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Synthesis and characterization of nanoencapsulated herbicide using direct and indirect method

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Abstract
Nanoencapsulated herbicide materials were synthesized using direct and indirect encapsulation techniques at the Department of Nano Science and Technology, Tamil Nadu Agricultural University, Coimbatore. Ammonium bi carbonate was mixed with manganese sulphate monohydrate solution and ethanol solution the $MnCO_3$ microcapsules are prepared by altering layer by layer (LbL) adsorption of opposite charge polyelectrolyte. Thus direct and indirect nano encapsulated herbicide particles were analysed using various instruments. The porous rough surface characteristic of $MnCO_3$ core particles aided in loading of herbicides due to the physical adsorption and also by covalent bonding. The remarkable size, shape, physico-chemical properties of nanoparticles have fascinated and inspired research activity in this direction.

Keywords: $MnCO_3$ microcapsules, layer by layer, encapsulation, Nanoherbicide

Introduction
Smart delivery nano systems will help the agricultural industry combat against yield minimizing factors. In the near future nano structured catalysts will be available which will increase the efficiency of pesticides and herbicides allowing lower doses to be used [1]. At this scale, the physical, chemical and biological properties of materials may be fundamentally different from their corresponding bulk materials. Microencapsulation is a well-established dedicated to the preparation, properties and uses of individually encapsulated novel small particles, as well as significant improvements to tried and tested techniques relevant to micro and nano particles and their use in a wide variety of research applications [2]. The right choice of the encapsulation materials and methods are very important because it influences the encapsulation efficiency and stability of the microcapsule. The ideal encapsulation materials and methods should have the following characteristics like not reactive with the core, ability to cover and maintain the core inside the capsule, ability to provide maximum protection to the core against adverse conditions [3].

Material and Methods
Nanoencapsulation of pendimethalin herbicide by direct method
Synthesis of $MnCO_3$ core material: Equal volume of 0.33 M ammonium bi carbonate (NH_4HCO_3) was mixed with equal volume of 0.33 M manganese sulphate monohydrate solution ($MnSO_4$). Equal volume of 0.5 per cent ethanol solution was added to the above mixture in the round bottom flask. The resulting solution was vigorously stirred for 10 min. It was then left undisturbed for 10 min and incubated for 1 hour in water bath at 75 ^oC.
The solution was centrifuged to settle down the particles completely and the particles were washed thrice with distilled water followed by centrifuging after each wash. Then the particle was isolated by filtering the outcome of final water wash with filter paper Whatman no. 41. The filter paper along with particles settled on it was dried in compact vacuum desiccators. After drying the particles were scrapped and stored in a vial.

Loading pendimethalin in the $MnCO_3$ core template
Took 20 mg of $MnCO_3$ core particles and added 25 ml of 20 ppm pendimethalin and stirred it for 15 min in magnetic stirrer. Then the suspension was allowed to dry for overnight. This enables pendimethalin to adsorb on the $MnCO_3$ core particles surface. The dried particles were collected and stored in vial.

Encapsulation of pendimethalin adsorbed $MnCO_3$ core material
$MnCO_3$ microcapsules are prepared by altering layer by layer (LbL) adsorption of opposite charge polyelectrolyte onto the $MnCO_3$ microsphere templates.

Prepared polyelectrolyte solutions like Poly (allylamine hydrochloride) and Sodium poly (styrene sulfonate) weighing each 20 mg was added to the 20 ml of 0.5 N NaCl solutions in separate beakers and dissolved it completely. Then pH was adjusted for the solution to 6.5-7.0 by using hydrochloric acid and sodium hydroxide.

Typically, 20 ml of polyelectrolyte solution was added to 40 mg of dry pendimethalin adsorbed $MnCO_3$ microparticles and the suspension was gently stirred in magnetic stirrer for 15 min. Then the suspension was centrifuged at 1000 rpm for 15 min. Later the centrifuged particles rinsed three times with 0.1 N NaCl to remove the unbounded particles. The same procedure was repeated with oppositely charged polyelectrolyte. Then the suspension was centrifuged and allowed to dry for overnight. The particles were collected and stored in a vial.

Nanoencapsulation of pendimethalin herbicide by indirect method

Preparation of core-shell and hollow-shell particles

Typically, 20 ml of polyelectrolyte solution (PAH) was added to 40 mg of dry $MnCO_3$ microparticles and the suspension was gently stirred in magnetic stirrer for 15 min. Then the suspension was centrifuged at 1000 rpm for 15 min and rinsed for three times with 0.1 N NaCl to remove the unbounded particles. The same procedure was repeated with oppositely charged polyelectrolyte (PSS). Then alternate layer was formed using PAH and PSS for two or three times. After defined number of polyelectrolyte layer reached, $MnCO_3$ core was removed by adding 0.1 M HCl and stir it for 15 min. Then the suspension was centrifuged and rinsed with water for three times with water. Then the suspension was allowed to dry for overnight. The particles were collected and stored in a vial [4].

Loading of pendimethalin in hollow-shell

Take 20 mg of hollow-shell and add 25 ml of 20 ppm pendimethalin and stirred it for 15 min in magnetic stirrer. Then the suspension was allowed to dry for overnight. The particles were collected and stored in a vial.

Thus, synthesised nanoherbicide particles were characterized using TEM, SEM, particle size analyzer, XRD and TGA for size determination and loading efficiency.

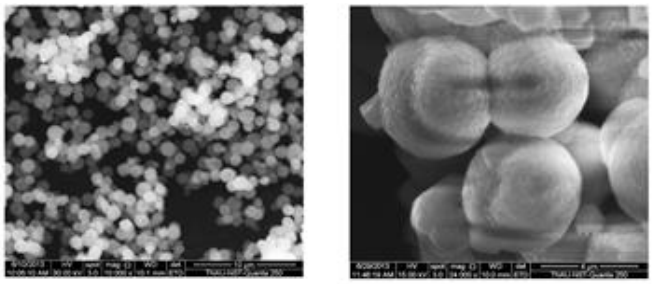
Results and Discussion

The direct and indirect nano encapsulated herbicide particles were analysed using various instruments and the results are discussed here under.

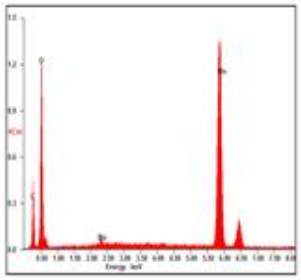
Scanning Electron Microscope (SEM)

$MnCO_3$ Core

$MnCO_3$ microparticles were prepared by mixing $MnSO_4$ and NH_4HCO_3 solutions. Ethanol was added to decrease the dielectric constant of the system and the solubility of the inorganic salts and results in the formation of modified porous surfaced $MnCO_3$. The SEM image shows (Fig. 1) the surface topography of the manganese carbonate ($MnCO_3$) particles. The porous rough surface characteristic of $MnCO_3$ core particles aided in physical adsorption targeted herbicides. Further the presence of the $MnCO_3$ core was confirmed with characteristic peak obtained in SEM-EDX. The porous rough surface characteristic of $MnCO_3$ core particles aided in loading of herbicides due to the physical adsorption and also by covalent bonding [4].



(a)



(b)

Element	Wt%	At%
CK	30.21	44.05
OK	43.60	47.72
MoL	00.85	00.16
MnK	25.33	08.07
Matrix	Correction	ZAF

(c)

Fig 1: SEM image of $MnCO_3$ core, EDX graph and composition

Direct method

In the direct encapsulation method the target per-emergence herbicide was implanted directly on the $MnCO_3$ core template synthesized already. Thus formed herbicide embedded core were encapsulated with two layers of polymers. The surface morphology of bilayers (PAH + PSS) nanoencapsulated herbicide formed by Direct method was observed in SEM (Fig. 2). The porous nature of the core materials played an important role for adsorbing the herbicide molecules.

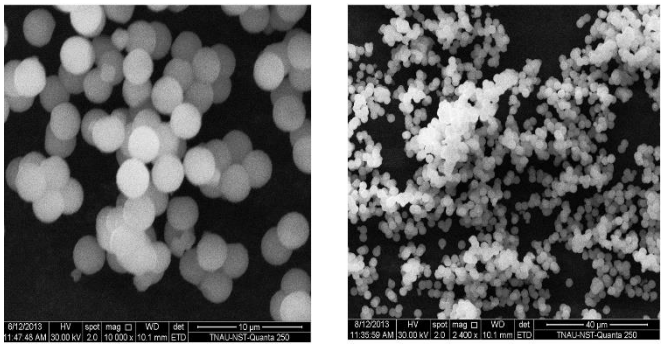


Fig 2: SEM images of direct method of nanoencapsulated herbicide

Indirect method

Uniform spherical sized particle of $MnCO_3$ were obtained with layer-by-layer (LbL) assembly method. It is evident from the images obtained with scanning electron microscope (Fig.3). The $MnCO_3$ core was synthesized first and coated with bilayers of polymers *viz.*, poly styrene sulfonate (PSS) and poly allyl amine hydrochloride (PAH). Thus formed core-shell was treated with HCL to etch out core and to form hollow-shell. The hollow-shell was then loaded with pendimethalin active ingredients passively by the utilizing permeability of the polymer layer in the presence of solvent used for dissolving the herbicide. The image obtained from the SEM clearly shows the spherical shape of core-shell with PSS and PAH polymer layer and the $MnCO_3$ core etched out hollow-shells. The result was in conformation with the SEM and SEM-EDX studies [5].

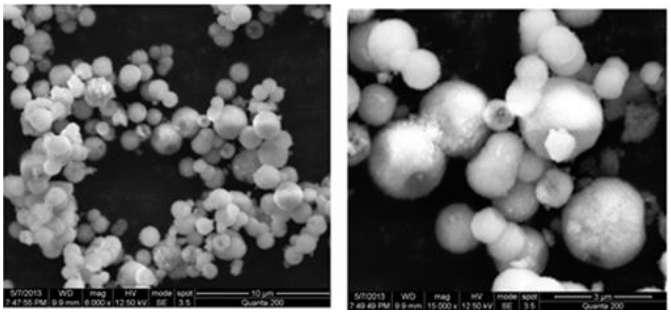


Fig 3: SEM images of indirect method of nanoencapsulated herbicide

Particle size

The particle size analyzer was used to analyze the particle size using laser scattering principle for estimating the particles size and size distribution pattern for nanoencapsulated herbicide fabricated using Direct (DC) and Indirect (ID) methods with pendimethalin active ingredient. .

The particle size distribution gives the average minimum and maximum diameter of various particles using laser scattering principle. The particles size varied at different intensity of distributions. The particle size distribution of the $MnCO_3$ core was 127.9 nm. The particle size distribution of the encapsulated herbicides by DC and ID methods were 298.4 nm and 427.4 nm diameters, respectively with 100 per cent intensity. The 100 per cent intensity shows the fabrication of uniform sized particles in all the methods. Fabrication of uniform particles is very much important with respect to release of encapsulated active ingredient in a designated period of time. The particle size distribution of the pendimethalin active ingredient was 48.3 nm dia with 80.0 per cent intensity. The smaller size of pendimethalin herbicide particles was beneficial in the encapsulation because $MnCO_3$ core particles size was more compare to pendimethalin active ingredient. The small size pendimethalin particles easily breach in to the porous natured $MnCO_3$ core.

X-ray diffraction

X-ray crystallography is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their ailment and various other information. The X-ray diffraction was carried out to identify the $MnCO_3$ particles and nanoencapsulated herbicide materials prepared using different methods.

The X-ray diffraction patterns of $MnCO_3$ core, encapsulated materials via direct and indirect methods and active ingredient loaded particles were shown in the diffractograms. From the X-ray diffractograms for $MnCO_3$ core, characteristic peaks are seen at 24°, 32° and 52° and 100% peak was seen at 32° which match with the standard pattern of rhodochrosite [4]. The $MnCO_3$ core pattern is in good agreement with the JCPDS card No. 86-0173 and the previous reports [6]. Similarly, for direct and indirect method of encapsulated particle peak was observed at 24°, 28°, 32°, 37° 45° and 52° (Fig.4). However peak 28° represent the pendimethalin active ingredient with the conformation of JCPDS card no. 33-0664. After adding to pendimethalin and polymers, three maximum peaks added to the $MnCO_3$ core material could be observed from the X-ray diffractrogram of direct and indirect encapsulation methods. This alteration confirms the pendimethalin herbicide had been loaded into the $MnCO_3$ carrier material.

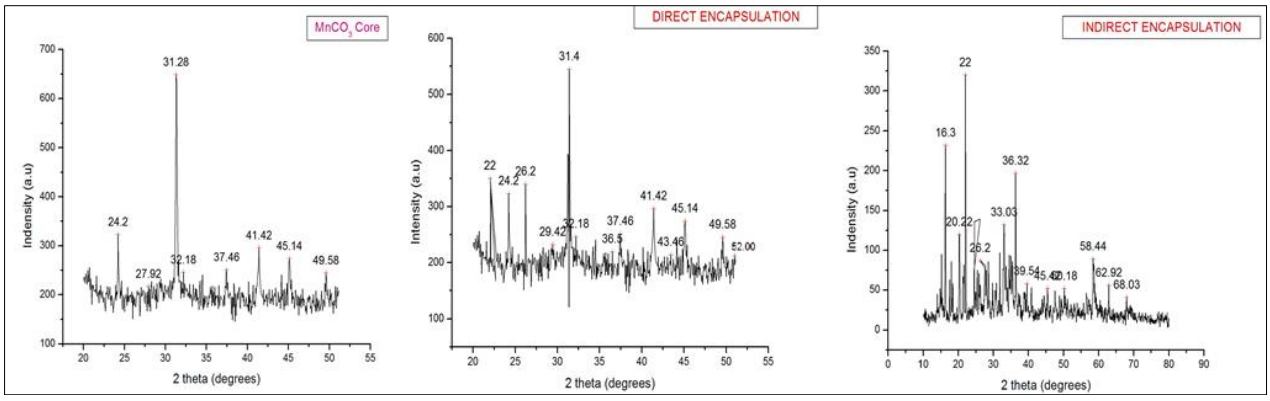


Fig 4: XRD- diffractograms of $MnCO_3$ core, direct and indirect method of nanoencapsulated herbicide

Thermo Gravimetric Analysis (TGA)

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate). TGA can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption. TGA is done to find out the stability of the materials used for encapsulation and herbicide against the raising temperature gradually.

The thermogram of $MnCO_3$ shows single stage decomposition with high stable temperature at 350°C. The TGA curves for manganese carbonate are recorded and thermal decomposition process of manganese carbonate has only one step i.e., $MnCO_3 \rightarrow MnO + CO_2$. On the basis of the TGA curve, the thermal decomposition reaction is an endothermic reaction. The calcite type rhombohedral structure of manganese carbonate starts to decompose at around 370 °C. The reaction finishes at about 430 ^{0}C with a total weight loss of 49.81% [7]. Similarly TGA for direct encapsulated materials shows two stage decomposition at 180 °C and 320 °C and followed a steady decomposition pattern. This may be due to the encapsulated pendimethalin with layer-by-layer assembly of polymers. The first stage decomposition may correspond to the herbicide which has been loaded and second one for polymers.

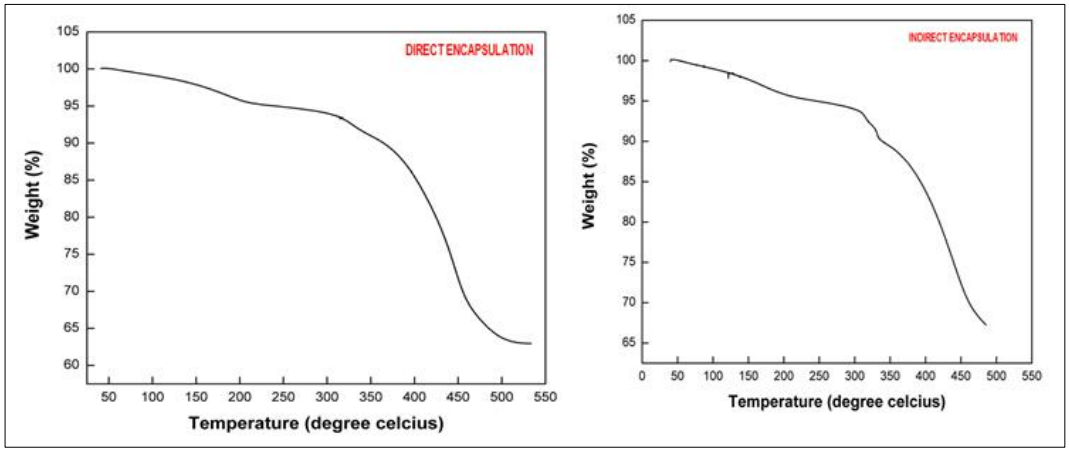


Fig 5: TGA thermogram of direct and indirect method of nanoencapsulated herbicide

Whereas a different pattern of TGA was observed for the herbicide encapsulated via indirect method due to the solid nature of herbicide. The TGA thermogram of pendimethalin loaded indirect sample depicts two stages decomposition at 180 °C and 320 °C and followed a steady decomposition pattern.

Conclusion

In conclusion, we have developed a nanoencapsulated pendimethalin using direct and indirect method of encapsulation with appropriate developed procedures. Furthermore, present procedure resulting in the formation of nano pendimethalin shows the porous nature and spherical shape of core-shell with PSS and PAH polymer layer. The nanosized particle with 100 per cent intensity shows the fabrication of uniform sized particles in both the methods. The X-ray diffraction patterns of encapsulated materials active ingredient loaded particles were shown in the diffractograms matched with JCPDS card number. Finally TGA thermogram depicts steady decomposition pattern present in the nanomaterials.

References

1. Biswal SK, Ashok Kumar Nayak, Umesh Kumar Parida, Nayak PL. Applications of nanotechnology in agriculture and food sciences. International Journal of Science Innovations and Discoveries. 2012; 2(1):21-36.
2. Nitika Agnihotri, Ravinesh Mishra, Chirag Goda, Manu Arora. Microencapsulation- A novel approach in drug delivery: A review. Indo Global Journal of Pharmaceutical Sciences. 2012; 2(1):1-20.
3. Filomena Nazzaro, Pierangelo Orlando, Florinda Fratianni, Raffaele Coppola. Microencapsulation in food science and biotechnology. Current Opinion in Biotechnology. 2012; 23:182–186
4. Tong W, Gao C. Selective removal of particle cores to fabricate manganese carbonates hollow spheres and composite microcapsules. Colloids Surfaces A: Physicochem. Eng. Aspects. 2007; 295:233-238.
5. Kanimozhi V, Chinnamuthu CR. Engineering core/hallow-shell nanomaterials to load herbicide active ingredient for controlled release. Res. J Nanosci. Nanotechnol. 2012; 2(2):58-69.
6. Lianyi Shao, Jie Shu, Rui Ma, Miao Shui, Lu Hou, Kaiqiang Wu, Dongjie Wang *et al*. Electrochemical characteristics and intercalation mechanism of manganese carbonate as anode material for lithium-ion batteries. Int. J Electrochem. Sci. 2013; 8:1170-1180.
7. Lianyi Shao, Jie Shu, Rui Ma, Miao Shui, Lu Hou, Kaiqiang Wu, Dongjie Wang *et al*. Electrochemical characteristics and intercalation mechanism of manganese carbonate as anode material for lithium-ion batteries. Int. J Electrochem. Sci. 2013; 8:1170-1180.