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Study on flavonoid migration from active low-density polyethylene film into aqueous food simulants

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ABSTRACT

The migration of flavonoids from low-density polyethylene (LDPE) film (0.4%, w/w) to aqueous food simulants over 16 weeks at 0, 15, and 30 °C was investigated. The migration amount of total flavonoids was calculated based on the rutin contents determined by high-performance liquid chromatography (HPLC). Diffusion and partition coefficients, along with the activation energy (E_a) were calculated based on Fick's second law. The results showed that the migration of flavonoids was influenced by temperature, time and the simulants. The E_a values for flavonoid diffusion were 49.2, 55.9, and 25.8 kJ mol^{-1} in distilled water, 4% acetic acid and 30% ethanol, respectively. This study indicated that the flavonoids in LDPE film easily migrated into food simulants; and this behaviour was related to the low E_a values of flavonoid diffusion, especially in ethanol at 0–30 °C, when the antioxidants were released from the film.

1. Introduction

Flavonoids are the main naturally occurring compounds of pharmacological and nutritional interest, and are widely found in the flowers, leaves and seeds of many plants (Kosalec et al., 2013; Momtaz, Hussein, Ostad, Abdollahi, & Lall, 2013; Petlevski, Flajs, Kalođera, & Končić, 2013). García-Mateos, Aguilar-Santelises, Soto-Hernández, and Nieto-Angel (2013) reported that the flavonoid extracts of some Mexican flowers have antioxidant activities and their compositions were identified by HPLC-MS. Among the flavonoids, quercetin 3-O-glucoside, quercetin 3-O-rhamnoside, quercetin 3-O-rhamnosyl-(1-6)-glucoside and quercetin 3-O-rhamnosyl-(1-2)-[rhamnosyl-(1-6)]-glucoside were assigned. Li et al. (2014) reported that celery flavonoid extracts exhibited a strong total antioxidant capacity, with IC_{50} values of 68.0 μg/ml^{-1} in the DPPH assay, 0.39 μg/ml^{-1} in the $O_2^{-\cdot}$ assay and 48.0 μg/ml^{-1} in the OH· assay, respectively. Saroja and Annapoorani (2012) found that the flavonoid fractions of Cynodon dactylon and Terminalia catappa leaves had antioxidant activity and could potentially be used as a source of natural antioxidants. Kredy et al. (2010) researched the potential antioxidant activities of flavonols from lotus seeds. This antioxidant potential in terms of IC_{50} values were 5.48, 40 ± 0.14 and 0.62 ± 0.05 (dry fraction 2) μg/ml^{-1} in the DPPH radical, hydroxyl radical and hydrogen peroxide assays, respectively. Flavonoids therefore have potential applications as new food additives with high antioxidant capacities.

Antioxidant active packaging is a promising technology for food protection (Barbosa-Pereira et al., 2013; Bodaghi et al., 2013; Martínez-Camacho et al., 2013; Núñez-Flores et al., 2013; Salgado, López-Caballero, Gómez-Guillén, Mauri, & Montero, 2013). The major antioxidants added to films include: α-tocopherol, butylated hydroxytoluene, I-1076 and I-168. Graciano-Verdugo et al. (2010) reported that the concentration of α-tocopherol in low-density polyethylene (LDPE) films, as well as the storage temperature, directly affected the migration of α-tocopherol into corn oil and its oxidative stability. Granda-Restrepo et al. (2009) studied the migration of α-tocopherol from multilayer active packaging materials into whole milk powder. The packaging materials were made of high-density PE (HDPE), ethylene vinyl alcohol and a layer of LDPE containing the antioxidant. Nerín et al. (2006) researched the stabilization of beef using a new active packaging containing natural antioxidants and showed that the active film containing natural antioxidants efficiently enhanced the stability of both the myoglobin and fresh meat against oxidation processes. Garde, Catalá, Gavara, and Hernandez (2001) investigated the migration of antioxidants from polypropylene (PP) films into fatty food simulants and found that heptane could fully extract the antioxidants from the polymer. All the above studies provide a great deal of valuable information and promote the research and development of active packaging. However, there is little data available in scientific literature regarding the migration of flavonoids from LDPE

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films into food. In this study, the characteristics of flavonoid migration from active LDPE films into several aqueous food simulants (distilled water, 4% acetic acid, and 30% ethanol) were investigated to understand the interaction of food and plastic packaging and provide information for the development of the active packaging industry.

2. Materials and methods

2.1. Film manufacture

Granular LDPE (1 kg) mixed with flavonoids (5 g) was manufactured into the experimental film using a laboratory film-blowing machine (PTF-IBS-20/28, Guangzhou, China). The running temperature of machine was 120 °C and the air pressure was 0.2 MPa. The film thickness was 4×10^{-3} cm, and the flavonoid content was 0.4% (w/w, partially loss during manufacture) as determined using the Soxhlet extraction method. Flavonoids were extracted from Chinese lotus leaves by ultrasonication. The rutin content in the flavonoid extracts was determined by high-performance liquid chromatography (HPLC, Agilent 1200, USA). And the concentration of rutin in theflavonoid extracts was 68.0%. The film was cut into pieces with dimensions of 0.5 cm × 0.5 cm after being cleaned with distilled water.

2.2. Migration experiments

Distilled water, 4% acetic acid and 30% ethanol were chosen as the aqueous food simulants. For each simulant, 144 LDPE film samples (16 weeks, three replicates) were accurately weighed as 0.2 g. Each sample was placed in a beaker with a cover. Fifty ml of the simulants were added to these beakers. The mixtures were stored under different temperatures (0, 15, and 30 °C). A total of 432 samples were obtained.

2.3. Quantification of flavonoids in aqueous simulants

The beakers were taken out of storage and the volume was immediately made up to 50 ml. Samples (10 ml) were evaporated to dryness and the residue was redissolved in methanol (10 ml). The rutin content was determined by HPLC, and the migration of total flavonoids was calculated (68.0% of the rutin concentration in flavonoids). Three replicates were carried out for each sample; the mean values and standard deviations were calculated, denoted by $X \pm s$. Analysis of variance and *t*-tests were conducted using SAS 9.13 software (SAS Institute Inc.), and pair comparisons were made using the Duncan method.

2.4. Chromatographic conditions

The HPLC system (Agilent 1200, USA) was fitted with an auto sampler and diode array ultraviolet detector. Chem-station chromatographic software was used for data acquisition. Chromatographic separation was performed using a Lichrospher C18 column (25 cm × 0.21 cm inner diameter). Isocratic elution was performed using acetic acid (0.4% w/w)–methanol (9/1, v/v); the column temperature was 30 °C and the flow rate was 0.3 ml/min^{-1}.

2.5. Mathematical models and determination of key parameters

Migration processes in films can be fully described by the kinetics of migrant diffusion (expressed by the diffusion coefficient, D) and the chemical equilibrium (expressed by the partition coefficient, K).

An analytical solution of Fick's second-law equation for diffusion in one dimension, limitless volumes of food, and lengthy contact was used for the determination of D using Eq. (1) (Crank, 1975):

$$\frac{M_{F,t}}{M_{F,\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2_{\pi^2}} \exp\left[-\frac{(2n+1)^2\pi^2}{4d_p^2} Dt\right] \quad (1)$$

where $M_{F,t}$ is the amount of migrant in the food at a particular time t (s); $M_{F,\infty}$ is the amount of migrant in the food at equilibrium; d_p (cm) is the polymer thickness; D (cm^2 s^{-1}) is the diffusion coefficient of migrant in the polymer and t (s) is the time.

The beginning of migration process can be described by a simplified expression (Eq. (2)) (Crank, 1975):

$$\frac{M_{F,t}}{M_{F,\infty}} = \frac{4}{d_p}\left[\frac{Dt}{\pi}\right]^{0.5} \quad (2)$$

To fit the data to Eq. (2), the mass of the flavonoids diffused at time t divided by the mass of the flavonoids diffused at equilibrium (M_t/M_∞ or M_t/M_{eq}) was plotted versus time t (s), and then D was calculated. The MATLAB (Math Works, Natick, MA, USA) program was used to find the best fit of the data to Eq. (2), using the nlinfit (non-linear regression) function in MATLAB R2012a.

The partition coefficient, K, is expressed by

$$K = \frac{C_{P,\infty}}{C_{f,\infty}} \quad (3)$$

where $C_{p,\infty}$ (μg g^{-1}) and $C_{f,\infty}$ (μg g^{-1}) are the equilibrium concentrations of the component in polymer and food, respectively (Siró et al., 2006).

2.6. Diffusion activation energy (E_a)

The E_a values for the diffusion of flavonoids from films to simulants was determined using the Arrhenius equation for diffusion (Garde et al., 2001; Limm & Hollifield, 1996):

$$D = D_0 \exp(-E_a/RT) \quad (4)$$

where E_a is the diffusion activation energy; R is the ideal gas constant (8.314 J K^{-1} mol^{-1}); and T is the absolute temperature (K). The logarithms of D values were plotted versus the reciprocal of absolute temperature; E_a was obtained using the slope of line ($=-E_a/2.303R$).

3. Results and discussion

3.1. Influence of temperature on migration of flavonoids

The increase in the amount of flavonoids in the distilled water, 4% acetic acid, and 30% ethanol during storage at 0, 15 and 30 °C is presented in Fig. 1. It was obtained from Fig. 1 that the amount of flavonoid migration in the three simulants was lowest at 0 °C and highest at 30 °C at the same time before it reached equilibrium. For example, during the first week of storage in distilled water, the migration of flavonoids increased to 4 ± 0.01 μg, 14 ± 2.01 μg, and 29 ± 10.1 μg at 0, 15, and 30 °C, respectively. The amount of migration at 15 °C was triple that at 0 °C, and at 30 °C was twice that at 15 °C. Therefore, the temperature significantly influenced the migration of the flavonoids into the stimulants during storage.

The systems reached equilibrium at almost the same percentages (70.3%, 72.5%, and 73.7%) of the amount of migration flavonoids from the total because of the similar dissolutions between the films and liquids. The equilibrium was not related to the storage temperature, as would be expected from the physicochemical properties. However, the equilibrium time had an inverse relationship with temperature and was about a week shorter when