Journal of Food Engineering 116 (2013) 195–201

Contents lists available at SciVerse ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

# Adsorption isotherm, thermodynamics and kinetics studies of polyphenols separation from kiwifruit juice using adsorbent resin

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ARTICLE INFO

*Article history:*
Received 10 July 2012
Received in revised form 10 September 2012
Accepted 23 October 2012
Available online 6 November 2012

*Keywords:*
Polyphenols
Kiwifruit juice
Adsorption
Isotherm
Thermodynamics
Kinetics

ABSTRACT

In this study, the adsorption characteristics of polyphenols in kiwifruit juice were investigated using AB-8 resin, with the aim to separate the polyphenols from kiwifruit juice to prevent astringency and browning during processing and storage. Results showed that the adsorption ability ($q_e$) of the resin increased with an increase in temperature. The adsorption equilibrium was best described by the Freundlich isotherm ($R^2 > 0.98$). Thermodynamic parameters including the changes of enthalpy ($\Delta H$), free energy ($\Delta G$), and entropy ($\Delta S$) were evaluated at 25, 30 and 35 °C. From the enthalpy change ($0 < \Delta H < 5$), the adsorption was endothermic in nature and involved physical adsorption. The result of free energy change ($\Delta G < 0$) demonstrated a spontaneous adsorption process. The pseudo first-order model was found to describe the kinetic data satisfactory. The adsorption mechanism was not limited solely by intra-particle diffusion as shown by the Weber and Morris model.



## 1. Introduction

Juice browning and severe astringency are common technical problems in the kiwifruit juice industry. A high content of polyphenols substances in kiwifruit juice is the main factor contributing to the above phenomena. These problems are obstacles to produce high quality kiwifruit juice in China. Currently, non-commercial and hard kiwifruits are the main source of kiwifruit juice concentrate and the average polyphenols content in the fresh and hard kiwifruit is 273 mg/100 g (Cieslik et al., 2006). Removal of polyphenols from kiwifruit juice is essential to enhance sensory properties and to extend shelf life of the juice, facilitating the development of the kiwifruit juice industry. Several adsorbents, such as activated carbons and resins have been reported for polyphenols removal in fruit (Arslanoglu et al., 2005; Luisa et al., 2011). Adsorbent resins have been widely applied especially in waste water treatment to remove contaminants due to their high adsorption ability and the ease to regenerate the adsorbate through desorption. However, their use in fruit juice processing is still limited. Using an optimal resin to treat kiwifruit juice will enable the separation of the polyphenols that caused browning and astringency of kiwifruit juice, and thereby improved the flavour and maintain the color of kiwifruit juice as mentioned above. In addition, the polyphenols substances which are adsorbed can be desorbed and recovered from the adsorbent resin for other applications. Polyphenols comprise of flavonoids, phenolic acids and tannins which are excellent healthcare products that exhibit a wide range of pharmacological effects (Martins et al., 2011). In recent years, the effects of polyphenols on various physiological activities were studied including antioxidant activity, antibacterial action, antihypertensive and carcinogenesis inhibitory effects (Luisa et al., 2011).

Adsorbent resin has been applied to remove components that caused browning and post-turbidity in apple juice and peach pulp (Qiu et al., 2007; Ibarz et al., 2008). However, the application of adsorbent resin for separation of polyphenols from kiwifruit juice has not been reported in literature. The overall goal of this work was to systematically evaluate the adsorption characteristics of polyphenols of kiwifruit juice using the AB-8 resin to provide a theoretical basis on the separation of polyphenols from kiwifruit juice. To achieve this, the following specific objectives were set: (1) To obtain experimental equilibrium data at different temperatures and to simulate these data with isotherm models including Langmuir and Freundlich models; (2) to evaluate the thermodynamic parameters including adsorption enthalpy ($\Delta H$), adsorption free energy ($\Delta G$) and adsorption entropy ($\Delta S$), which are basic principles in thermodynamics; (3) to obtain experimental kinetics data at optimum temperature and to simulate the data with different

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http://dx.doi.org/10.1016/j.jfoodeng.2012.10.037

**Nomenclature**

| | | | |
|---|---|---|---|
| $q_e$ | adsorption capacity of resin at equilibrium (mg/g resin) | $\Delta H$ | enthalpy change (kJ/mol) |
| $C_0$ | initial concentration of polyphenols (mg/mL) | $k_2$ | rate constant for pseudo second-order model (g/(mg min)) |
| $C_e$ | equilibrium polyphenols concentration after adsorption (mg/mL) | $R$ | gas constant (8.314 J/mol K) |
| $V_0$ | volume of initial kiwifruit juice (mL) | $C$ | integration constant |
| $V_1$ | volume after adsorption (mL) | $\Delta G$ | free energy change (kJ/mol) |
| $m$ | weight of dry resin (g) | $\Delta S$ | entropy change (kJ/mol K) |
| $q_d$ | desorption capacity (mg/g resin) | $q_t$ | amount of polyphenols absorbed at time $t$ (mg/g resin) |
| $C_d$ | polyphenols concentration in the desorption solution (mg/mL) | $t$ | time (min) |
| $V_2$ | volume of the desorption solution (mL) | $n$ | constant in Freundlich model |
| $D$ | ratio of desorption (%) | $T$ | absolute temperature (K) |
| $q_m$ | maximum adsorption capacity (mg/g resin) | $k_i$ | intra-particle diffusion rate constant (g/(mg.min$^{1/2}$)) |
| $K_L$ | Langmuir constant (mL/mg) | $I$ | intra-particle diffusion constant |
| $K_f$ | Freundlich constant (mL/mg) | | |
| $k_1$ | rate constant for pseudo first-order model (min$^{-1}$) | | |

kinetics models; (4) to interpret the kinetics mechanism and rate-limiting step of the adsorption process. It is proposed that a theoretical basis for the polyphenols adsorption of kiwifruit juice onto AB-8 resin can be established for industry applications through these objectives.

## 2. Materials and methods

### 2.1. Materials

Kiwifruit (*Actinidia deliciosa 'Hayward'*) were from a local market at Auckland, New Zealand (NZ). Gallic acid, Folin Ciocalteu's phenol reagent, pectinase (from *Aspergillus niger*), amylase (from *Aspergillus oryzae*) were purchased from Sigma Chemical Company (St. Louis, MO, USA). Anhydrous sodium carbonate monohydrate, sodium hydroxide, ethanol (ECP Ltd., NZ) and hydrochloric acid (Adrew, NZ) used were of analytical grade. Food-grade synthetic adsorbent resins, AB-8 (surface area 480–520 m$^2$/g, average pore diameter 13.0–14.0 nm, particle size 0.3–1.25 mm, density 1–1.10 g/mL, weak polar) was from Nankai Bohong Sci. & Tech. Co., Ltd. (Tianjin, China). Mili-Q water (18.2 MΩ) was used in all experiments.

### 2.2. Methods

#### 2.2.1. Resin preparation

The resins were soaked in 95% ethanol for 24 h followed by washing by deionized water thoroughly. The resins were treated by 1 mol/L HCl and NaOH solutions successively to remove any monomers trapped inside the resin pores during the synthesis process. It was then washed with deionized water thoroughly before drying at 70 °C under vacuum (Fu et al., 2007).

#### 2.2.2. Kiwifruit juices preparation

The kiwifruit was washed and then mashed using a laboratory blender (7011S, Waring commercial, USA) after the skin was peeled. Pectinase (300 mg/kg) and Amylase (200 mg/kg) were added to the pulp at 50 °C for 120 min, followed by centrifugation (Labofuge 400 centrifuge, Thermo scientific, USA) at 3500 rpm for 10 min, and filtration (VE-11 electric aspirator, Jeio tech Co., Korea). The clear kiwifruit juice was heated to 95 °C for 5 min in a water-bath to inactivate the remaining enzyme in the juice. Finally, the juice was concentrated (Buchi Rotavapor R-210, Buchi, Australia) at 50 °C under vacuum for 1–2 h.

#### 2.2.3. Total polyphenols determination

The total polyphenols in kiwifruit juice was determined by Folin–Ciocalteu method (Waterhouse, 2003) using gallic acid as standard.

#### 2.2.4. Total soluble solids and pH

The total soluble solids (°Brix) of kiwifruit juices were measured using a refractometer (ATC-1E, Atago Co. Ltd., Tokyo, Japan) before and after adsorption experiments. The pH was measured using a pH meter (Orion320 PerpHecT, Orion Research Inc., USA).

#### 2.2.5. Static adsorption and desorption test

Preconditioned resin (0.5 g) was introduced into a 250 mL flask and 80 mL kiwifruit juice was added. The flask was shaken at 300 rpm using a constant temperature water-bath shaker (Model SWB20D, Ratek, Australia) at 25 °C for 12 h. The polyphenols content of kiwifruit juice was determined before and after adsorption as described in Section 2.2.3. After equilibrium was reached, desorption was conducted with 80 mL ethanol–water (70:30, v/v) with constant shaking at 300 rpm for 12 h at 25 °C. The polyphenols content in the desorbed solution was determined (Section 2.2.3). The experiments were conducted in duplicate. The adsorption capacity ($q_e$) of resin at equilibrium (mg/g resin) and desorption capacity ($q_d$, mg/g resin) were calculated as in Eq. (1) and (2) (Fu et al., 2006):

$$q_e = \frac{C_0V_0 - C_eV_1}{m} \tag{1}$$

$$q_d = \frac{C_d \times V_2}{m} \tag{2}$$

The ratio of desorption ($D$, %) was calculated as followed:

$$D = \frac{C_d \times V_2}{C_0V_0 - C_eV_1} \times 100\% \tag{3}$$

#### 2.2.6. Adsorption isotherms

An amount of 0.5 g AB-8 resin was added to a 250 mL conical flask with 40 mL kiwifruit juice containing different concentrations of polyphenols (ranged from 217.39 to 1304.35 μg/mL). The flasks were shaken thoroughly at 300 rpm using a constant temperature water-bath shaker at 25, 30 and 35 °C for 8 h. The kiwifruit juices were filtered and the equilibrium concentrations of polyphenols were calculated (Section 2.2.3). Triplicate experiments were performed.