Industrial Crops and Products 80 (2016) 93–100

Contents lists available at ScienceDirect

Industrial Crops and Products

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

The green generation of sunscreens: Using coffee industrial sub-products

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ARTICLE INFO

Article history:
Received 6 July 2015
Received in revised form 4 November 2015
Accepted 9 November 2015
Available online 6 December 2015

Keywords:
Spent coffee oil
Green coffee oil
Supercritical fluid extraction
Water resistant
Pickering emulsion sunscreen

ABSTRACT

Spent coffee grounds and green coffee defective beans, which are industrial sub-products of coffee processing, have a potential use for cosmetic applications, due to their safety and high content in lipids that present interesting physicochemical properties. Sunscreen formulations in the form of water-in-oil emulsions might be a suitable application for these sub-products because providing a higher sun protection factor (SPF) for the same concentration of sunscreen activities than oil-in-water emulsions.

The purpose of this work was to assess the biological effects of using the oil fraction of spent coffee grounds extracted with supercritical CO_2 and green coffee oil in the development of new generation of sunscreens with improved sun protection performance. The oil fractions were used to prepare w/o sunscreens involving a cold emulsification process, with purified water as disperse aqueous phase and TiO_2 and ZnO particles as stabilizers. The sunscreens were characterized in terms of mechanical, rheological and skin adhesion properties. In addition, the *in vitro* and *in vivo* biological properties of the formulations were evaluated, including safety and sunscreen water resistance tests.

The use of two types of solid particles proved to be useful in the developed formulations, ensuring a high SPF with UVB/A protection, conferred by TiO_2 and ZnO, respectively. Moreover, the emulsion containing 35% w/w of the spent coffee grounds oil fraction presented promising characteristics in the improvement of water performance with a broad spectrum sun protection when compared to an emulsion containing 35% w/w of green coffee oil which improved the SPF in physical sunscreens. The formulations are industrial-scalable and suitable for topical use according to the rheological, mechanical and safety assessment.

The use of spent coffee oil in cosmetic industry seems to be a suitable approach for the valorisation of waste from the coffee industry and presents promising characteristics in the improvement of sunscreen performance.

1. Introduction

The efficacy of sunscreen products has been recognized as an important public health issue and is usually expressed by the sun protection factor (SPF), which is calculated as the ratio between the UV energy required to produce a minimal erythema dose of protected and unprotected skin (Dutra et al., 2004; Ribeiro et al., 2013).

Avoiding sun exposure, covering the skin or applying sunscreens with a high SPF are the main strategies strongly recommended to prevent UV-induced cell damage. The UV filters can be divided in two groups: (a) chemical filters which absorb UV radiation (UVR); and (b) physical filters, such as, titanium dioxide (TiO_2) which reflect UVR (Ascenso et al., 2014).

Sunscreens are normally based on synthetic chemicals with high capacity to absorb sun light at the region of UVB (320–290 nm) and UVA (400–320 nm) spectrum. Several synthetic UV filter molecules (*e.g.* benzophenones, anthranilates, PABA derivatives, salicylates, cinnamates and camphor derivatives) are available as photoprotective agents, but due to their harmful effects they are becoming less popular. The main problem of the chemical sunscreen agents

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http://dx.doi.org/10.1016/j.indcrop.2015.11.033
0926-6690/

are the photoirritation, photosensitization and contact dermatitis. Reducing the concentration of such chemicals in cosmetics is a strategy to improve their quality, without affecting their properties (Serpone et al., 2007).

In recent years, the use of natural agents has been attracting significant attention, due to their safety, multiple biological actions on the skin and cost effectiveness. Consequently, an oily vehicle with antioxidant activity could be an excellent approach for its important role on the product efficacy by improving the products' photoprotective activity (Calixto et al., 2011; Couto et al., 2009). In addition to bioactivity, natural products are, in general, not harmful for humans, not expensive, suitable to be used in a wide range of applications, and are obtained from renewable sources. In this context, green coffee oil and spent coffee grounds oil have arisen as potential candidates to replace synthetic chemicals in sunscreens since they are a rich source of antioxidants and polyphenols (Ribeiro et al., 2013). Phenolic compounds are excellent candidates for the prevention of the harmful effects of UV radiation on the skin. More specifically, flavonoids have photoprotection potential due to their UV absorbing capacity, ability to act as antioxidants and anti-inflammatory, and immunomodulatory agents (Saewan and Jimtaisong, 2013).

Coffee consumption is growing worldwide, being extremely embedded in the cultural habits of many countries, so the total import and export of coffee has been increasing. Spent coffee grounds (SCG), which are the residue obtained after the treatment of coffee with hot water or steam for extracting flavour substances, can be used for industrial applications such as high quality biodiesel production (Couto et al., 2009). Nevertheless, due to their high content in lipids, particularly fatty acids, SCG might also find a suitable application in cosmetic products where these lipid compounds can be used as valuable excipients. Therefore, the lipid fraction of SCG extracted with supercritical CO_2 can be used in the development of new, improved sunscreens. On average, a fifth of the Brazilian coffee production consists of defective beans, and several studies have been developed in order to find an alternative use for sub-product, including the cosmetic application of the extracted oil (Preedy, 2014; Ribeiro et al., 2013).

Titanium dioxide has been incorporated in sunscreen formulations for more than 25 years, being regarded as safe and effective, thus bringing together two of the most desirable features in cosmetic market (Renner, 2009). It is especially preferred by people with a high propensity for skin irritation, such as patients undergoing oncological chemotherapy. Moreover, TiO_2 particles are a UV-B filter, suitable for developing physical sunscreens combining both increasing stability and high SPF properties (Wang and Tooley, 2011). The introduction of ZnO ensures an adequate protection in the range of UVA. Due to its multifunctional nature, ZnO particles have been shown to be effective as antibacterial and antifungal agent (Singh et al., 2012; Smijs and Pavel, 2011).

On the other hand, TiO_2 particles can be also used as solid particles for stabilization of surfactant-free emulsions stabilized by solid particles (*i.e.* Pickering emulsions). This type of emulsions have important advantages over the classical surfactant-based emulsions, such as higher resistance to coalescence due to an improved stability, and a higher tolerability (Laredj-Bourezg et al., 2012). The stabilization of emulsion droplets takes place by means of adsorption of solid particles at the surface of emulsion droplets. It can be assumed that a stable water-in-oil (w/o) Pickering emulsion is a function of particles concentration, pH and ionic strength. This adsorption mechanism is quite different compared to surfactants since partial wetting of the solid particles surface by water and oil is the reason of the strong anchoring of these particles at the water–oil interface. Few fully natural and biocompatible materials are available for the effective stabilization of these emulsions since severe requirements must be simultaneously met, including insolubility in both fluid phases and intermediate wettability (Folter et al., 2012).

The purpose of this work was to develop and characterize a w/o emulsion stabilized by physical sunscreens containing 35% of the lipid fraction of spent coffee grounds extracted with supercritical CO_2 and green coffee oil obtained from defective beans with improved sunscreen performance. Sunscreen formulations might be a suitable application for these types of sub-products because w/o emulsions are water resistant and provide greater efficacy (a higher SPF) for the same concentration of sunscreen actives than their o/w counterparts (Couteau et al., 2012).

2. Material and methods

2.1. Materials

Spent coffee grounds oil (SCO) was supplied by LAQV-REQUIMTE – Departamento de Química, Faculdade de Ciências e Tecnologia (Caparica, Portugal). Green coffee oil (GCO) was supplied by Cooxupé – Cooperativa de Cafeicultores de Gauxupé, (Minas Gerais, Brazil). Triethoxycaprylylsilane titanium dioxide ($mTiO_2$) (Unipure White LC 987) was a gift from Sensient (Milwaukee, USA). The starch used was aluminum starch octenylsuccinate (ASt) (DryFlo® Plus) obtained from AkzoNobel (Amsterdam, Netherlands). Zinc oxide (ZnO) (Tego® Sun Z 500) was obtained from Evonik Industries AG (Essen, Germany). Purified water was obtained by inverse osmosis (Millipore, Elix® 3).

2.2. Methods

2.2.1. Characterisation of the formulation ingredients

2.2.1.1. Wettability measurements. Contact angles of water, green coffee oil and spent coffee oil on ZnO, $mTiO_2$ and ASt in air atmosphere were measured at room temperature by using ConAnXL—a Microsoft Excel based workbook and add-in software (freely available upon request) as described in detail elsewhere (Marto et al., 2015). All measurements were performed in triplicate.

2.2.1.2. Particle size distribution. Particle size distribution was determined using a Malvern Mastersizer 2000 (Malvern Instruments, UK), coupled with a Hydro S accessory. Data were expressed in terms of relative distribution of volume of particles in the range of size classes, and given as diameter values corresponding to percentiles of 10, 50 and 90. The Span value is a useful parameter to characterize the particle size distribution broadness.

2.2.1.3. Natural oils.

2.2.1.3.1. Oil extraction. SCG oil was obtained by supercritical CO_2 extraction as described elsewhere (Ribeiro et al., 2013). Supercritical fluid extraction can be an environmentally friendly alternative to traditional organic solvent extraction processes whereby extraction/separate recovery of oil and bioactive compounds from agro-industrial residues can be done without their degradation (Brunner, 2013). Mass transport is highly facilitated owing to favourable transport properties (high mass and thermal diffusivities coupled with low viscosities) and the solvation capacity of the supercritical fluid is tuneable by changing the operating conditions of pressure and temperature. The most commonly used supercritical fluid, carbon dioxide, is non-toxic, non-flammable, non-corrosive, relatively inert from a chemical point of view and environmentally friendly. Its relatively low critical temperature (304.3 K) allows extraction of thermolabile substances without degradation.

The supercritical CO_2 extraction of SCG oil was done in a high pressure extraction pilot unit. SCG were first dried in an oven at