Chemical Engineering Journal 215–216 (2013) 113–121

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Adsorption of soy isoflavones by activated carbon: Kinetics, thermodynamics and influence of soy oligosaccharides

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HIGHLIGHTS

- Systematic studied the adsorption of soy isoflavones by activated carbon.
- The adsorption characters vary with the chemical forms of soy isoflavones.
- The adsorption of soy isoflavones by activated carbon is endothermic.
- Soy oligosaccharides have negative influence to the diffusion of isoflavones.

ARTICLE INFO

Article history:
Received 12 September 2012
Received in revised form 10 October 2012
Accepted 11 October 2012
Available online 10 November 2012

Keywords:
Adsorption
Activated carbon
Isoflavones
Soy molasses

ABSTRACT

Adsorption behavior of daidzin, genistin, 6″-*O*-malonyldaidzin and 6″-*O*-malonylgenistin, the four major soy isoflavones presented in soy molasses centrifugation supernatant on activated carbon was studied in this paper so as to provide theoretical basis for the purification of soy oligosaccharides from soy molasses. Kinetic experiments showed that the adsorption processes obeyed pseudo-second-order kinetics and equilibrium was nearly achieved in 90 min. Weber–Morris model fitting showed that adsorption process consisted of 3 stages: boundary layer diffusion and two intra-particle diffusions. Experimental adsorption data for every isoflavone components could be described separately by the Langmuir isotherm model and the calculated maximum adsorptions were in the order of genistin > daidzin > 6″-*O*-malonylgenistin > 6″-*O*-malonyldaidzin, indicating that the adsorption driving forces were due to dispersion interactions between the aromatic ring of isoflavone and the aromatic structure of the activated carbon. Adsorption behaviors of isoflavones on activated carbon in sugar free solutions were compared. It was found that, by removing sugar from the system, diffusion rate constants and the sum of the maximum adsorption capacity increased.

1. Introduction

Soy molasses is a by-product generated in the production of soy protein concentrate, in which soy oligosaccharides, isoflavones, saponins, and other phytochemicals are enriched [1,2]. The by-product has been a popular fermentation medium for bio-ethanol [3] as well as lactic acid [4] production and a good resource of soybean phytochemicals. Several researchers reported isolating isoflavones and other phytochemicals from the insoluble precipitates of soy molasses suspension [5–7] while there are few reports concerned with the centrifugation supernatant of soy molasses. The supernatant contains most of the water soluble components existed in soy molasses, predominantly sucrose, raffinose and stachyose. Raffinose and stachyose have been proved to be functional oligosaccharides, as they can stimulate the growth of bifidobacteria and other kinds of lactic acid bacteria, promote the competitive exclusion of potential pathogens [8] and reduce the levels of some colonic enzymes (β-glucuronidase, nitroreductase, azoreductase and glycoholic acid hydrolase) which are implicated in the conversion of procarcinogens to carcinogens [9].

Currently, commercial soy oligosaccharides are isolated from soybean whey which is generated from soy protein isolate production [10]. Extraction of soy oligosaccharides from soy molasses supernatant could be more beneficial economically because of its higher oligosaccharide concentration, thus less energy is needed in water evaporation. As Galanakis [11] pointed out, recovery of high-added value compounds usually follows 4–5 stages of macroscopic pretreatment, macro- and micro-molecules separation, extraction, isolation and purification, as well as finally product

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http://dx.doi.org/10.1016/j.cej.2012.10.100

Nomenclature

P	pressure of N_2 (MPa)
P_o	saturated vapor pressure of N_2 (MPa)
$pH_{(PZC)}$	point of zero charge
Q_e	adsorbed isoflavones on activated carbon at equilibrium (mg/g)
C_o	initial concentration of isoflavone in solution (mg/L)
C_e	equilibrium concentration of isoflavone in solution (mg/L)
V	volume of solution (L)
A	dry mass of activated carbon (g)
Δq	standard deviation
S^2	model variance
Q_{em}	adsorbed isoflavones on activate carbon calculated from model
N	number of experimental data
F-test	Fisher statistical test
S_{BET}	BET surface area of activated carbon (m^2/g)
V_p	total pore volume of activated carbon (cm^3/g)
t	contact time (h)
Q_t	concentration of adsorbed isoflavone at contact time t (mg/g)
κ	pseudo-second order kinetic parameter (g/mg/h)
k_{id}	intra-particle diffusion rate constant ($mg/g/h^{1/2}$)
I	boundary layer constant (mg/g)
k_d	diffusion rate constant ($mg/g/h^{1/2}$)
C_i	initial concentration of isoflavone in solution at the start of the linear portion (mg/L)
K_F	Freundlich isotherm coefficient
n	Freundlich adsorption coefficient
Q_m	Langmuir maximum adsorption capacity (mg/g)
K_L	Langmuir adsorption coefficient (L/mg)
R^2	correlation coefficient
pKa	dissociation constant
ΔG	Gibs free energy (kJ/mol)
ΔH	enthalpy change (kJ/mol)
ΔS	entropy change (kJ/mol/K)
K_o	adsorption equilibrium constant
R	universal gas constant (J/mol/K)
T	adsorption temperature (K)

formation. In the purification process of oligosaccharides extracted from soy molasses, isoflavones are one of the major components which should be removed from the supernatant so as to prevent the development of bitter taste and dark color to the product. In nature, soy isoflavones exist predominantly as malonylglucosides forms, but acetylglucosides, glucosides and aglycons forms generated from the malonylglucosides during processing of soybeans or sample preparation and analysis [12]. Thus, four different chemical forms of soy isoflavones could be found in processed soy products, i.e. the aglycons (daidzein, glycitein and genistein), the glucosides (daidzin, glycitin and genistin), the acetylglucosides (6″-*O*-acetyldaidzin, 6″-*O*-acetylglycitin and 6″-*O*-acetylgenistin), as well as the malonylglucosides (6″-*O*-malonyldaidzin, 6″-*O*-malonylglycitin, and 6″-*O*-malonylgenistin) [13,14].

Adsorptions using activated carbon, resins and other porous substances are commonly practiced in product decoloration and purification. Several studies reported the adsorption behavior of dyes [15,16], phenolic compounds [17,18], organic acid [19,20] and metal ions [21,22] on activated carbon. On the other hand, Gugger et al. [23] reported the adsorption of soy isoflavone in ultrafiltration permeate fraction of soy molasses or soybean whey using resins (divinylbenzene, ethylvinylbenzene copolymer resin). At present, there are no systematic studies about the adsorption of soy isoflavones on activated carbon. This paper reports the adsorption behavior of four predominant isoflavones, daidzin, genistin, 6″-*O*-malonyldaidzin and 6″-*O*-malonylgenistin in soy molasses centrifugal supernatant on the activated carbon. The kinetic and thermodynamic characteristic adsorption constants were determined using accepted theoretic models. Effects of the presence of soy oligosaccharides on the adsorption behavior were also studied.

2. Materials and methods

2.1. Chemicals and regents

Activated carbon (AC) powder (purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was dried at 105 °C overnight for pre-activation. Oligosaccharides standards (sucrose, raffinose and stachyose) were purchased from Sigma Chemical Co. Ltd. Commercial soy oligosaccharides syrup was purchased from Shansong Biological Product Co. Ltd. (Linyi, China). Soy isoflavone standards (daidzin, glycitin, genistin, 6″-*O*-malonyldaidzin and 6″-*O*-malonylgenistin) were purchased from Wako Pure Chemical Industries, Ltd.

2.2. Analysis and measurement methods

The high-performance liquid chromatography (HPLC) apparatus (Hitachi, Tokyo, Japan) consisted of a HITACHI L-2490 RI detector, a HITACHI L-2400 UV detector, a HITACHI L-2300 column oven, and a HITACHI L-2130 pump.

Reversed-phase HPLC analysis of isoflavones was carried out on a 250 × 4.6 mm, 5 μm YMC-Pack Pro C18 column (YMC Co., Ltd., Kyoto, Japan). A linear HPLC gradient was composed of (A) 0.05% trifluoroacetic acid in water and (B) 0.05% trifluoroacetic acid in ACN. Following injection of 20 μL of sample, solvent B was increased from 15% to 20% over 15 min with the flow rate 0.8 mL/min. In the second 15 min, solvent B was increased from 20% to 30%. In the third 15 min, solvent B was increased from 20% to 35%. In the following 20 min, solvent B was decreased from 35% to 15%, and then held at 15% for 5 min. The flow rate was kept at 1.0 mL/min between 15 min and 70 min. Eluted isoflavones were detected by their absorbance at 254 nm. The experiment was carried out at 34 °C.

Analysis of carbohydrates was conducted on a 250 × 4.6 mm, 5 μm Alltima Amino column (Grace, Waukegan, USA). The mobile phase was solvent of 68% ACN in water, and the flow rate was 1.0 mL/min. Eluted carbohydrates were detected by RI detector and the analysis was performed at 40 °C.

The textural characterization of the activated carbon was carried out by N_2 adsorption at 77 K using an ASAP 2020 Micromeritics instrument. The surface area was calculated using BET method and the total pore volume was calculated from the amount of N_2 adsorbed at $P/P_o = 0.95$ [24].

The $pH_{(PZC)}$ (point of zero charge) of the activated carbon was measured using the method suggested by Franz et al. [25].

2.3. Preparation of soy molasses centrifugation supernatant

Soy molasses (kindly provided by Wonderful Industrial Group Co., Ltd., Shandong, China) was diluted with distilled water and