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Kinetics and thermodynamics adsorption of carotenoids and chlorophylls in rice bran oil bleaching

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ABSTRACT

The adsorption characteristics of carotenoids and chlorophylls in the rice bran oil bleaching at different temperatures (100–120 °C) and activated earth concentrations (0.5–2.5% w/w) were investigated. The kinetic study showed that, after 20 min the adsorption capacity tends to stay constant. Pseudo-second order model was more appropriate to describe the adsorption kinetics for both pigments, especially at higher temperatures. The use of 1% (w/w) of activated earth at 120 °C led to a high decrease in chlorophyll content, while the decrease in carotenoids content was less pronounced. Freundlich model was suitable to represent the equilibrium experimental data for the pigments. The activation energy values showed that the chlorophyll molecules required more energy to be removed from the oil. The rice bran oil bleaching was considered an endothermic, favorable and spontaneous process, and the isosteric heat of adsorption indicated that the activated surface of the earth was heterogeneous.

1. Introduction

World production of rice (*Oryza sativa* L.) has increased in recent years, mainly, due to the expansion of planted area and increased productivity. The south of Brazil is the largest producer of rice outside Asia and has an average productivity about 20% above the worldwide. This is mainly due to climatic factors, availability of lowlands and water. However, with the fluctuation of commodity prices, a way to add value is the utilization of byproducts of culture, such as rice bran (FAO, 2015). This byproduct corresponds from 8 to 11% (w/w) of the grain, and it has interesting characteristics for the food oil industry (Gopinger et al., 2015; Pourali et al., 2009). The rice bran oil contains proteins (12–13%, w/w), carbohydrates (48–60%, w/w) and lipids (18–25%, w/w) (Silva et al., 2006). Although being obtained from a by-product of rice processing, the rice bran oil has a high content of bioactive phytochemicals and monounsaturated fatty acids, which confers to the oil high oxidative stability. Rice bran oil contains too ɣ-oryzanol, which is a natural antioxidant composed mainly of esters of phytosterols with *trans*-ferulic acid. The ɣ-oryzanol content found in the oil ranges from 0.9 to 2.9% (w/w), and the tocopherols (vitamin E) content ranges from 0.10 to 0.14% (w/w) (Lerma-García et al., 2009). According to Wilson et al. (2000), the rice bran oil may assist in reducing LDL cholesterol due to its fatty acid profile and high quantity of unsaponifiable compounds.

The vegetable oil refinement, including rice bran oil, can be done by chemical or physical methods. The steps of chemical refinement typically include degumming, neutralization, bleaching, dewaxing and deodorizing. The degumming is typically carried out using phosphoric acid or hot water to remove phospholipids and mucilaginous gums (Kreps et al., 2014). In the neutralization, removal of free fatty acids is realized through the addition of an alkali solution of sodium hydroxide (Marrakchi et al., 2015). Bleaching is an adsorption operation that aims at removing pigments, oxidation products and traces of metals using adsorbing substances (Ribeiro et al., 2001). Some vegetable oils have a high content waxes which are separated from the oil in the winterization step (dewaxing) through the oil cooling and crystallization of waxes or via solvents (Baümler et al., 2007). Finally, the deodorization removes volatile compounds, such as, aldehydes, ketones and alcohols by vacuum distillation (Silva et al., 2014). The physical refinement has been reported in rice bran oil to reduce losses ɣ-oryzanol during the chemical refinement, especially in the neutralization step (Pestana-Bauer et al., 2012).

Bleaching is an important step because it removes the excess of pigments, metals and oxidation products. The main pigments found

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in vegetable oils are the carotenoids and chlorophylls. Carotenoids are red pigment, precursors of vitamin A and have antioxidant activity. They can be divided into carotenes and xanthophylls. The carotenes most known are α-carotene, β-carotene, ɣ-carotene and lycopene. The β-carotene is normally the most abundant carotenoid found in vegetable oils (Rodriguez-Amaya, 1996). The carotenoids removal is important only to improve the visual appearance to the consumer, since its permanence assists in oxidative stability of the oil and provide health benefits. However, more important than the carotenoids is the removal of chlorophyll, which by the heat action decomposes into pheophytins, which give the oil an opaque and dark color (Sabah, 2007).

Several studies have investigated the bleaching step of oils from different sources, such as, hazelnut oil (Bayrak, 2003), soybean oil (Liu et al., 2008), rapeseed oil (Su et al., 2013), palm oil (Silva et al., 2013), sardine oil (García-Moreno et al., 2013) and cottonseed oil (Caglayan et al., 2005). However, few studies have reported the kinetic behavior and thermodynamic aspects associated with the compounds adsorption of oils.

The activated earths are widely used in bleaching of vegetable oil. They are mainly composed of clay minerals with surface activated by acid treatment. The use of bentonite, attapulgite and sepiolite has been reported in the literature for the adsorption of pigments in oils (Liu et al., 2008; Worasith et al., 2011). After the bleaching step, the extraction of adsorbent (spent bleaching earth) and the use of oil in the production of renewable diesel as also have been proposed in literature (Kuuluvainen et al., 2015).

The adsorbent-adsorbate interactions is a fundamental property in adsorption, and can be elucidated by equilibrium isotherms. The thermodynamic parameters are used in identify the nature of the process, and through of kinetic curves is possible to determine the processing time (Bayrak, 2003).

In this context, the aim was to study the kinetics, equilibrium and thermodynamics of the bleaching step of rice bran oil. The influence of temperature on adsorption kinetics of carotenoids and chlorophylls was evaluated by the Arrhenius relationship, and kinetic models of pseudo-first order, pseudo-second order and Elovich were fitted to experimental data. The equilibrium isotherms were obtained using different adsorbents concentrations, and the changes in thermodynamic parameters (Gibbs free energy, enthalpy, entropy and isosteric heat) were estimated.

2. Material and methods

2.1. Materials

The neutralized rice bran oil was obtained from a local industry and stored at −20 °C to avoid oxidation. Activated earth (Tonsil Supreme 110 FF) was used as commercial adsorbent in bleaching experiments.

2.2. Adsorbent characterization

Activated earth was characterized by scanning electron microscopy (SEM) (JEOL JSM-6060 model, Japan) and energy dispersive spectroscopy (EDS) (JEOL JSM-5800, Japan). The surface area of the adsorbent was determined by a volumetric adsorption analyzer (Quantachrome Instruments, New 2 Win, USA) using the method of Brunauer, Emmett and Teller (BET).

2.3. Carotenoids and chlorophylls analyses l

The determination of the carotenoids content was carried out by spectrophotometry (Quimis, Q108 model, Brazil). Rice bran oil samples were diluted in hexane (10% w/v) and filtered. The carotenoids content was obtained by absorbance at 446 nm and expressed in mg kg^{-1} (Eq. (1)), according to MPOB (2005).

$$C = \frac{383A_{446}}{Lc} \tag{1}$$

where C is the carotenoids content (mg kg^{-1}), A is the absorbance at 446 nm, L is the length of cuvette (cm), c is the oil concentration in hexane (g 100 mL^{-1}) and *383* is the extinction coefficient for carotenoids.

The chlorophyll content (predominantly pheophytin-*a*) was determined by absorbance at wavelengths of 630, 670 and 710 nm (Sabah, 2007), and calculated by Eq. (2).

$$Cl = \frac{[A_{670} - (A_{360} + A_{710})/2]V}{0,0964ML} \tag{2}$$

being, Cl the chlorophyll content (mg kg^{-1}), A_{630}, A_{670} and A_{710} the absorbances (nm), V the volume of hexane (mL), L the length of cuvette (cm) and M the mass of oil (g).

2.4. Adsorption assays

Samples (40 g) of neutralized rice bran oil were heated under constant stirring (40 rpm) using a magnetic stirrer with heating. The heating rate was 7 °C min^{-1}, and the oil was kept at absolute pressure of 70 mmHg. After reaching the desired temperature, the adsorbent was added to the oil. The kinetic curves were obtained during 60 min using 1% (w/w) of activated earth at 120 ± 1 °C. For the equilibrium curves were used different concentrations of adsorbent (from 0.5 to 2.5% w/w) at different temperatures (from 100 to 120 °C). The contact time between adsorbent and the oil was of 120 min (Bayrak, 2003). The adsorbent was immediately separated from the oil by centrifugation (3500 × g for 3 min). The parameters used in this study were based on preliminary tests and literature (Ribeiro et al., 2001; Silva et al., 2013). The experiments were performed in triplicate. The samples were analyzed for carotenoids and chlorophylls contents.

The adsorption capacities at any time (q_t) and in equilibrium (q_e) were determined by Eqs. (3) and (4):

$$q_t = \frac{M_o(C_i - C_t)}{M_a} \tag{3}$$

$$q_e = \frac{M_o(C_i - C_e)}{M_a} \tag{4}$$

being, M_o the oil quantity (kg), M_a the amount of adsorbent (kg), C_i the initial adsorbate concentration (mg kg^{-1}), C_t and C_e are the adsorbate concentrations (mg kg^{-1}) at time t and at equilibrium, respectively. Usually the concentration is expressed in mg L^{-1}, but in this study the concentration of the solution is equivalent to the pigments content in the oil, which in literature is expressed in basis weight.

2.5. Kinetic and equilibrium models

The adsorption kinetics of the pigment was obtained by fit of pseudo first order (Equation (5)), pseudo-second order (Equation (6)) and Elovich (Equation (7)) models. These models are based on the adsorption capacity rather than the solution concentration (Silva et al., 2013).

$$q_t = q_1(1 - \exp(-k_1 t)) \tag{5}$$