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CONTROLLED RELEASE OF A MODEL BIOACTIVE COMPOUND FROM - CARRAGEENAN/CHITOSAN NANOLAYERED FILMS

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KEYWORDS

Multilayers, layer-by-layer, transport modeling

ABSTRACT

Nanotechnology holds a great potential to generate very innovative solutions for the food industry and packaging is one of the many areas that can benefit from this new technology. The main goal of this work is to prepare nanofilms by layer-by-layer deposition using κ-carrageenan and chitosan, incorporate the model compound methylene blue and to evaluate its loading and release behaviour. The developed biodegradable nanofilms are a promising delivery system for application in food products, as a strategy for shelf-life extension.

INTRODUCTION

Layer-by-layer (LbL) assembly is based on the alternating deposition of oppositely charged polyelectrolytes and can be used to produce multilayers of nanometer thickness. Nanolayered films have promising applications on food products, as a strategy for shelf-life extension. However, there is a need to create multilayer systems that combine both biofuncionality and edibility. Chitosan, a natural cationic polysaccharide, is an excellent edible film component due to its good oxygen barrier properties and due to its intrinsic antimicrobial activity (Bégin & Van Calsteren, 1999). Κ-carrageenan, an anionic polysaccharide, is extensively used in food industry as gelling and stabilizing agent and has been reported as having excellent film forming properties (Park et al., 1996). In recent years, LbL nanolayered films have been investigated due to the possibility of controlling drug release (Wang et al., 2007). Furthermore, drug molecules can act as either functional drugs or components of the film. The release behaviour of bioactive compounds from nanolayered films depends on the permeability, on the disassembly or erosion of the multilayer structure and on other experimental variables (e.g. pH) (Jiang & Li, 2009). Methylene blue (MB), a monovalent cation of 374 Da, is a suitable model for loading and release experiments due to its large absorption peak in the visible range. MB has been used to investigate multilayer surface properties due to its ability to bind to available negatively charged functional groups (Chung & Rubner, 2002).
In this work multilayer nanofilms were prepared by LbL deposition using κ-carrageenan and chitosan onto a substrate (polyethylene terephthalate - PET). MB was incorporated in the nanolayered film and its loading and release behaviour was evaluated.

METHODS

Preparation of nanolayered film: The κ-carrageenan and the chitosan solutions were prepared at a concentration of 0.2 % (w/v) in distilled water and 1 % acid lactic, respectively. The solutions' pH was adjusted to 7 and 3, respectively. MB solution was prepared at a concentration of 0.3 % (w/v) in 50 % (v/v) PBS and the pH was adjusted to 7. The nanolayered film was composed by an aminolyzed PET sustaining layer adsorbed with 5 layers (3 κ-carrageenan and 2 chitosan layers). The MB was incorporated in the film, forming the second, the fourth or the sixth layer, thus replacing the corresponding chitosan layer in those positions. The formation of nanolayered film was performed according to Carneiro-da-Cunha et al. (2010).

MB loading: The loading of MB on each position of the multilayer structure was monitored by UV-VIS spectroscopy (Jasco 560, Germany). Real time deposition of MB on the coated electrode was recorded by a Quartz Crystal Microbalance (QCM 200 purchased from Stanford Research Systems, SRS, USA), equipped with AT-cut quartz crystals (5 MHz) with optically flat polished titanium/gold electrodes on contact and liquid sides.

MB release: The MB release from the multilayer coating on PET was evaluated by incubating the loaded film in 40 mL of PBS of a certain pH (2 or 7) and temperature (4 and 37 ºC). The release medium was continuously stirred. At preset intervals, 0.25 mL supernatant was taken and 0.25 mL of fresh PBS was added. The sample solutions were analyzed using UV-VIS spectroscopy (at 600 nm). In order to evaluate the MB release mechanism, the kinetic model of Korsmeyer & Peppas (1981) was applied. Non-linear regression analysis was performed using STATISTICA 7.0.

RESULTS & CONCLUSIONS

MB loading: The MB loading at different positions of the κ-carrageenan/chitosan multilayered film was evaluated by UV–Vis spectroscopy. The amount of MB loaded increased with the distance from the first layer. Similar results were obtained by Chung and Rubner (2002). The real-time adsorption of MB on κ-carragenan/chitosan pre-coated gold electrode surface was monitored using a QCM. It was found that MB loaded mass increased with the incubation time, exhibiting a very fast initial adsorption phase followed by a slower phase upon approaching a steady state. After 15 min (time used for MB loading) the maximum adsorption of MB was guaranteed. In addition, it was observed that the MB had a higher adsorption in the sixth layer than in the other positions.

MB release: The effects of temperature, pH and layer position on MB release were studied. It was observed that diffusional exponent values are within the limiting value of 0.5, suggesting that the MB release kinetics is Fickian in nature. Further, the values of correlation coefficient R^2 shows a fairly good fit of the model to the experimental data. It was observed that the MB position on the nanolayered film influences its release. At the same release conditions, the MB in the sixth layer enabled a fast release of this compound. Moreover, the rate of diffusion of MB from the κ-carrageenan/chitosan nanolayered film increased with increasing temperatures, from 4 to 37 °C. This behaviour can be explained by temperature effects on the solubility of diffusing molecules in films, on the nature of adhesive forces at interfaces and on molecular mobility (Vojdani and Torres 1990). The decrease of pH of the surrounding environment, from 7 to 2, also resulted in a faster MB release. At pH 2 the electrostatic interaction between κ-carrageenan and MB is very low, since the pKa value of the anionic sulfate groups on κ-carrageenan is around pH 2 and at this pH the sulfate groups on the κ-carrageenan molecules are protonated and consequently uncharged (Gu et al., 2005). Therefore, the pH decrease promotes the release of MB molecules from the nanolayered film.

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