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Adsorption of carotenes and phosphorus from palm oil onto acid activated bleaching earth: Equilibrium, kinetics and thermodynamics

Simone M. Silva [a,c], Klicia A. Sampaio [c], Roberta Ceriani [b], Roland Verhé [c], Christian Stevens [c], Wim De Greyt [d], Antonio J.A. Meirelles [a,*]

[a] EXTRAE, Department of Food Engineering, School of Food Engineering, UNICAMP, Campinas, SP, Brazil
[b] Department of Chemical Processes, School of Chemical Engineering, UNICAMP, Campinas, SP, Brazil
[c] Department of Sustainable Organic Chemistry and Technology, Faculty of Bioscience Engineering, University of Ghent, Ghent, Belgium
[d] Desmet Ballestra, Zaventem, Belgium

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ABSTRACT

In this work, the adsorption of carotenes and phosphorus from crude palm oil onto acid activated bleaching earth was investigated under bleaching conditions, i.e. high temperature (90, 105 and 115 °C) and low pressure (less than 50 mbar). Bleaching earth was added to palm oil in a range of 0.5–3.0 wt%. Results presented in this work suggest that adsorption of β-carotene increases with temperature, while phosphorus adsorption was less affected. Both the pseudo-first-order and the pseudo-second-order kinetic model describe efficiently the β-carotene experimental data. Intra-particle diffusion is involved in β-carotene adsorption mechanism, although it is not the sole rate limiting step in the adsorption onto acid activated bleaching earth. Phosphorus adsorption was too fast resulting in a lack of kinetic data. The equilibrium data were described better by Langmuir and Freundlich models, for β-carotene and phosphorus, respectively. A multi-component Freundlich type isotherm was tested. Its competition coefficients were too low, and it assumed the same form as the monocomponent Freundlich. A thermodynamic study demonstrated that β-carotene and phosphorus adsorption is spontaneous, endothermic and an entropy-driven process. Isosteric heat values suggest that the interactions between adsorbate and adsorbent are heterogeneous.

1. Introduction

Adsorption is a complex chemical process employed in the refining of vegetable oils during which oil impurities are removed by adsorbent materials after alkali or before physical refining (Proctor and Brooks, 2005). During bleaching, compounds such as phospholipids, colorants, soaps, contaminants and lipid peroxidation products are removed to obtain desirable characteristics in edible oils (Zschau, 2001). Adsorptive bleaching is mostly affected by temperature and humidity, but structure and type of bleaching earth also plays a role (Gibon et al., 2007). Activated bleaching earth is the most common adsorbent used in edible oil bleaching. It adsorbs preferentially those components which are cationic or polar in nature (Zschau, 2001). Furthermore, adsorptive processes can also be used in vegetable oil industry for the removal of free fatty acids (Cren et al., 2009; Cren and Meirelles, 2005, 2012).

Crude Palm Oil (CPO) is purified by physical refining, meaning that the free fatty acids (FFAs) are removed in the last refining step at high temperature (240–260 °C) and low pressure (less than 5 mbar), avoiding excessive loss of neutral oil during alkali neutralization (chemical refining) (Rossi et al., 2001; Sampaio et al., 2011).

To avoid color fixation during the deodorization step, bleaching needs to reduce phosphorus and iron to sufficiently low levels and minimize oxidation products (Gibon et al., 2007). In the case of carotenes, full reduction by bleaching is not necessary, as they can be thermally decomposed during the subsequent deacidification (so-called heat bleaching) (Gibon et al., 2007). In fact, in some refining processes, only 20% of the carotenoid-related color is removed during bleaching. Remaining carotenoids are then destroyed during heat bleaching: after 20 min at 240 °C, more than 98% of the total carotenoids are destroyed (Maclellan, 1983).

Usually, work on bleaching is dealing with color/pigments removal by physical adsorption on the bleaching earth surface. Some authors have suggested that pigments and phospholipids removal is performed through chemisorption and that bleaching earth acidity is related with its adsorption capacity for pigments (Taylor, 2005). β-carotene adsorption was studied for different types of oil such as soya (Ma and Lin, 2004), palm oil (Low et al.,

* Corresponding author. Address: Departamento de Engenharia de Alimentos, Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas – UNICAMP, 13083-862 Campinas, SP, Brazil. Tel.: +55 (19) 3521 4037; fax: +55 (19) 3521 4027.
E-mail address: tomze@fea.unicamp.br (A.J.A. Meirelles).

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1998), rapeseed oil (Sabah et al., 2007), maize and sunflower (Christidis and Kosiari, 2003). None of these studies looked at the adsorption under bleaching conditions, i.e. high temperature, low pressure and without solvent addition.

Besides pigments removal, the bleaching process is responsible for removing trace amounts of metals, adsorption of phosphorus, soaps and for decomposing primary oxidation products (Taylor, 2005).

There is a lack of scientific knowledge on phosphorus adsorption onto bleaching clays. Gutfinger and Letan (1978) studied phospholipids removal from soybean oil onto various adsorbents and proposed the Freundlich model to describe the equilibrium isotherm. However, they did not determine thermodynamics parameters. (Brown and Snyder, 1985) studied the removal of phospholipids from miscellas by adsorption onto silica.

Although adsorption is used on industrial scale for bleaching of edible oils, the understanding of its thermodynamic basis is still very restricted. One of the reasons for this lack of understanding is that the proposed adsorption is multicomponent, involving at least carotenes, phospholipids and, eventually, metals removal. Furthermore, the use of model systems able to correctly mimetize the studied vegetable oil is difficult due to the unavailability of pure compounds and/or the difficult solubilization of the compounds in solvent-free systems. For these reasons, the use of model systems cannot properly represent all events that occur in the real system.

In this context, the objective of this work was to evaluate the adsorption of carotenes and phosphorus from Crude Palm Oil (CPO) onto acid activated bleaching earth under industrially applied conditions, i.e. high temperature, low pressure and without solvent. Acid activated bleaching earth was chosen as it is the most common adsorptive agent used industrially (Taylor, 2005). Through batch adsorption experiments, the kinetics (pseudo-first-order and pseudo-second order) and mechanism (intra-particle diffusion) of removal were evaluated. The effect of temperature on the adsorption process was also studied. Moreover, thermodynamic parameters as Gibbs Free Energy, enthalpy and entropy were calculated. Those results are important to better understand and to improve palm oil refining.

2. Material and methods

2.1. Adsorbent

Tonsil OPT 210 FF (Süd Chemie, Germany), a commercial bleaching earth, was used for the adsorption experiments. It is a highly acid activated bleaching earth manufactured by acid activation of calcium bentonite with a surface area (B.E.T.) of 200 m^2/g. Particle size was characterized by a sieve analysis of the dry powder, presenting the following average values: 60% >25 μm, 40% >45 μm, 29% >63 μm, 17% >100 μm and 5% >150 μm. (Süd-Chemie, 2011). Table 1 presents the bleaching earth physical chemical characterization.

Table 1
Physical chemical characterization of Tonsil OPT 210 FF (Süd-Chemie, 2011).

Apparent bulk density (g/l)	550
Free moisture (2 h, 110 °C) (%)	~10
Loss on ignition (predried, 2 h, 1.000 °C) (%)	8.0
pH (10% suspension, filtered)	2.2–4.8
Acidity (mg KOH/g)	4.5
Chloride content (mg Cl/g)	0.5
Surface area (B.E.T.) (m^2/g)	200
Micropore volume	
0–80 nm ml/g	0.29
0–25 nm ml/g	0.25
0–14 nm ml/g	0.23

2.2. Oil characterization

Crude palm oil was obtained from a local processor in Belgium and it was characterized in terms of free fatty acids (FFAs) (4.6 wt%, expressed as palmitic acid) and phosphorus content (19.1 ± 0.02 mg/kg). Carotenes, which are susceptible to degradation due to oxidation, were determined before each experimental set. The initial carotenes concentration was 454 ± 5.5 mg/kg, but this initial value decreased along the storage time to 399 ± 3.3 mg/kg.

2.3. Batch adsorption

Batch adsorption experiments were carried out in a rotary evaporator at a constant speed, reproducing the bleaching process of palm oil. In each test, 0.400 kg of crude palm oil was placed into 500 mL flasks and the following procedure was performed: heating the crude palm oil to 85 °C (Rotavapor, BUCHI, B-480, Switzerland); adding 0.09% citric acid, as 30% aqueous solution (Sigma–Aldrich ACS reagent, >99%, Germany); high shear mixing at 16,000 rpm during 1 min (mixer, IKA-WERKE Digital, EURO-ST D, Germany); adding adsorbent (bleaching earth); 15 min of maturation at 85 °C and atmospheric pressure; applying vacuum (50 mbar) and maintaining the bleaching for 30 min at the selected temperature (Rotavap, BUCHI, R-124, Switzerland); removing the bleaching earth by filtration over a Buchner funnel and paper filter (pore size 11 μm, Whatman). In this way, the bleaching earth contact time with palm oil sums 45 min. For adsorption kinetics, time zero was considered immediately after the bleaching earth (BE) addition, before the 15 min maturation step. Sampaio et al. (2013) found that carotene loss during dry pretreatment with silica gel under 85 °C was less than 5%. Moreover, a blank run was made to evaluate the thermal degradation during this procedure. The experiment was performed in triplicate according to the procedure previously described and using 105 °C of bleaching temperature. The initial and final concentrations of carotenes were measured. It was obtained a loss in carotenes of 6.3 ± 1.3 wt%. Based on the small amounts of carotenes lost by thermal degradation, it is assumed that almost all carotene removal is due to the adsorption process.

The kinetics of adsorption was determined at 105 °C and using 3.0 wt% of bleaching earth. To determine this value, preliminary experiments were performed using bleaching earth in a range of 0.5–3.0 wt%. The bleached oil was deodorized afterwards, and Lovibond color was analyzed. The experiment using 3.0 wt% of acid activated bleaching earth resulted in a fully refined oil with a light color (3.4 R) as specified by PORAM (Palm Oils Refiners Association of Malaysia) for processed palm oil (Taylor, 2005). To obtain the adsorption isotherms, different concentrations of bleaching earth were added (ranging from 0.5 to 3.0 wt%) and agitated at 90, 105 and 115 °C. The adsorbate concentrations in solid phase q_t (mg/kg) at time t, and at equilibrium, q_e (mg/kg), were obtained by mass balance, according to the following equation:

$$q_t = \frac{W_{oil}(C_0 - C_t)}{W_{BE}} \quad (1)$$

$$q_e = \frac{W_{oil}(C_0 - C_e)}{W_{BE}} \quad (2)$$

where W_{oil} is the weight of crude palm oil treated in kg, W_{BE} is the weight of bleaching earth in kg, C_0 is the initial concentration of adsorbate (carotenes or phosphorus) in (mg/kg), C_t and C_e are the