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Sustained release of pesticide (Cypermethrin) from nanocarriers: An effective technique for environmental and crop protection

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ABSTRACT

Cypermethrin loaded calcium alginate nanocarriers were prepared and characterized by various techniques such as FTIR, FESEM, TEM, XRD, DSC, SEM-EDX, ED, particles size and zeta potential analysis. Whereas the FTIR spectral analysis confirms the presence of cypermethrin and alginate in the nanocarriers, the FESEM suggests for heterogeneous morphology of the nanocarriers surfaces when pesticide is loaded. The TEM analysis reveals that the native alginate nanocarriers have dimensions in the range of 108–127 nm while encapsulation of cypermethrin changes their sizes to fall in the range of 115–119 nm which is also accompanied by change in their shape. The loading of pesticide also results in slight shift of surface potential of nanocarriers from −25 to −21 mV. The study showed that cypermethrin is well encapsulated (encapsulation efficiency approx 95% and cypermethrin loading approx 78%) within calcium alginate nanocarriers without any chemical deformation. The release of cypermethrin from calcium alginate nanocarriers was evaluated under varying experimental conditions. The mechanism of release of cypermethrin from alginate nanocarriers was found to follow non Fickian behavior i.e anomalous transport governed by diffusion and relaxation of the alginate chains. The whole study suggested that cypermethrin loaded calcium alginate nanocarriers could be a promising and safe candidate for sustained and slow release of cypermethrin and helpful in reducing the environment pollutions caused by excessive use of cypermethrin.

1. Introduction

The food demand has tremendously increased with increasing human population and it is, therefore, necessary to protect agricultural crops from the infestation by different groups of insects. It is now globally recognized that extensive use of pesticides in agriculture contributes to over production but adversely affects humans and the natural environment. The allowed concentrations of pesticides in drinking water and in the environment are 0.1 mg L^{-1} and 0.5 mg L^{-1}, respectively (Raileanu et al., 2010). At present various fertilizers and pesticides are being used for improving crops yield, however, their excessive application has originated several severe environmental problems such as soil erosion (Green and Heffernan, 1987), salinization and flooding of heavily irrigated soils (Ceuppens et al., 1996), aquifer depletion (Wagner, 2017), deforestation and environmental pollution (Lewis et al., 1999). Furthermore, it also causes developmental and reproductive anomalies because only 0.1% of the chemicals used in crop protection reach at the target pests while the rest enter in to the environment as 90% of the applied conventional pesticides are lost or decomposed (Getzin and Shanks, 1970). These problems can be effectively reduced by the development of sustained release nano-formulations utilizing the application of nanotechnology in pesticide delivery because they are able to transfer predetermined concentration of pesticides from a reservoir to a targeted surface for a specified period of time and also reduce the indiscriminate use of conventional pesticides and ensure their safe application (Grillo et al., 2014).

Cypermethrin is a widely used synthetic pyrethroid pesticide, showing genotoxic (Bolognesi, 2003), neurotoxic (DeMicco et al., 2010), immunotoxic and carcinogenic properties (Rehman et al., 2014) and used for crop protection (Clair et al., 2008). In recent years, cypermethrin residues were found to be reported in most of the tested samples (sediments) from urban creek due to aerobic microbial degradation, hydrolysis, volatilization, and adsorption as well as photo-degradation of cypermethrin (half life is 8–16 days) causing severe environmental pollution (Tallur et al., 2015; Nair et al., 2010; FAO, 2011; Price et al., 2014a; Custódio et al., 2016).

Recently, there has been growing interest in application of nanotechnology in pesticide delivery to reduce the indiscriminate use of conventional pesticides as more than 90% of applied pesticides is

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unable to reach the target area due to leaching (Bahri and Taverdet, 2007), evaporation (Nuruzzaman et al., 2016a), deposition (Yin et al., 2018), hydrolysis (Nuruzzaman et al., 2016b), aerobic and photo degradation (Ravier et al., 2005). Therefore, using nanotechnology a sustained delivery system may be developed for pesticides that may overcome these problems.

Presently, biopolymers based nanoparticles have gained much attention among researchers due to their low cost, ease of availability, biodegradability, nontoxicity, biocompatibility and ability to form gels with a variety of crosslinking agents under mild and aqueous conditions (Donald et al., 2017). In the present study, our main aim was to develop biodegradable nanocarriers for sustained release of cypermethrin using calcium alginate nanocarriers due to the fact that alginate can easily be crosslinked with calcium chloride. Cypermethrin was encapsulated into the nanocarriers during preparation of nanocarriers. The other objectives include determination of particle size, morphological features, encapsulation efficiency and release of cypermethrin from calcium alginate nanocarriers. The suitability of developed slow releasing nanoformulation to agricultural fields was also judged by carrying out soil-pot experiments.

2. Materials and methods

2.1. Materials

Sodium alginate and calcium chloride (dihydrate) were obtained from Merck India and used without pretreatment. Cypermethrin (Unikil Pesticide Pvt. Ltd., Mumbai, India) was purchased from a local agrochemical supplier. Paraffn oil (Merck, India) was used to prepare microemulsion while double distilled water was used throughout the experiments. For conducting soil-pot experiments the sandy soil was collected from the Leh-Laddakh region of India. The moisture content in the soil was determined by a Digital Moisture-meter (Universal Traders, New Delhi, India).

2.2. Preparation of cypermethrin loaded Ca-alginate nanocarriers

Cypermethrin loaded calcium alginate nanocarriers were synthesized by emulsion crosslinking method (Roy et al., 2012). In a typical experiment, 2.5 g of sodium alginate was dissolved in 30 mL distilled water at 60 °C, and to this solution of sodium alginate, 10 mL paraffn oil was added with vigorous stirring (Capacity 5 MLH 300 rpm, Remi India) for 40 min to produce a stable emulsion. Now, for crosslinking of sodium alginate emulsions and subsequent loading of cypermethrin, 10 mL of calcium chloride solution (0.5 M) and an equal volume of 0.5 M cypermethrin (15 mL) were added to sodium alginate emulsion under constant stirring. The reaction mixture was continuously stirred for 3 h at room temperature so that alginate was completely crosslinked by Ca^{2+} ions to form cypermethrin loaded calcium alginate nanocarriers which were precipitated at the bottom of the reaction vassal. The as prepared cypermethrin loaded calcium alginate nanocarriers were left in solution for 24 h at room temperature and thereafter filtered and intensively washed with water and acetone, respectively to remove unreacted chemicals and paraffn oil. Following the same procedure, unloaded calcium alginate nanocarriers were also prepared.

2.3. Characterization of cypermethrin-loaded Ca-alginate nanocarriers

2.3.1. Fourier transforms infrared (FTIR) spectroscopy

The FTIR spectra of native alginate, cypermethrin, and cypermethrin loaded ca-alginate nanocarriers were recorded on a FTIR-8400S, Shimadzu spectrophotometer. Prior to analysis KBr pellets were prepared by mixing the sample and KBr in the ratio 1:10 (wt/wt) followed by uniaxial pressing the powder under vacuum. The spectra were obtained in the range 4000–400 cm^{-1} at 2 cm^{-1} resolution.

2.3.2. Field emission scanning electron microscopy analysis (FESEM)

0.1 mL of alginate suspension was prepared in distilled water and Field Emission Scanning Electron Microscopy (FESEM) was performed using a Leo/Zeiss 1530 Field Emission Scanning Electron Microscope with an acceleration voltage of 5.0 kV.

2.3.3. Transmission electron microscopy (TEM)

The shape and size of the nanocarriers were determined from the TEM images. Transmission electron microscopy (TEM) was performed using a Morgagni-268-D transmission electron microscope with an acceleration voltage of 80.0 kV. The samples for the TEM measurements were prepared by dispersing a drop of the sample solution on Formvar-coated C grids.

2.3.4. X-ray diffraction analysis

The crystalline nature of the native sodium alginate and cypermethrin loaded ca-alginate nanocarriers was studied on a rotating X-ray diffractometer scanned at 0.0050, (2θ)/s in the 2θ range of 10–60°.

2.3.5. DSC (differential scanning calorimetry)

DSC measurements were carried out using NET2SCH DSC 204 F1 machine. The studies were performed in the temperature range 0–350 °C under nitrogen atmosphere (flow rate 40 mL min^{-1}), and the heating rate was 2.5 K/min.

2.3.6. SEM analysis and energy dispersive analysis of x-ray spectroscopy (EDAX)

A scanning electron microscope fitted with an electron dispersive X-ray spectrometer (SEM/EDX, JEO, JSM-5800LV) was used to study the surface morphologies and elemental analysis of the native and cypermethrin loaded ca-alginate nanocarriers.

2.3.7. Electron diffraction analysis

Electron diffraction study was performed to investigate the crystalline nature of native alginate nanocarriers and cypermethrin loaded Ca-alginate nanocarriers using a Morgagni 268-D Transmission Electron Microscope.

2.3.8. Particle size distribution and zeta potential measurements

The average size and surface potentials of cypermethrin-loaded calcium alginate nanocarriers were measured using a Zetasizer (Malvern Instruments, Malvern, UK). All experiments were done in triplicate.

2.4. Evaluation of encapsulation efficiency and cypermethrin loading

The methods of determination of encapsulation efficiency and cypermethrin loading (Bahri and Taverdet, 2005; Korsmeyer et al., 1983) have been described in supplementary sections S1 and S2, respectively.

2.5. In vitro release study of cypermethrin-loaded Ca- alginate nanocarriers

In vitro release assays was used to study the release profiles of cypermethrin encapsulated in the nanoparticles. In brief, cypermethrin-loaded nanocarriers (0.1 g) were added in to 25 mL of distilled water taken as release medium under static conditions. The released amounts of pesticides at different time intervals