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Complex coacervation of collagen hydrolysate extracted from leather solid wastes and chitosan for controlled release of lavender oil

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ABSTRACT

In the world, approximately 600 000 metric tonnes of chromium-containing solid wastes are generated by the leather industry each year. Environmental concerns and escalating landfill costs are becoming increasingly serious problems to the leather industry and seeking solutions to these problems is a prime concern in much research today. In this study, solid collagen-based protein hydrolysate was isolated from chromium-tanned leather wastes and its chemical properties were determined. Microcapsules of collagen hydrolysate (CH) – chitosan (C) crosslinked with glutaraldehyde (GA) containing Lavender oil (LO) were prepared by complex coacervation method.

The effects of various processing parameters, including the CH to C ratio, LO content, and GA, on the oil load (%), oil content (%), encapsulation efficiency (%) and release rate of LO from microcapsules were investigated. As the ratio of C present in the CH/C mixture and crosslinking density increased, the release rate of LO from microcapsules slowed down. Optical and scanning electron microscopy images illustrated that the LO microcapsules were spherical in shape. Fourier transform infrared spectroscopy (FTIR) studies confirmed that there was no significant interaction between CH/C complex and LO.

1. Introduction

Solid wastes of chromium-tanned leather generated in the leather industry derive mainly from the treatment of chromium-tanned leathers by mechanical processes such as shaving, buffing, splitting and trimming (Lipsett, 1982; Aslan et al., 2007; Przepiorkowska et al., 2007; Castiello et al., 2009; Haroun, 2010; Ocak et al., 2011a). These solid leather wastes are composed of a large amount of structural fibrous proteins called collagen and contain 3–6% chromium III. These wastes require special attention because chromium III can oxidize to toxic chromium VI which may endanger ecological life and human health (Taylor et al., 1990; Przepiorkowska et al., 2007; Fuck et al., 2011; Ocak et al., 2011a). Solid leather wastes have become an important problem for the leather industry in the last few years because of the increase in dumping charges, the difficulty of finding new landfills, and environmental concerns (Taylor et al., 1990; Aslan et al., 2006, 2007; Przepiorkowska et al., 2007; Ocak et al., 2011a).

Facing this challenge, numerous efforts have been made to develop alternative applications including the promotion of collagen hydrolysate (CH) to reduce both the environmental impact of waste and depletion of natural resources (Suresh et al., 2001; Sundar et al., 2002; Aslan et al., 2007; Haroun, 2010; Ocak et al., 2011a).

Microencapsulation is defined as a technology of packaging individual droplets or particles of solid, liquid or gaseous materials in capsules in the micrometre to millimetre range, which can release their contents at controlled rates under specific conditions (Li et al., 2009; Ocak et al., 2011b). Among the microencapsulation methods, complex coacervation is the most commonly used to produce microcapsules (Cabeza et al., 1999; Maji et al., 2007; Hussain and Maji, 2008; Ma et al., 2009; Gu et al., 2010; Ocak et al., 2011b). The major advantage of complex coacervation over other methods is its very high payload (up to 99%) and controlled release possibilities (Gouin, 2004; Jun-xia et al., 2011). In summary, this method is a phase separation process based on the simultaneous desolvation of oppositely charged polyelectrolyte and the composition of wall-forming polymers, which play an important role because they are responsible for the protection and release properties of the encapsulated active compounds (Ducel et al., 2004; Fuguet et al., 2007; Hussain and Maji, 2008; Leclercq et al., 2009; Ma et al., 2009).

An area of research of increasing interest in the last few years is the development of alternative, inexpensive and natural polymeric wall materials for microencapsulation (Beristain et al., 2001; Elzatahry and Eldin, 2008). The wall material of the capsules can be formulated by a variety of materials including natural and synthetic polymers (Alencastre et al., 2006; Hussain and Maji,

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2008; Rodrigues et al., 2008; Devi and Maji, 2009). The use of natural polymeric wall materials in the microencapsulation process has received considerable attention in recent years, especially from the viewpoint of cost, environmental concerns and safety, because under natural conditions, the biodegradation of synthetic polymers is very slow, and some of them do not undergo biodegradation at all (Remunan-Lopez and Bodmeier, 1996; Patil et al., 2000; Chiellini et al., 2001; Kandil et al., 2004; Devi and Maji, 2009; Haroun, 2010).

Chitosan (C) is the second most abundant polysaccharide in the world, and is obtained by alkaline N-deacetylation of chitin, and produced commercially from waste shells of crabs and shrimps (Agnihotri et al., 2004; Hu et al., 2004; Espinosa-Andrews et al., 2007; Gupta and Jabrail, 2008). Relative to other polymers available for microencapsulation purposes, gelatin, a collagen hydrolysis product, and C have been widely studied as means of obtaining long-term, sustained active compound release from microcapsules because the amino groups of C carry positive charges at pH values below 6.5 and gelatin is associated with C to neutralize its charge and thereby form a complex (Remunan-Lopez and Bodmeier, 1996; Soppimath et al., 2001; Agnihotri et al., 2004; Ducel et al., 2004; Hsieh et al., 2006; Kim et al., 2006; Ma et al., 2009; Haroun and El-Halawany, 2010; Nagpal et al., 2010).

In recent years, there has been an increasing interest in the uses of essential oils due to their eco-friendly and biodegradable natures (Maji et al., 2007; Maji and Hussain, 2009). Lavender oil (LO) is the most used and the most versatile of all the essential oils (Wang and Chen, 2005; Chograni et al., 2010). Studies on LO have been performed due to its applicability in the perfumery industry as a pleasant fragrance or antimicrobial agent (Cavanagh and Wilkinson, 2002; Badulescu et al., 2008; Ocak et al., 2011a). The release speeds of these volatile essential oils are usually affected by different application environment conditions, and they are volatile and chemically unstable in the presence of air, light, moisture and high temperatures (Beristain et al., 2001; Adamiec and Kalemba, 2006; Hsieh et al., 2006; Hussain and Maji, 2008; Rodrigues et al., 2008; Maji and Hussain, 2009; Ocak et al., 2011b). Microencapsulation of volatile essential oils by polymeric wall materials seems to be an effective solution for increasing the stability of these compounds in order to improve their efficiency and minimize environmental damage, thus providing them with a longer shelf-life (Wang and Chen, 2005; Lameiro et al., 2006; Maji et al., 2007; Hussain and Maji, 2008; Maji and Hussain, 2009; Haroun and El-Halawany, 2010; Ocak et al., 2011a, 2011b). Recently, microencapsulation of active compounds has become an interesting area in fiber, leather, textile and coating technologies (Nelson, 2002; Wang and Chen, 2005; Sohn et al., 2007; Badulescu et al., 2008; Rodrigues et al., 2008; Ma et al., 2009; Renzi et al., 2010).

The use of CH as a wall material in the simple coacervation process was reported in our previous paper (Ocak et al., 2011a). However, no previously reported work deals with the use of CH and C in a complex coacervation process. Therefore, the aim of this study was to investigate the ability of CH obtained from shavings and C as a polymeric wall material to microencapsulate LO using the technique of complex coacervation. Different factors affecting the release characteristics of LO from microcapsules such as CH/C ratio, oil loading, and GA concentration were studied.

2. Materials and methods

2.1. Materials

Chrome shavings were obtained from a commercial tannery in Izmir, Turkey. The following chemicals were obtained from commercial suppliers and used as received: chitosan (medium molecular weight, viscosity 200 cps) (Sigma–Aldrich, USA), magnesium oxide (Merck, Germany), Rodazym ML (Rohm, Darmstadt), glutaraldehyde 25% w/v (Merck, Germany), sodium hydroxide (Merck, Germany), silicone antifoam 30% w/v (Sigma–Aldrich, USA), Tween 80 (Sigma–Aldrich, USA), anhydrous sodium sulphate (Sigma–Aldrich, USA), lavender oil (*Lanvandula angustifolia*, Sigma–Aldrich, USA), acetic acid (Merck, Germany). Double-distilled water was used throughout the study.

2.2. Methods

2.2.1. Preparation of collagen hydrolysate

CH was prepared by the controlled enzymatic hydrolysis of collagen waste. First, chromium-tanned leather wastes were soaked in water five times their weight and treated with 4% MgO at 65 °C for 30 min. In the following step, the enzyme Rodazym ML was added to this solution at a concentration of 1% (w/v) and the mixture was digested for 4 h. This mixture was then filtered under vacuum through Whatman # 1 filter paper to separate the chrome cake, and the liquid CH was dried to powder form in a spray drier (Niro Atomizer brand) (Aslan et al., 2006; Ocak et al., 2011b).

2.2.2. Determination of chemical characteristics of collagen hydrolysate

CH was analyzed in order to determine volatile matter (moisture) (IUC 5), sulphated total ash and sulphated water insoluble ash (IUC 7), chromic oxide content (IUC/8:4), nitrogen and hide substance (protein) (IUC 10) and pH (IUC 11) (SLTC, 2009). The chromium content of the CH was measured with Perkin Elmer Optima 2100 DV ICP-OES.

2.2.3. Coacervation behaviour study

Aqueous solutions of CH in deionized water and of C in 1% (v/v) acetic acid were prepared. An Erlenmeyer flask containing CH and C solutions mixed at different ratios (1.0/0.0, 0.75/0.25, 0.50/0.50, 0.25/0.75 and 0.0/1.0) was immersed in a thermostatic water bath at room temperature under stirring conditions. A predetermined amount of aqueous sodium sulphate solution (10% w/v) was added dropwise to each different polymer mixture. The temperature of the water bath was then increased by 1 °C per minute. The ratio of total polymer to sodium sulphate and the temperature were varied from 1:2 to 1:30 and from 30 to 45 °C respectively. The minimum temperature and polymer-salt ratio at which clear phase separation occurred were recorded.

2.2.4. Preparation of collagen hydrolysate-chitosan microcapsules

A CH solution was prepared with 5.0 g of CH in 100 ml of double-distilled water and heated until the clear solution appeared. C (2.5 g) was dissolved in 100 ml of 1% (v/v) acetic acid solution by stirring in an Erlenmeyer flask until the solution was transparent. Variable amounts of CH/C solutions (1.0/0.0, 0.75/0.25, 0.50/0.50, 0.25/0.75 and 0.0/1.0) were taken into the reaction vessel (250 ml working volume) placed in a temperature-controlled water bath, and the internal temperature of the reaction vessel was adjusted to 30 ± 1 °C. The CH/C solution in the reaction vessel was stirred at 800 rpm with a mechanical stirrer. One drop of silicon-based antifoaming agent was added, and the internal temperature of the reaction vessel was raised to 42 ± 1 °C. Then the LO (2–10 ml) used as the active substance was added dropwise into the reaction vessel. Coacervation was achieved by gradual addition of aqueous sodium sulphate solution (10% w/v) for about 120 min. The pH of the emulsion was brought to the range of 6.5–7.0 using 0.1 N NaOH to attain maximum coacervation, and the internal temperature of the reaction vessel was brought to 30 ± 1 °C to harden the microcapsules. The CH–C walled microcapsules were crosslinked through the slow addition of GA solution (0.1–0.3 mmol/g of