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Interfacial properties of green leaf cellulosic particles

A. Tamayo Tenorio [a], J. Gieteling [a], C.V. Nikiforidis [a, b], R.M. Boom [a], A.J. van der Goot [a, *]

[a] Food Process Engineering, Wageningen University, P.O. Box 17, 6700 AA, Wageningen, The Netherlands
[b] Biobased Chemistry and Technology, Wageningen University, P.O. Box 17, 6700 AA, Wageningen, The Netherlands

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ABSTRACT

Cellulosic pulp from sugar beet leaves was fractionated and assessed on its interfacial properties. After pressing leaves to express the juice, the press cake was washed at alkaline pH (pH 9) to remove residual protein, dried, milled and air classified. The obtained cellulosic particles mainly consisted of insoluble dietary fibre (77.8% w/w) with remaining proteins (6.3% w/w) and exhibited considerable interfacial activity. The protein impurities contribute to the surface charge of the particles and provide surface activity, leading to spontaneous diffusion of the particles during the interfacial tension analysis; whereas the particle adsorption kinetics were characteristic of soft particles or Pickering emulsifiers. The interfacial rheology measurements showed abnormal behaviour and unusual drop shape upon deformation, hindering interpretation of the analysis but still suggesting a rigid interface with strong physical particle-particle interactions. Stable oil-in-water emulsions were produced using cellulosic particles, and despite phase separation, the emulsions were stable against coalescence. The results suggested that mostly fine particles (0.04–1.0 μm) were responsible for the interfacial stabilisation, given the small oil droplets obtained (2–5 μm); whereas larger particles (>10 μm) created a network in the continuous phase, which was responsible for the emulsion phase separation. It was concluded that the cellulosic particles had a soft nature and suitable shape to produce stable Pickering emulsions, which can be used as food-grade particles for food and pharma applications.

1. Introduction

The use of solid particles as emulsion stabilisers is highly promising in many applications (e.g. food, pharma, cosmetics) because of their outstanding stabilisation against coalescence compared to low molecular weight emulsifiers (Tcholakova, Denkov, & Lips, 2008). The stabilising mechanism of solid particles in Pickering emulsions is due to the accumulation of particles at the oil-water interface as a densely packed layer, which is determined by the particle properties and emulsification conditions (Binks, 2002; Tzoumaki, Moschakis, Kiosseoglou, & Biliaderis, 2011; Wu & Ma, 2016). The particles are irreversibly adsorbed at the interface, and the mechanical properties of the adsorbed layer contribute to the long-term stability of emulsions (Dickinson, 2012). The particles may be synthetic or obtained from different types of biobased feedstocks (Rayner et al., 2014), which can be extended to leaves and leaf by-products.

Leaves and leaf by-products are available on massive scale from industrialized crops. Using leaves that are now discarded, may at least partly provide a sustainable alternative to producing more food from existing resources (Dijkstra, Linnemann, & van Boekel, 2003). For this, leaves are processed to extract valuable components such as proteins. The extraction involves a pressing/grinding step that separates the intracellular fluids from the leaf fibrous pulp. So far, most scientific interest is focussed on further juice purification, thereby neglecting the fact that the pulp represents nearly 25% w/w of the starting biomass (Tamayo Tenorio, Gieteling, Nikiforidis, Boom, & van der Goot, 2016), and giving added value to this large side stream would contribute to a more complete use of the green leaves.

The leaf fibrous pulp is rich in dietary fibres like cellulose, hemicellulose and lignin, with the amounts present varying between crops (Siqueira, Bras, & Dufresne, 2010). A simplified scheme of a plant cell wall is depicted in Fig. 1, identifying the major components and structural arrangements. The plant cell wall constitutes an ordered network of cellulose microfibrils coated with hemicellulosic polysaccharides, a gel-like matrix made of pectic polymers, and a network consisting of structural proteins that hold

* Corresponding author.
E-mail address: atzejan.vandergoot@wur.nl (A.J. van der Goot).

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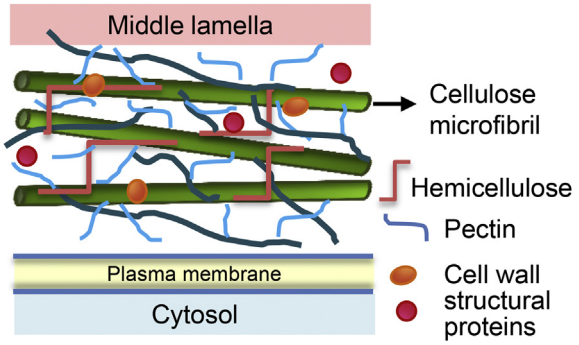

Fig. 1. Simplified scheme of the primary cell wall structure, adapted from (Labavitch et al., 2015).

the polymers in place (Held, Jiang, Basu, Showalter, & Faik, 2015). Dietary, fibre rich materials have multiple uses, including clouding of beverages, thickening and gelling, and also low calorie bulking (Galanakis, 2012). Moreover, fibre rich biomass is a potential source of Pickering emulsion stabilisers. Such materials have been produced from other agro-industrial waste like orange peel (Wallecan, McCrae, Debon, Dong, & Mazoyer, 2015), mango peel (Serna-Cock, García-Gonzales, & Torres-León, 2016), celery and spinach (Göksel Saraç & Dogan, 2016) and cocoa fibres (Gould, Vieira, & Wolf, 2013).

The type of particles produced is related to the cell wall structure and to the processing conditions that disrupt the cell wall. In general, plant cell walls are networks of interconnected biopolymers such as polysaccharides (cellulose, hemicelluloses, pectin), glycoproteins (i.e. extensins), and lignin (Beck, 2005). With harsh processing conditions (i.e. high pressure, high temperature, chemical hydrolysis), pure crystalline cellulose can be obtained, which has been used in particle stabilised emulsions (Pickering) and composites (Siqueira et al., 2010). With milder mechanical processing, the resulting particles are rich in cellulose but still contain other cell wall components, like polysaccharide-protein complexes (Harris & Smith, 2006), which can provide additional Pickering stabilisation (Wallecan et al., 2015).

In this study, cellulosic particles were extracted from sugar beet leaves (SBL), using mild aqueous extraction. Our objective was to characterise these particles and to study their interfacial behaviour. Composition and size characterisation were followed by interfacial tension and interfacial rheology analysis, and the particles were finally added to oil-water emulsions as stabilisers. We concluded that fibrous leaf pulp is a potential source of cellulosic particles that can be used as Pickering emulsifiers in food applications.

2. Materials and methods

2.1. Purification of leaf fibres

Sugar beet leaves from mature plants were harvested from a sugar beet production field in Wageningen, The Netherlands. The leaves were pressed with a screw press (Angelia juicer II 7500 from Angel Juicers, Queensland, Australia) to separate the leaf juice from the fibrous pulp. The pulp was then processed until a fine powder as depicted in Fig. 2. The fibrous pulp was washed 5 times for 1 h with alkaline deionised water (pH 9.0) in a pulp-to-water weight ratio of 1:5. NaOH 1M was used for adjusting the pH. The material was dialysed against MilliQ water with a cellulose membrane (MW cut-off of 14 kDa) (Sigma-Aldrich, St. Louis, MO, USA). The dialysed pulp was filtered through four layers of cheese cloth, followed by freeze drying. The dried pulp was milled with a rotor mill (Pulverisette 14, Fritsch, Germany) using a sieve-size of 0.08 mm. The

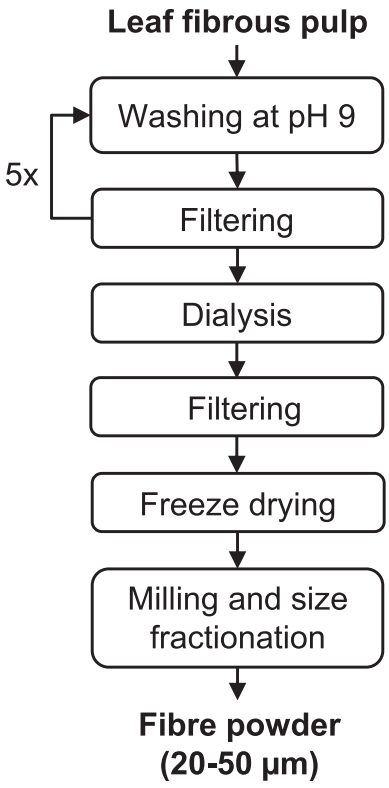

Fig. 2. Diagram of purification of fibre particles from sugar beet leaves.

resulting powder was separated by air-jet sieving (Alpine200 LS-N, Hosokawa-Alpine, Augsburg, Germany), collecting four fractions $\leq$ 20, 20–50, 50–100 and $\geq$ 100 μm. The fraction between 20 and 50 μm was used for further experiments. All processing steps were done at room temperature.

2.2. Compositional analysis

The moisture content was determined with an infrared moisture analyser MA35 (Sartorius weighing technology GmbH, Göttingen, Germany) at 105 °C. The nitrogen content of the dry samples was measured in duplicate by Dumas analysis (NA 2100 Nitrogen and Protein Analyser, ThermoQuest-CE Instruments, Rodeno, Italy). A conversion factor of 6.25 was used to convert nitrogen values to protein and to enable comparison with previous leaf protein studies, although lower conversion factors (4.32–4.95) have been recently defined for SBL (Kiskini, Vissers, Vincken, Gruppen, & Wierenga, 2016). Total dietary fibre was determined with a Megazyme assay kit (Megazyme International, Bray, Ireland) according to AACC method 32–05.01 (AACC, 1983c). The ash and fat content were determined with official AACC method 08–01 and method 30–25, respectively (AACC, 1983a, 1983b).

2.3. Zeta potential measurements

The ζ-potential was measured in triplicate as a function of pH with a Zetasizer (Malvern Instruments, Worcestershire, UK) coupled with an autotitrator (Malvern Instruments, Worcestershire, UK) at pH between 1.0 and 10.0. A cellulose particle dispersion (0.5% w/v) was prepared by vortexing and was analysed after 1 h of rest at 20 °C. Samples were diluted ~1000 times in Milli-Q water before the analysis. Additionally, a particle sample with extra purification was analysed. The extra purification consisted of