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# Effect of pectins on the mass transfer kinetics of monosaccharides, amino acids, and a corn oil-in-water emulsion in a Franz diffusion cell



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# ABSTRACT

The effect of high (HMP) and low (LMP) methoxylated pectins (2% *w/w*) on the rate and extent of the mass transfer of monosaccharides, amino acids, and a corn oil-in-water emulsion across a cellulose membrane was evaluated. A sigmoidal response kinetic analysis was used to calculate both the diffusion coefficients (rate) and the amount of nutrients transferred through the membrane (extent). In all cases, except for lysine, HMP was more effective than LMP in inhibiting both the rate and extent of the mass transfer of nutrients through the membrane. LMP and HMP, *e.g.*, reduced 1.3 and 3.0 times, respectively, the mass transfer rate of glucose, as compared to control (containing no pectin), and 1.3 and 1.5 times, respectively, the amount of glucose transferred through the membrane. Viscosity, molecular interactions, and flocculation were the most important parameters controlling the mass transfer of electrically neutral nutrients, electrically charged nutrients, and emulsified lipids, respectively.

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#### 1. Introduction

There is a growing interest among consumers about the nutritional, therapeutic, and functional properties of foods consumed in the diet (Mohamed, 2014). The current trend of consumers is based on the consumption of foods with functional components beneficial for human health, such as phytosterols, polyphenolics, anthocyanins, carotenoids, and dietary fibres (Bigliardi & Galati, 2013). In recent years, dietary fibre has received important attention from the food industry and consumers due to the health benefits associated with the consumption of dietary fibre-rich foods (Brownlee, 2014). Dietary fibre components possess distinctive physicochemical and structural characteristics determining their functionality, and they can be categorized as either insoluble or soluble dietary fibres (Phillips, 2013). The consumption of insoluble dietary fibre has been associated with increasing bulkiness of the digesta content and improvement of the gastrointestinal tract (GIT) mobility (Edwards, Johnson, & Read, 1988), whereas the consumption of soluble dietary fibre has been associated with a wider variety of physiological functions, such as control of postprandial glycemic and lipid response (Pasquier et al., 1996), decrease of blood lipid and glucose levels (Ye, Arumugam, Haugabrooks, Williamson, & Hendrich, 2015), inhibition of the GIT enzyme activities (Espinal-Ruiz, Parada-Alfonso, Restrepo-Sánchez, & Narváez-Cuenca, 2014),

\* Corresponding author. E-mail address: cenarvaezc@unal.edu.co (C.-E. Narváez-Cuenca). Parada-Alfonso, Restrepo-Sanchez, Narvaez-Cuenca, & McClements, 2014a, 2014b; Espinal-Ruiz, Restrepo-Sánchez, Narváez-Cuenca, & McClements, 2016), increase of the viscosity of the GIT content (Edwards et al., 1988; Elleuch et al., 2011), and retardation of the mass transfer process of nutritional compounds to be absorbed by enterocytes (Fabek, Messerschmidt, Brulport, & Goff, 2014; Srichamroen & Chavasit, 2011). Among the aforementioned properties of soluble dietary fibre, the ability to modulate the viscosity of the GIT content stands out because this feature is related to the control of the mobility of nutrients and their further digestion and absorption (Fabek et al., 2014). The functional properties of soluble dietary fibres (*e.g.*, gums, mucilages, and pectins) rely on their ability to gel into hydrated

control of the rate and extent of lipid digestion (Espinal-Ruiz,

The functional properties of soluble dietary fibres (*e.g.*, gums, mucilages, and pectins) rely on their ability to gel into hydrated three-dimensional networks and their subsequent increasing of viscosity, determining their potential to exert physiological effects along the GIT, specifically through the stomach and small intestine (Brownlee, 2014). The proposed mechanism by which viscosity may induce physiological responses includes increasing of luminal bulk (Ye et al., 2015) and inhibiting of nutrient diffusion across the unstirred water layer (UWL) of the mucosal membrane (Fabek et al., 2014; Gunness, Flanagan, Shelat, Gilbert, & Gidley, 2012). Viscous soluble fibres may hinder the mass transfer process of nutritional compounds from the lumen to the UWL of the mucosal membrane by reducing the mixing between them and reducing the time available for intestinal absorption by enterocytes (Fabek et al., 2014; Gunness et al., 2012). Therefore, an increase in digesta







viscosity, arising from the soluble dietary fibre consumption, might influence the processes occurring during the nutrient digestion and adsorption (Espinal-Ruiz, Parada-Alfonso, Restrepo-Sanchez, Narvaez-Cuenca, & McClements, 2014a, 2014b).

Among the different sources of soluble dietary fibre available, pectin is a polysaccharide obtained from fruits and vegetables and it is widely used in the pharmaceutical and food industries for its thickening, gelling, and texturing properties (Maxwell, Belshaw, Waldron, & Morris, 2012). Pectin is a biopolymer, mainly formed from galacturonic acid (GalA) units joined in chains by  $\alpha$ -D-(1,4) glycosidic linkages. Three pectic structures [homogalacturonan (HG), rhamnogalacturonan-I (RG-I), and rhamnogalacturonan-II (RG-II)] have been isolated and structurally characterized (Mohnen, 2008). HG corresponds to the linear chain of  $\alpha$ -(1,4) GalA units in which the carboxyl group (-COO<sup>-</sup>) of GalA moieties can be partially esterified with methanol (methoxylated), forming the carbomethoxyl group (-COOCH<sub>3</sub>). An important characteristic of HG is the methoxylation degree, defined as the percentage of carboxyl groups which have been methoxylated. If more than 50% of the carboxyl groups are methoxylated, the pectin is called high methoxylated pectin (HMP), and if less than that methoxylation degree, it is called low methoxylated pectin (LMP). RG-I is a pectic structure containing a linear backbone of the disaccharide  $[\rightarrow 4)$ - $\alpha$ -D-GalA- $(1 \rightarrow 2)$ - $\alpha$ -L-Rha- $(1 \rightarrow ]$ , where Rha corresponds to rhamnose, and RG-II consists of a HG backbone substituted with side branches, consisting of twelve different types of monosaccharides in up to twenty different linkages (Maxwell et al., 2012). The most abundant pectic structure is HG that comprises ~65% (mol/mol) of pectin, whereas RG-I and RG-II comprise ~25 and ~10% (mol/mol), respectively (Yapo, 2011). It is important, however, to stress that the ratios of HG, RG-I and RG-II may vary greatly, depending on both the source and the extraction method (Mohnen, 2008). Many functional properties of pectin (e.g., viscosity, solubility, as well as waterholding, texturing, and gelling capacities) are dependent on its structural parameters such as molecular weight, methoxylation degree, and the distribution pattern of methoxylation within the GalA chains (Mohnen, 2008; Ryden, MacDougall, Tibbits, & Ring, 2000; Yapo, 2011). In previous studies, we have demonstrated that pectin inhibits the activity of some digestive enzymes (Espinal-Ruiz, Parada-Alfonso, Restrepo-Sánchez, & Narváez-Cuenca, 2014) and interferes with the digestion process of emulsified lipids (Espinal-Ruiz, Parada-Alfonso, Restrepo-Sanchez, Narvaez-Cuenca, & McClements, 2014a, 2014b; Espinal-Ruiz et al., 2016) by interacting with several GIT components, such as digestive enzymes, bile salts, and electrolytes (Espinal-Ruiz, Parada-Alfonso, Restrepo-Sanchez, Narvaez-Cuenca, & McClements, 2014a, 2014b).

Although studies regarding the mass transfer control of some nutritional compounds (e.g., glucose and bile salts) have been carried out by using different sources of dietary fibres, no information is currently available concerning the influence of pectins on the mass transfer process of the primary nutritional compounds consumed in the diet or produced after the digestion process, such as monosaccharides, amino acids, and lipids. The objective of this study was, therefore, to determine the effect of HMP and LMP on the rate and extent of the mass transfer process of the main nutritional compounds consumed in the diet or obtained after the digestion process, e.g. monosaccharides, amino acids, and lipids (represented by a corn oil-in-water emulsion). The mass transfer profiles of monosaccharides, amino acids, and a corn oil-in-water emulsion in the absence (control) or presence of pectins (LMP or HMP) reported a possible interaction mechanism between pectin and the evaluated nutritional compounds. These results might lead to the design, formulation, and fabrication of functional foods developed to control postprandial blood concentrations of the monosaccharides, amino acids, and lipids consumed in the diet.

## 2. Materials and methods

# 2.1. Chemicals and materials

D-(+)-Glucose, D-(+)-galactose, D-(-)-fructose, and D-(-)-ribose were purchased from Panreac Química SLU (Barcelona, Spain). L-lysine, L-glycine, L-aspartic acid, L-tyrosine, ninhydrin monohydrate, Tween 80, and a dialysis tubing cellulose membrane (cut-off 14 kDa) were purchased from Sigma-Aldrich Chemical Company (St Louis, MO, USA). Corn oil was purchased from a commercial food supplier (Grasco LTDA, Bogotá DC, Colombia) and stored in darkness at room temperature until used. The manufacturer reported that the corn oil contained approximately 14, 35, and 51% (*w/w*) of saturated, monounsaturated, and polyunsaturated fatty acids, respectively. Commercial powdered LMP was donated by TIC Gums Inc. (Belcamp, MA, USA) and was used without further purification, with methoxylation degree and average molecular weight previously reported as 30% (mol/mol) and 130 kDa, respectively (Espinal-Ruiz et al., 2016). Commercial powdered HMP (Genu Citrus Pectin USP/100) was donated by CP Kelco Co. (Lille Skensved, Denmark) and was also used without further purification, with methoxylation degree and average molecular weight previously reported as 71% (mol/mol) and 181 kDa, respectively (Espinal-Ruiz et al., 2016). All other chemicals were purchased from Merck KGaS (Darmstadt, Germany). Deionized water was used to prepare all solutions. Franz diffusion cells (Fig. 1) were fabricated by Siliser LTDA (Bogotá DC, Colombia). The volumes of the donor and receptor compartments were 3 and 17 mL, respectively. The effective area of mass transfer (A)was 1.33 cm<sup>2</sup>.

#### 2.2. Sample preparation

LMP and HMP stock solutions (4% w/w) were prepared separately by dispersing 2 g of powdered pectins into 48 g of deionized water. These solutions were stirred at 1000 rpm overnight at room temperature to ensure complete dispersion and dissolution. LMP and HMP solutions were then adjusted to pH 7.0 by using 0.1 M NaOH.

A monosaccharide stock solution (280 mM of each compound) was prepared by dissolving together glucose, galactose, fructose, and ribose in deionized water. These monosaccharides were selected because of their nutritional relevance and because they are monosaccharides composing digestible carbohydrates the most (Asp, 1996). The monosaccharide stock solution (2.5 mL) was then



**Fig. 1.** Structural design of a Franz diffusion cell. Donor compartment with a nominal volume of 3 mL (a), receptor compartment with a nominal volume of 17 mL (b), position for a semipermeable cellulose membrane (c) with an effective area of mass transfer (A) of 1.33 cm<sup>2</sup> (diameter of 1.30 cm), sampling port (d), magnetic stir bar (e), thermostatted chamber at 37 °C (f), water inlet (g), and water outlet (h).

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