Colloids and Surfaces B: Biointerfaces 83 (2011) 148–154

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

journal homepage: www.elsevier.com/locate/colsurfb

Novel photodegradable insecticide W/TiO_2/Avermectin nanocomposites obtained by polyelectrolytes assembly

Hua-Nan Guan, De-Fu Chi*, Jia Yu, Si-Yu Zhang

Department of Life and Sciences, Northeast Forestry University, HeXing Road 26, Harbin, China

ARTICLE INFO

Article history:
Received 28 July 2010
Received in revised form 9 November 2010
Accepted 9 November 2010
Available online 17 November 2010

Keywords:
Avermectin
Layer-by-layer (LbL) self-assembly
TiO_2
W-doped
Photodegradable insecticide

ABSTRACT

Stable and even microcrystals of Avermectin (AVM) were produced by recrystallization in presence of a stabilizer. Sequential layer growth was achieved by the layer-by-layer (LbL) self-assembly of biocompatible polyelectrolytes (PEs). The coated colloids were characterized using confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM). The in vitro release of Avermectin from microcapsules was studied under the simulated insect midgut conditions. W-doped TiO_2 photocatalysts were synthesized by a simple hydrothermal method, and characterized by Brunauer–Emmett–Teller (BET) surface area measurements and SEM. The photocatalytic activities of photocatalysts, which were undoped with TiO_2 and W-doped TiO_2, were evaluated by the photocatalytic oxidation degradation of AVM microcapsules in aqueous solution under UV illumination. The toxicity of the photodegradable insecticide was evaluated by the adult stage *Martianus dermestoides*. The results showed that AVM microcrystals which were obtained by association had a mean length of 13.8 μm and a zeta potential of −34.7 mV. The drug loading and encapsulation efficiency were 65.57 ± 0.96% and 46.15 ± 0.96%, respectively. The in vitro release experiments revealed that the polyelectrolytes prolonged the release time of the encapsulated AVM microcrystals. The sample which was prepared at 120 °C with 4.0 mol% W-doped amount had the highest photocatalytic activity. Toxicity of the novel photodegradable insecticide was higher in the adult stage compared to the 95% AVM as indicated by the lower LC_{50} value.

1. Introduction

Pesticides are widely used in agriculture although their usage may create hazards to both humans and the environment. Their toxicity, stability to natural decomposition and persistence in the environment have aroused wide attention to societies and authorities around the world. In addition, depending on the method of administration and climate conditions, as much as 90% of the applied conventional pesticide is lost or decomposed, which not only increases the cost but also leads to environmental pollution [1–4].

To reduce the harmful effects and the impacts of these compounds on the non-target organisms, controlled release formulations were developed using various methods of which microencapsulation is one [5,6]. Controlled release of pesticides can remarkably reduce the amount of active agent required for treatment by maintaining an effective concentration in the target for longer periods of time. This can be achieved by using microencapsulation which is able to protect the pesticide against degradation, control the release rate and prolong the duration of agrochemicals [7]. Toxicity enhancement via successful delivery of a therapeutic agent is the principal target of insecticide delivery research. The most important commercially recognized technologies are available for delivery of large quantities of water-insoluble insecticides with improved performance characteristics [8]. Recently, some novel controlled release carriers have been developed. The layer-by-layer surface nano-engineering is a novel strategy for direct surface modification of colloidal entities, which utilizes sequential adsorption of oppositely charged polyelectrolytes (PEs) to form a complex assembly via electrostatic interactions [9].

The other way to minimize the pollution problem is developing new and reasonable technologies which can promote the degradation of these bio-recalcitrant organic compounds [10–12]. A promising way to perform the degradation of biologically and chemically stable molecules is the application of advanced oxidation processes (AOPs) that all have in common the “in situ” production of hydroxyl radicals under mild experimental condition. Semiconductor photocatalysts belong to AOPs [13]. Among various oxide semiconductor photocatalysts, titanium oxide (TiO_2) has been proven so far to be the most promising material used for both fundamental research and practical applications because

* Corresponding author. Tel.: +86 451 82191792.
E-mail addresses: guanhuanan3@163.com (H.-N. Guan), Chidefu@126.com (D.-F. Chi).

0927-7765/$ – see front matter.
doi:10.1016/j.colsurfb.2010.11.013

of its high photoreactivity, biological and chemical inertness, cost effectiveness, non-toxicity, and long-term stability against photo corrosion and chemical corrosion. Anatase TiO_2 has been identified as the most effective and useful photocatalyst under near UV illumination [14]. To improve photocatalytic activity of TiO_2 for wide range applications, several approaches have been developed, including doping techniques, and nanosized process of enhancing the specific surface area of catalysts [15–17]. Recently, most studies have been focused on the photocatalytic properties of metal ion-doped TiO_2, such as Fe, Cr, Co, Mn, Ag and V ions. The doping of metal ions, especially transition metal ions, makes it possible for TiO_2 to absorb visible light. Introducing WO_3 into TiO_2 was proved to be attractive for photocatalysis research. The results showed that coupling TiO_2 with WO_3 presented improved photocatalytic performances compared with the corresponding bare oxides, and the mixed-oxide could be excited using visible light [18,19].

Avermectins (AVMs) are biological agents that contain a macrocyclic lactone and produced by *Streptomyces avermitilis* [20]. AVM has been used widely to control parasites and pests of human being, animals and crops. In the production process, fermentation wastewater which contains 100–300 mg AVM residues L^{-1} is a kind of recalcitrant wastewater and causes an important environmental problem because of its toxic residues. The bacterial toxicity and recalcitrance may play an important role in decreasing the chemical oxygen demand (COD) removal efficiency in affected treatment systems [21].

In this paper, the main purpose of present work is to obtain the novel photodegradable insecticide microcapsules. For the purpose, we investigated the experimental conditions of preparing AVM microcapsules, which was used as a model pesticide. AVM has been microencapsulated with chitosan (CHI) and alginate (ALG) by layer-by-layer (LbL) technique. Then, W-doped TiO_2 photocatalysts were successfully synthesized by a simple hydrothermal method at a low synthetic temperature. W/TiO_2 has been constructed for photocatalytic degradation and mineralization of the AVM microcapsules. According to the studies, a model has been successfully established for the prediction of W/TiO_2/AVM–(CHI/ALG) microcapsules process with any kinds of insecticides.

2. Materials and methods

2.1. Insects

Martianus dermestoides (Coleopteran, Tenebrionidae, a kind of pest in storage), was originally collected from Shenyang city, LiaoNing province, China, and raised in laboratory without any contact with insecticides from 2005. These insects were fed on the rice, and placed in the 15 cm diameter plastic Petri dishes. The rearing conditions were $25 \pm 1\,^{\circ}C$, photoperiod 12 L:12 D and the relative humidity 60–70%. The most of sensitive adults were used for photodegradable AVM microcapsules toxicity tests in the laboratory. All the experiments were carried out under the dark conditions.

2.2. Insecticides and chemicals

Chitosan (CHI) and sodium alginate (ALG) were purchased from Aldrich, Germany (Aldrich, Germany). The stabilizing agent used was hydroxypropyl methyl cellulose (HPMC, type 2910, USP, Tokyo, Japan). Avermectin (purity, 99.9% by HPLC) and $Ti(SO_4)_2$ were obtained from Pestanal Sigma–Aldrich (Aldrich, Germany). $Na_2WO_4{\cdot}2H_2O$, was purchased from Alfa Aesar (Tianjin, China). Other chemicals were purchased from Merck China (Shanghai, China). The deionized water used in experiments was purified with a Millipore purification apparatus as the resistivity higher than 18 MΩ cm.

2.3. Crystallization procedure

The AVM microcrystals were prepared with the crystallization procedure as described previously [22]. Briefly, AVM was dissolved in acetone (1%). The stabilizing agents (HPMC) were dissolved in water (0.025%). Afterwards, 400 mL of the aqueous solution were poured rapidly with stirring into the 100 mL of the drug solution. The particle size in the resulting dispersions was determined after 60 min. The AVM microcrystals were finally collected by centrifugation at 8000 rpm for 10 min and rinsed twice with AVM-saturated aqueous solution (pH 6.0, adjusted with acetic acid) to remove the impurities. Microcrystals were lyophilized using Freeze Dry Systems Vacuum Pump (Labconco FreeZone™, America) and then stored at 4 °C prior to use. The shape and surface texture of microcrystals were examined by scanning electron microcopy (SEM) (JEOL JSM-6460LV SEM, Japan). Size distributions of unrecrystallized AVM and recrystallized AVM were determined in washing media by laser diffractometry (Fraunhofer model) using a Coulter LS130 particle analyzer, with a size range from 0.1 to 1000 μm. Particle size was expressed as volume mean diameter (μm) values related to mean.

2.4. Encapsulation by polyelectrolyte multilayers

Polyelectrolyte multilayers of CHI/ALG were deposited on the AVM microparticles through layer-by-layer self-assembly in aqueous solution. To prevent AVM dissolving during the layer-by-layer process, all the polyelectrolyte solutions and the rinsing water used were adjusted to pH 6.0 with acetic acid. The first layer was deposited by adding 50 mg of AVM microparticles to 1 mL of CHI solution (cationic polyelectrolyte, 1 mg/mL, 0.5 mol/L NaCl). The mixture was incubated for 15 min under gently shaking. The excess CHI was removed by two repeat refining circles of centrifugation (8000 rpm, 10 min)/washing/re-disperse in water at pH 6.0. The following ALG layer was deposited using the same procedure with 1 mL of ALG solution (anionic polyelectrolyte, 1 mg/mL). This process would continue until a desired level of coating was achieved. Microcapsules made of five pairs of chitosan/sodium alginate were denoted as $(CHI/ALG)_5$

2.5. Drug content and entrapment efficiency

Estimation of AVM content was done according to the method adopted earlier [23]. The % drug loading and encapsulation efficiency were calculated, respectively, using Eqs. (1) and (2):

$$\%\,\text{drug loading} = \left(\frac{\text{weight of AVM in microcapsules}}{\text{weight of microcapsules}}\right) \times 100 \quad (1)$$

$$\%\,\text{entrapment efficiency} = \left(\frac{\text{weight of AVM in microcapsules}}{\text{initial weight of AVM}}\right) \times 100 \quad (2)$$

2.6. Charaterization

The ζ-potential values of the coated microcrystals were measured using BROOKHEVEN Zeta PALS. The size distributions of AVM–$(CHI/ALG)_n$ were determined in washing media by laser diffractometry. Particle size was expressed as volume mean diameter (μm) values related to mean. Confocal laser scanning microscopy (CLSM) images were captured with a Leica TCS NT confocal scanning system (leica, Germany) equipped with a 100×/1.4–0.7 oil immersion objective. Scanning electron microcopy (SEM) observation was performed with a JEOL JSM-6460LV