Utilization of Surface-active Compounds and Microfibrillated Cellulose Particles from Argan Processing Residue as Sustainable Natural Emulsifiers

Meryem BOUHOUTE

Summary of thesis

The utilization of natural ingredients derived from biomass is a promising path toward sustainability. In recent years, consumers are more aware about the resources and ingredients formulating their products and the challenges facing today's food engineering field is to provide healthy sustainable products while regaining consumer trust. Sustainability approach is based on three main pillars, environment, social and economic. For a product to be sustainable, it has to satisfy those three pillars. In addition, the development of functional food, dietary supplements, nutraceuticals and product reformulation for favorable health impact (salt reduction, calorie reduction) for an aging population is also a challenge toward healthiness. Finally, to regain consumer trust, food formulations require the incorporation of natural ingredients and providing clean label products.

Considering the above-mentioned aspects, the choice of argan oil industry made a lot of sense for this study to tackle the challenges of product formulation. This industry is unique to the Moroccan country because the species Argania spinosa is endemic to its desert. Argan tree plays an important environmental role in the region, because of its high resistance to environmental stress (water draught, arid land) therefore procuring a barrier to desertification and erosion of the soil. Argan plays also an important socio-economical role in the region, considering that Argan is a wild species that have been present for centuries in southwestern Morocco. Today, 2-3 million people rely on argan tree as a source of income, in fact, all the parts of the tree are used today by the local population. The main product of argan fruit is the oil, however, this product represents only 3% of the total mass of the fruit. The remaining are, agan press cake, argan pulp and argan shell that are considered by-products and are used by the locals as cattle feed (press care and pulp) or burned for heat generation (shell).

Argan shell is a lignocellulosic biomass rich in fibers, which led to few research centered toward this material to prepare composites or to be used as biochar. However, considering that argan oil made a real breakthrough to international markets (argan oil is known for its unique cosmetic and edible features), this thesis was inspired to valorize argan by-product (argan shell) within food, cosmetic or pharmaceutic industries. By providing new compounds acting as natural emulsifiers.

Emulsifiers global market represents 8.4 billion $, this market is divided between food market (30%),

cosmetics (20%) and pharmaceutic and agrochemicals (50%). This market is expected to grow by 5.6 points in 2050. Mostly, when considering emulsifiers, it is more common to find a synthetic emulsifier used rather than a natural one. In fact, synthetic emulsifiers represent 70% of emulsifiers against only 30% of natural emulsifiers in the global market. The reason behind this difference is the inhomogeneous and high cost of natural emulsifiers when compared to their synthetic counterparts. Therefore, industrial are less attracted to their utilization when formulating products. But this trend is now changing, and industrials and manufacturers have to adapt to the new aspirations of consumers, thus, providing acceptable products for them to use.

Oil-in-water (O/W) emulsion is a system encountered in many commercial products such as food, cosmetic and pharmaceutic industries. This system is thermodynamically unstable consisting of two immiscible liquids, one dispersed into the other, that would rapidly separate to the initial homogenized components in the absence of stabilizers. Emulsion stabilizers can be categorized into surface-active emulsifiers (surfactants) and thickening or gelling agents. Furthermore, solid particles were also described to stabilize emulsions forming the so-called 'Pickering emulsions' that were first reported by Pickering (1907). Our research focus was to identify a new natural source of surface-active compounds and microfibrillated cellulose and utilize them to formulate and stabilize emulsions.

The thesis highlighted an exhaustive extraction of natural compounds from argan shell biomass and applied them in the formulation of O/W emulsions. The first extraction consisted on solid-liquid extraction using aqueous-ethanol as solvent. Five extracts were characterized in this study then compared for their emulsifying performance. The obtained residue of aqueous-ethanol extraction was used for the preparation and purification of cellulose. The pulping process consisted of alkali treatment and we studied the effect of four different concentration of sodium hydroxide on argan shell purified cellulose. After reaching satisfying properties of argan shell cellulose microfibrillated cellulose was prepared using mechanical disintegration.

First, a characterization of the extracted compounds using spectrophotometric methods, Fourier Transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), interfacial tension and contact angle, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), was conducted. Then, we focused on the utilization of the identified compounds to formulate and stabilize (O/W) emulsions, this involved high energy emulsification and monitoring physical stability under different environmental stress conditions. Our results were successful and could lead to the formulation of emulsions

using natural emulsifiers from argan shell.

Emulsions formulation and stability using natural emulsifiers is varying considerably due to the source and the type of surface-active compounds. This is even more the case when using crude extracts from plant material as emulsion stabilizers. Mostly, interfacial tension and composition are used to confirm the tendency of an emulsifier to formulate a stable emulsion. However, systemic studies also offer more reflection on the mechanism behind a successful stability. Our study showed the possibility of using crude argan shell extracts as natural emulsifiers. We confirmed that with the same starting material, under different extraction conditions, all extracts were capable of producing submicron emulsions with a highly negative charge and good physical stability despite the variation in the composition of surface-active compounds. However only one extract (20-ASE) could form an emulsion with the lowest mean droplet size d43 < 200 nm. This means that the whole composition contributes to emulsion formation when using complex mixtures of surface-active compounds and emulsion trials have to be conducted in order to reveal this tendency.

The use of argan shell microfibrillated cellulose (AS-MFC) as oil-in-water (o/w) emulsions stabilizer was investigated. The effect of particles concentration was assessed and led to long term stability (15 days) of o/w emulsions at high concentration of AS-MFC confirmed by droplet size d4,3 and creaming index. This study also shows the oil concentration suitable to reach the maximum volume of emulsion using 1% w/w AS-MFC. The results show AS-MFC could stabilize 70% w/w MCT oil. Finally, CLSM shows the adsorption of AS-MFC at the oil-water interface and the formation of a 3D network surrounding oil droplets by larger fibrils.

Based on this research we provide evidence to predict an added value of argan shell for food, cosmetic or pharmaceutic industries. However, more research is required regarding toxicity of the compounds extracted from argan shell. In addition, for an industrial use, an economical based study is required for scaling up the production and reaching homogeneous compounds ready for utilization by the above-mentioned industries.

Besides the industrial application of surface-active compounds and microfibrillated cellulose, there are many scientific topics in which argan shell may offer new research opportunities. First, the chemical stability of bio-active compounds encapsulated by surface-active compounds or microfibrillated cellulose could be elucidated. Next, digestive stability of emulsions can be studied. Furthermore, it would be interesting to study the interfacial composition of emulsions stabilized by argan shell extracts. Another intersting topic would be the complexation of microfibrillated cellulose and surface-active compounds to deliver enhanced emulsifying properties.