Encapsulation of Pesticide Nanoparticles Using Polymerized Carbon Nanotubes and Application of Synthesized Nanocomposite for Alternaria Alternata Fungi

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ABSTRACT

Polymerization of citric acid onto the surface of oxidized multi wall carbon nanotubes was led to MWCNT-graft-poly (citric acid) (MWCNT-g-PCA) hybrid materials. Trapping of pesticides such as Benomyl, Trichlorfon and Pymetrozine (chess) in aqueous solution by MWCNT-g-PCA hybrid materials was led to Encapsulated Pesticide (EP) into polycitric acid shell. Optimum condition for encapsulation of Benomyl, Trichlorfon and Pymetrozine in hyper branch polycitric acid such as pH, stirring time and temperature was investigated by UV-Vis spectroscopy method. Also encapsulation of pesticides on CNT-g-PCA hybrid material were confirmed via TEM analysis. Furthermore the effect of encapsulated Benomyl on Alternaria alternate fungi was investigated. Experiments indicated that encapsulated Benomyl in comparison with bulk Benomyl had superior toxic influence on Alternaria alternata fungi.

Keywords: Pesticide nanoparticles, Encapsulation, Trichlorfon, Benomyl, Pymetrozine (chess)

1 INTRODUCTION

Organic pesticides including insecticides and herbicides are widely used in agriculture because of their powerful biological activity [1]. Benomyl is a general use pesticide (GUP). It is used against a wide range of fungal diseases of field crops, fruits, nuts, ornamentals, mushrooms, and turf [2, 3]. Trichlorfon is an organophosphate insecticide used to control cockroaches, crickets, silverfish, bedbugs, fleas, cattle grubs, flies, etc. It is also used for treating domestic animals for control of internal parasites [4, 5]. Pymetrozine is in class of pyridine azomethine. It is used to control aphids and whiteflies in vegetables, potatoes, tobacco, citrus, fruit, hops and ornamentals [6].

Encapsulated Pesticides to be released over the time and allowing farmers to apply the pesticides less often rather than requiring very highly concentrated and perhaps toxic initial applications followed by repeated applications to battle the loss of efficacy due to leaching, evaporation, and degradation [7]. Protecting the pesticides from full contact to the elements lessens the risk to the environment and those that might be exposed to the chemicals and provides a more efficient strategy to pest control [8].

In tis study Benomyl, Trichlorfon and Pymetrozine was encapsulated into MWCNT-g-PCA hybrid material which this process leads to bulk pesticide convert to pesticide nanoparticles. This technique has specific advantages as follows:

1-Encapsulated pesticide into CNT-g-PCA hybrid material is more stable and effective than bulk pesticide. 2-Pesticides usage will be decreased in agriculture. 3-Water solubility of encapsulated pesticides will be increased. 4-Multiwall carbon nanotubes will be solved in the water. This product can be used extensively in greenhouse and Agriculture.

2 EXPERIMENTAL

2.1 Reagents and Apparatus

The MWCNT was purchased from Nutrino. The outer diameter of MWCNT was between 20–40 nm. Monohydrate citric acid, sulfuric and nitric acid, tetrahydrofurane and cyclohexane were purchased from Merck. Pesticides standard was purchased from Delta Green South Corporation of Iran. A shimadzu model UV-1650PC UV-Visible spectrophotometer with 1-cm glass cells was used for recording the absorption spectra and absorbance measurements. Fourier transform infrared (FT-IR) spectroscopic measurements were performed using a FT-IR spectrometer (Thermo Nicolet Magna-IR 560 spectroscopy, USA).

2.2 Synthesis of MWCNT-g-PCA hybrid materials

CNTs were opened and citric acid Polymerized onto functionalized carbon nanotubes according to the reported procedures in literatures [9]. Briefly, MWCNTs were activated in nitric acid solutions to give carboxyl group modified MWCNTs (MWCNT-COOH), followed by reaction with monohydrate citric acid, resulting in hyperbranched poly (citric acid) grafted onto MWCNT (CNT-*g*-PCA).

2.3 Preparation of MWCNT-g-PCA-EP

Water solutions of MWCNT-g-PCA separately were mixed with each of pesticides and placed in an ultrasonic bath for 10 min in order to well disperse pesticides in the polymeric shell of hybrid material. Fig. 1 shows the synthetic scheme of the MWCNT-g-PCA-EP.

2.4 Preparation of medium Potato Dextrose Agar (PDA)

Usually for PDA medium preparation, 250 gr of potatoes was boiled for 20 min and the sap of potato was taken. Afterwards 20gr dextrose agar was added to the sap under continuous stirring and slowly warmed until it was well solved. Then the medium was diluted to 1 litter by warmed distilled water and autoclaved for 15 min at 121 $^{\circ}$C and pressure 1.5 kg/cm^2. Finally PDA medium was chilled until 45 $^{\circ}$C and was poured into Petri dish [10-12].

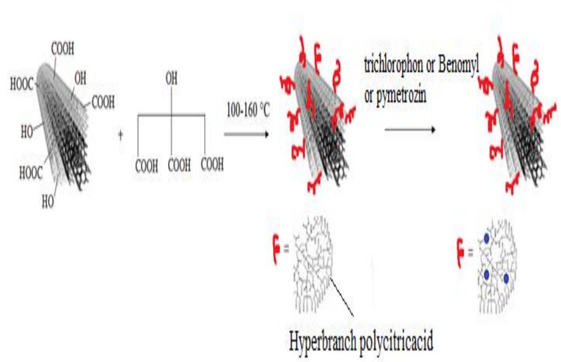


Figure 1: Synthetic scheme of CNT-g-PCA-EP.

3 RESULTS AND DISCUSSION

The encapsulation of the Benomyl, Trichlorfon and Pymetrozine by polymeric shell of CNT-g-PCA was investigated via UV-Vis spectroscopic technique (Fig. 2). In this procedure, pesticide was added to a water solution of CNT-g-PCA and the solution was stirred. UV spectra shows an increasing in the absorption peaks in the range of 200-285, 210-350 and 230-360 nm for Benomyl, Trichlorfon and Pymetrozine respectively. Probably increasing the intensity of UV spectra in these regions are due to charge transfer from implanted carboxylic acid groups on polycitric acid shell to pesticide molecules.

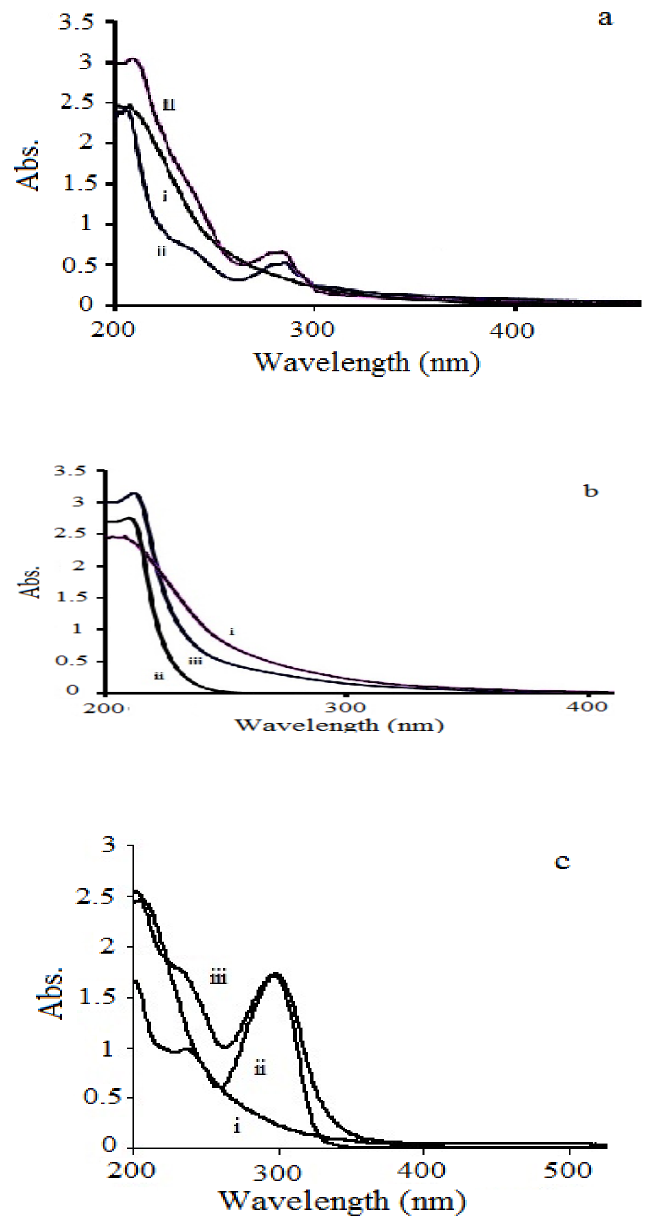


Figure 2: UV spectra for encapsulation of (a) Benomyl (b) Trichlorfon (c) Pymetrozine into CNT-g-PCA (i) aqueous solution of CNT-g-PCA (ii) aqueous solution of pesticide (iii) after addition of pesticide to CNT-g-PCA.

The encapsulation of Pymetrozine in CNT-g-PCA was accompanied with color change during time. The color change through the progression of the encapsulation reaction between Pymetrozine and CNT-g-PCA hybrid material was shown in Fig. 3. As shown in this picture, the light yellow color of solution turned gradually to pale yellow after 2 h. The darkening of the solution continued and fixed after 8 h which is an evidence for encapsulation of Pymetrozine into CNT-g-PCA.

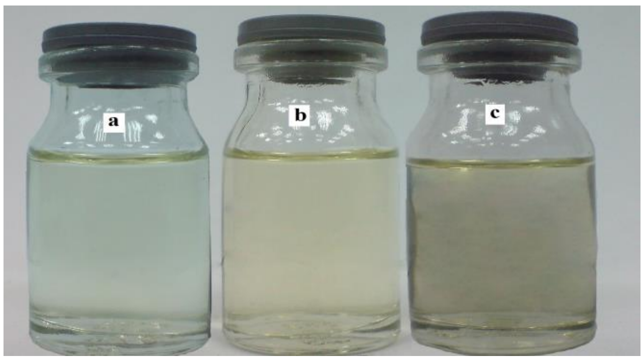
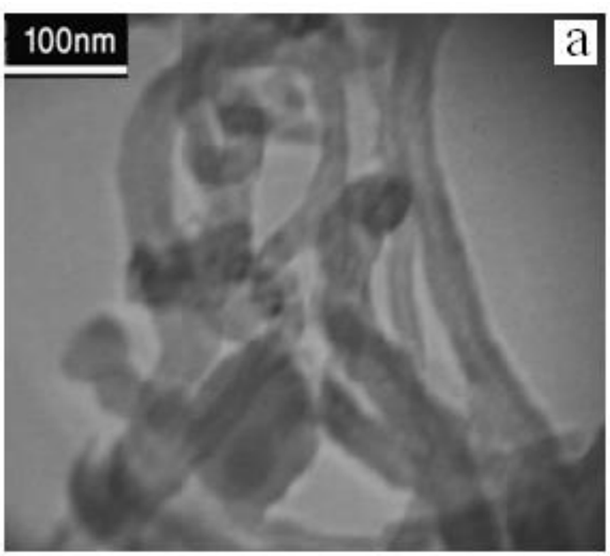


Figure 3: The color change during time progression of the encapsulation between Pymetrozine and MWCNT-g-PCA (a) initiate (b) after 2h (c) after 8h

Finally encapsulation of pesticides by CNT-g-PCA was confirmed with TEM analysis. Fig. 4 shows TEM images of Benomyl, Trichlorfon and Pymetrozine encapsulation by CNT-g-PCA hybrid material which clearly indicates polycitric acid (PCA) shell around CNTs and encapsulated pesticides. Also distribution of Pymetrozine in polycitric acid shell can be seen in Dark field image, which bright points in this image correspond to encapsulated Pymetrozine (fig. 5).



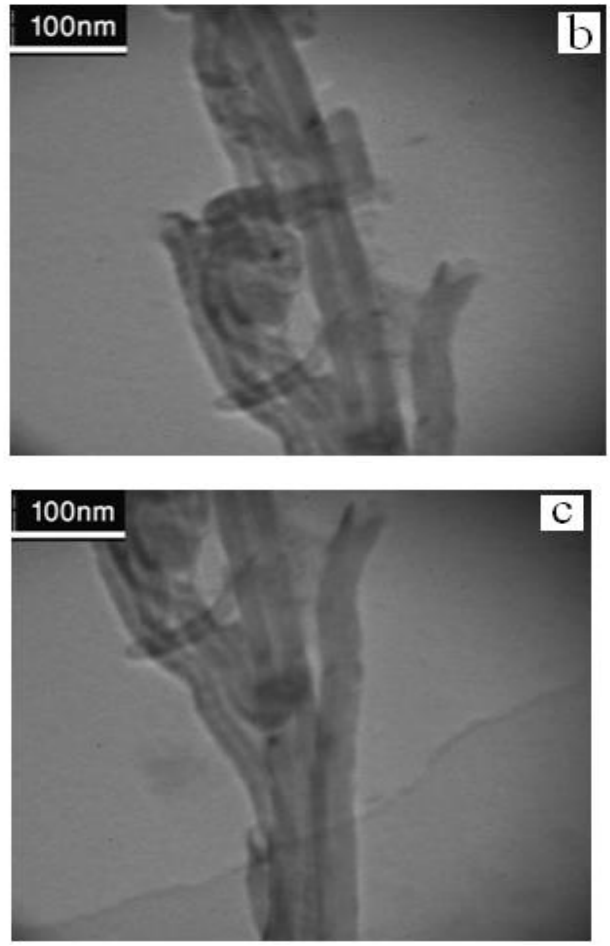


Figure 4: TEM images of encapsulation of (a) Benomyl (b) Trichlorfon (c) Pymetrozine into MWCNT-g-PCA.

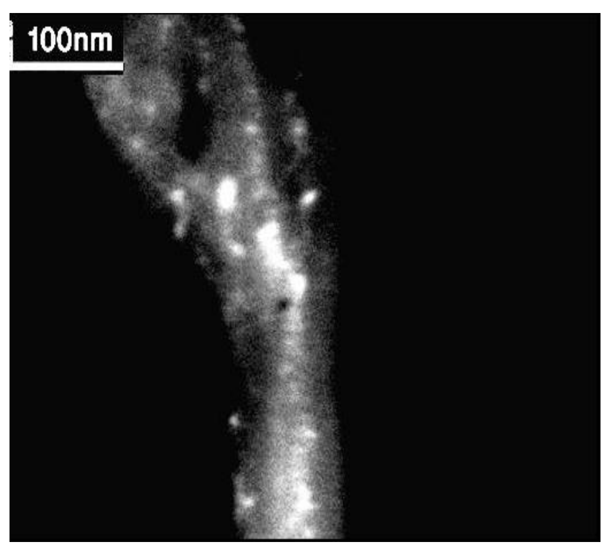


Figure 5: Dark field image of encapsulation of Pymetrozine with MWCNT-g-PCA.

The effect of Benomyl encapsulated in hyper branched polycitric acid was studied on malady Alternaria alternata fungi. Potato Dextrose Agar (PDA) medium was used to grow malady Alternaria alternate in this study. For this purpose, Bulk and encapsulated Benomyl were added to the control mediums and their effects on growth of colonies were studied after 10 days. Results shown encapsulated Benomyl had more effect on growth restriction in comparison to the bulk Benomyl. This effect after 10 days reached the maximum intensity as shown in fig. 6. Probably this phenomenon attributes to increasing the contact area which was formed between encapsulated pesticide and fungi.

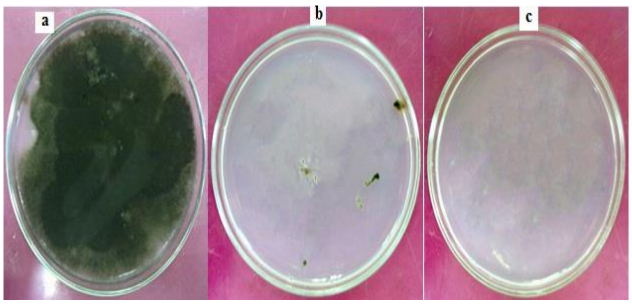


Figure 6: The influence of Benomyl encapsulation on Alternaria alternate fungi. (a) Potato Dextrose Agar (PDA) medium (bulk sample) (b) addition of bulk Benomyl and (c) encapsulated Benomyl to PDA medium after 10 day.

4 CONCLUSION

In summary, Benomyl, Trichlorfon and Pymetrozine were successfully encapsulated into CNT-g-PCA hybrid material. Results shown encapsulation of pesticides into hybrid material was dependent to pH and stirring time but temperature had no significant effect on encapsulation. Experiment shown the optimum pH for encapsulation of Benomyl, Trichlorfon and Pymetrozine were 7, 2 and 3 respectively. Furthermore the stirring time for complete encapsulation of Trichlorfon and Pymetrozine were 50 and 60 min respectively while encapsulation of Benomyl was constant during stirring time. In addition Benomyl encapsulated in comparison with bulk Benomyl showed extraordinary effect on malady Alternaria alternata fungi and its effect reached to maximum after 10 days.

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