTS) scavenging of the SeGO-3 at 300 μg/mL were 63.34 and 83.34 %, respectively. Besides, at 256 μg/mL, the SeGO-3 had the ability to inhibit 100 % of the *α*-glucosidase enzyme that causes hyperglycemia. Hence, the SeGO-3 material was chosen to synthesize the chitosan-poly(vinyl alcohol)-SeGO (CTS-PVA-SeGO) membranes.

CTS-PVA-SeGO membrane: Produced by solution casting method from three components of CTS, PVA, and SeGO-3 (SeGO). To figure out the optimal precursor ratio, simultaneous effects of three factors, comprising the volume of CTS, PVA, and SeGO over the antibacterial efficiency of the CTS-PVA-SeGO composite membrane were investigated by experimental design according to the response surface methodology (RSM). Accordingly, the experimental design based on the Box-Behnken model with the objective function being the antibacterial rate investigated by the agar disk diffusion method. The experimental design results showed that the composite membrane had the highest antibacterial effectiveness of 100 % at the CTS:PVA:SeGO volume ratio of 1.95:3.78:2.09, with respect to the membrane named CTS-PVA-SeGO-2. To verify the model, a control experiment was carried out, it indicated that the CTS-PVA-SeGO-2' (CPS) membrane was synthesized at a volume ratio of 2:4:2 (to suit the conditions) for antibacterial effectiveness reaching 99.9 %. This demonstrated the agreement between the model and experimental data. Furthermore, the characteristics of the CPS membrane were analyzed by FE–SEM, FTIR, XRD, and XPS; mechanical properties (modulus of elasticity and stress at maximum load), swelling, and water vapor permeability.

On the other hand, the biological activities of the membrane was also investigated through antibacterial, cytotoxic, and anti-inflammatory abilities by agar disk diffusion, MTT assay method, and inhibition of albumin denaturation, respectively. The results indicated that the CPS membrane has the ability to fight *E. coli* bacteria with an antibacterial diameter of 13 mm, capable of causing toxicity to Hep–G2 cells when diluted 20 times, and an anti-inflammatory effect of over 33 %. From the results of biological activity surveys, CPS composite membranes were applied to preserve sapoche fruit by dipping directly into CPS fluids. After 6 days of preservation, the sapoche still retained its original color and hardness, the weight of coated fruit decreased by 23.85 %, and the soluble solid content of the fruit reached 19 %. This proves that CPS membrane has potential for application in fruit preservation in Vietnam.

Advisors **Ph.D. candidate**

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