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Binary adsorption isotherm and kinetics on debittering process of ponkan (*Citrus reticulata* Blanco) juice with macroporous resins

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ABSTRACT

Selective removal of bitter components from ponkan juice with macroporous resins improved it sensory quality with scarcely effect on its nutritive value. Ten macroporous adsorbent resins were evaluated for their capacity in adsorbing the debittering component, and the adsorption selectivity for limonin against flavonids was estimated using coefficient $\alpha_{l/f}$. LX920 resin exhibited the highest adsorption capacity (7.96 mg/g wet resin) and selectivity coefficient $\alpha_{l/f}$ (99.42) at initial limonin concentration of 24 μg/mL. The adsorption equilibrium and kinetics were isothermally generated at 25 °C under static mode condition. Langmuir isotherm model and modified extended Langmuir model were well fitted with single and binary adsorption isotherms in binary system, respectively. The solute adsorptivity K_L of LX920 resin for limonin (2.81 L/g) was higher than that for flavonoids (1.10 L/g). limonin was more efficiently adsorbed onto the resin's surface. Furthermore, the pseudo-first, pseudo-second and intra-particle diffusion kinetic equations were employed to match the experimental adsorption data. Pseudo second-order and pseudo-first kinetic models were best fitted to the adsorption of limonin and flavonoids, respectively.

1. Introduction

As one of the most important centers of origin for the genus Citrus L., China is rich in ponkan (*Citrus reticulata* Blanco), which is one of the most popular citrus fruits for daily consumption and processing (Zhang et al., 2014). However, after squeezing or heating, ponkan juice exhibits an increase in bitterness just like other citrus fruits, which limits the industrial production of ponkan juice. Limonin (a limonoid) and naringin (a flavonoid) are recognized as the main reason for the bitterness of citrus juices (Cavia-Saiz, Muniz, Ortega, & Busto, 2011; Kola, Kaya, Duran, & Altan, 2010; Stinco et al., 2013). Our previous study showed that the content of narigin in ponkan juice was very low, and limonin was the main component of bitterness in ponkan juice (Bao, Yuan, Zhao, Liu, & Gao, 2013).

To improve the taste quality of citrus juices, several debittering techniques, including biodegradation by enzymes, addition of bitterness suppressing agents, ultra filtration, adsorption on certain adsorbents, and other methods, have been applied (Bassal & El-Hamahmy, 2011; Binello, Robaldo, Barge, Cavalli, & Cravotto, 2008; Cavia-Saiz et al., 2011; Lee & Kim, 2003; Stinco et al., 2013). Adsorbent resins are widely employed for the removal of limonin and the polystyrene divinyl benzene resins are preferred for citrus debittering (Chareonkit & Jirapakkul, 2011; Kranz, Adler, & Kunz, 2011).

Citrus fruit juices are rich in carbohydrates, vitamins, pigments and minerals, flavanones and phenolic acids (Zhang et al., 2014). Among these, cinnamic acid derivatives, coumarins and flavonoids (flavonones, flavones and flavonols) are the major phenolic compounds (Wang et al., 2013). Plant polyphenols are secondary metabolites which have positive effects on ameliorating some chronic diseases, such as type 2 diabetes, heart disease and various cancers because of their high antioxidant activities (Oboh & Ademosun, 2012) and other physiological activities like anti-inflammatory, anti-viral and anti-atherogenic functions (Chinapongtitiwat, Jongaroontaprangsee, Chiewchan & Devahastin, 2013). As flavonoids and limonoids have relatively similar structures and properties, the macroporous resins also adsorb some flavonoids during the debittering process and reduce the functional properties of ponkan juice. Unfortunately, no reference was available on the

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adsorption selectivity of debittering resins on limonin and flavonoids in citrus juices (Chinapongtitiwat et al., 2013).

We screened macroporous resins for high adsorption selectivity for limonin against flavonoids in the debittering process of ponkan juice. Furthermore, the adsorption properties of different resins including adsorption selectivity, adsorption kinetics and adsorption isotherm were investigated in detail.

2. Materials and methods

2.1. Chemicals

Limonin (>98.0%) and hesperidin (>98.0%) were obtained from Sigma Chemical Co. (St. Louis, MO). HPLC grade acetonitrile and methanol were purchased from Fisher Scientific Ltd. (Waltham, MA), purified water was obtained from Wahaha Co. Ltd. (Hangzhou, China). Other analytical grade chemicals and reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China).

2.2. Preparation procedure of ponkan juice

Ponkan were purchased from a local market in Huaihua City (Hunan Province, China) during its harvest season and peeled manually, then freshly squeezed using a screw press juicer. After that, ponkan juice was centrifuged at 2850 × g for 15 min to remove the flesh. The supernatant was collected and incubated at 85–90 °C for 60 s for enzyme inactivation. Thermally treated ponkan juice was cooled down and dispensed into 500 mL bottles and stored under −19 °C. Prior to adsorption experiments, the frozen ponkan juice was thawed at ambient temperature.

2.3. Activation and regeneration of adsorbent resins

The adsorbent resins used in this study are listed in Table 1. Prior to the adsorption, the resins were pretreated by a series of steps according to the method described by Bao et al. (2013) with minor modification. Firstly, resins were immersed in pure ethanol for 24 h, and then ethanol was replaced by distilled water through extensive washing. After that, the resins were regenerated in sequence by immersing in 40 g/L HCl for 4 h and 40 g/L NaOH for 4 h. After each immersion, the resins were washed to neutral by purified water.

2.4. Evaluation of resin adsorption capability

Static adsorption was employed to determine the adsorption capabilities of resins for limonin and flavonoids. Briefly, 0.15 g of each type of resins was accurately weighted and mixed with 50 mL ponkan juice prepared at an initial limonin concentration of 27.04 μg/mL in a 150 mL conical flask. The mixture was equilibrated for 24 h in a water bath at 25 °C with a shaking rate of 100 rpm. Then the juice was separated from the resins by filtering and collected for analysis. The adsorption capacity (Q_e mg/g wet resin) and removal rate (R_r) of limonin were calculated by Eq. (1) and Eq. (2). In order to optimize resins with the best adsorption selectivity for limonin against flavonoids, the selectivity coefficient$\alpha_{l/f}$ was defined as Eq. (3):

$$Q_e = (C_0 - C_e) \times \frac{V}{W} \tag{1}$$

$$R_r = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

$$\alpha_{l/f} = \frac{K_l}{K_f} \tag{3}$$

Here, C_0 (μg/mL) and C_e (μg/mL) are the liquid-phase concentrations of limonin (or flavonoid) at initial and at equilibration stages, respectively. V (mL) is the volume of ponkan juice and W (g) represents the mass of resins (Huang, Liu, Zhang, Xu, & Hu, 2012). K_l and K_f are the distribution ratios of limonin and flavonoids, respectively. The distribution ratio K (L/g) was calculated by using the following expression (Zhou, Shang, Liu, Huang, & Adesina, 2012):

$$K = \frac{Q_e}{C_e} \tag{4}$$

The adsorption capacity (Q_e mg/g wet resin) is calculated by Eq. (1), and C_e (μg/mL) is the liquid-phase concentrations of limonin (or flavonoid) at equilibrium stage.

Desorption experiments were performed in fixed-bed column. After washing with purified water, resins filtered from the ponkan juice were entirely transferred into a lab-scale column (10 × 200 mm). The experiments with dynamic column were carried out. An HL-2B constant flow pump (Huxi Instrument Ltd. Shanghai, China) was used to pump ethanol. The temperature of ethanol was maintained by a thermostatic bath (Taicang experimental equipment factory, Jiangsu, China). The effluent was collected for analysis.

The best desorption condition was 800 mL/L ethanol as an eluent, and 20 mL/h of the flow rate. The concentration of limonin in the effluent was monitored using high performance liquid chromatography (HPLC) analysis as described by Jayaprakasha, Dandekar, Tichy, and Patil (2011). The desorption capacity (Q_d μg/g wet resin) and desorption rate (D_r) were calculated as follows:

$$Q_d = C_d \times \frac{V_d}{W} \tag{5}$$

$$D_r = C_d \times \frac{V_d}{(C_0 - C_e) \times V} \times 100\% \tag{6}$$

Table 1
Physical properties of resins.

Resin type	Supplier	Structure	Polarity	Specific surface area (m^2/g)
EXA45	Residion, Mitsubishi Chem. Co., Japan	SDVB	apolar	1000
EXA50		SDVB	apolar	1000
EXA118		SDVB	apolar	1200
SP70		SDVB	apolar	1200
SP825		SDVB	apolar	1050
AB-8	Lukang Technology Ltd., Shandong, China	Polystyrene	low-polar	500
LX900	Lanxiao Technology Ltd., Xi'an, Shanxi, China	SDVB	apolar	≥1000
LX900*		SDVB	apolar	≥900
LX920		SDVB	apolar	≥850
LSA970		SDVB	polar	≥1200