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



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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  $\beta$ -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  $\beta$ -carotene experimental data. Intra-particle diffusion is involved in  $\beta$ -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  $\beta$ -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  $\beta$ -carotene and phosphorus adsorption is spontaneous, endothermic and an entropy-driven process. Isothermic heat values suggest that the interactions between adsorbate and adsorbent are heterogeneous.

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## 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).  $\beta$ -carotene adsorption was studied for different types of oil such as soya (Ma and Lin, 2004), palm oil (Low et al.,

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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<sup>2</sup>/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.

**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 <sup>2</sup> /g)	200
<i>Micropore volume</i>	
0–80 nm ml/g	0.29
0–25 nm ml/g	0.25
0–14 nm ml/g	0.23

(Süd-Chemie, 2011). Table 1 presents the bleaching earth physical chemical characterization.

### 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

liquid phase concentration of adsorbate at time  $t$  (min) and at equilibrium, respectively.

#### 2.4. Analytical measurements

Palm oil has a high carotenoid content,  $\beta$ -carotene being the most abundant (Gee, 2007). Total carotene content, expressed as  $\beta$ -carotene, was determined measuring the absorbance at 446 nm of samples homogenized and diluted in iso-octane (Spectrophotometer UV-240, Shimadzu Graphicord, Japan). In the same way, phosphorus in palm oil mostly occurs as inorganic phosphates (Goh et al., 1984a) and about 10–30% occurs as phosphatides (Gibon et al., 2007). In this work, phosphorus content was expressed as total phosphorus, measured using an Inductively Coupled Plasma (ICP) (Thermo Scientific, iCAP 6000 series, USA) method according to the AOCS Official Method Ca 20–99 (AOCS, 1998).

#### 2.5. Modeling

Adsorption models were fitted to experimental data using non-linear regression analysis performed using Origin<sup>®</sup> 8 and Levenberg–Marquardt interactive method (OriginLab, 2007). The parameters and coefficients of determination ( $R^2$ ) were obtained at 95% confidence interval.

### 3. Results

#### 3.1. Adsorption mechanism and kinetics

There are several mathematical models proposed to describe the kinetics of adsorption. They can be classified in two types: adsorption reaction models and adsorption diffusion models. Adsorption diffusion models are based on three consecutive steps, being (1) diffusion across the liquid film surrounding the adsorbent particle; (2) diffusion in the liquid contained in the pores and/or along pore walls, so called intra-particle diffusion; and (3) adsorption and desorption between adsorbate and active sites. The latter is a very rapid step in a physical process and can be negligible for kinetic studies (Qiu et al., 2009). Therefore, film liquid diffusion and/or intra-particle diffusion are always the limiting steps for the adsorption process and adsorption diffusion models are mostly constructed to describe one or both of those phenomena. Adsorption reaction models are based on the whole process of adsorption, without considering these steps mentioned above. In this work, we studied two reaction models and one diffusion model.

##### 3.1.1. Pseudo-first-order rate equation

The pseudo-first-order equation can be expressed in a non-linear Eq. (3) (Ho and McKay, 1998; Yousef et al., 2011).

$$q_t = q_e(1 - \exp(-k_1t)) \quad (3)$$

where  $q_t$  and  $q_e$  are sorption capacity at time  $t$  and at equilibrium  $e$ , respectively, i.e. the amount of adsorbate per unit of adsorbent;  $k_1$  is the pseudo-first-order constant  $t^{-1}$ . This model basically differs from first-order model of Lagergren as it is based on adsorption capacity instead of solution concentration. Mostly, this model is suitable to describe the initial 20–30 min of the adsorption process (Ho and McKay, 1998).

##### 3.1.2. Pseudo-second-order rate equation

The pseudo-second-order equation can be expressed in a non-linear equation (Eq. (4)) (Ho and McKay, 1998; Yousef et al., 2011).

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (4)$$

where  $k_2$  is the pseudo-second-order constant  $t^{-1}$ . The pseudo-second-order equation is based on the sorption capacity of the solid phase and it is in agreement with chemisorption being the rate controlling step (Ho and McKay, 1998). In the same way, Ho's second order-equation has been a so-called pseudo-second-order rate equation to distinguish from the one based on the solution concentration.

##### 3.1.3. Intra-particle diffusion

The Weber–Morris intra-particle diffusion model is expressed as;

$$q_t = k_{id}t^{0.5} + C_i \quad (5)$$

where  $k_{id}$  ( $\text{mg/kg min}^{0.5}$ ) is the intra-particle diffusion rate constant and  $C_i$  ( $\text{mg/kg}$ ) is associated to the boundary layer thickness. If intra-particle diffusion is the limiting step of adsorption process, the plot  $q_t$  against  $t^{0.5}$  is a straight line. According to the Weber–Morris model, it is essential that the plot goes through the origin if intra-particle diffusion is the only rate-limiting step (Alkan et al., 2007).

The concentration plot of adsorbed carotene and phosphorus versus contact time is shown in Fig. 1. For carotenes, the coefficient of determination were high for both pseudo-first-order and pseudo-second-order models ( $R^2 = 0.9992$  and  $0.9948$ , respectively) (Table 2). The  $T$ -test shows a high accuracy in parameter prediction for both kinetic models. The  $q_e$  values calculated by the pseudo-first-order model ( $14.25 \times 10^3 \text{ mg/kg}$ ) and the pseudo-second-order model ( $q_e = 14.10 \times 10^3 \text{ mg/kg}$ ) presented a good agreement

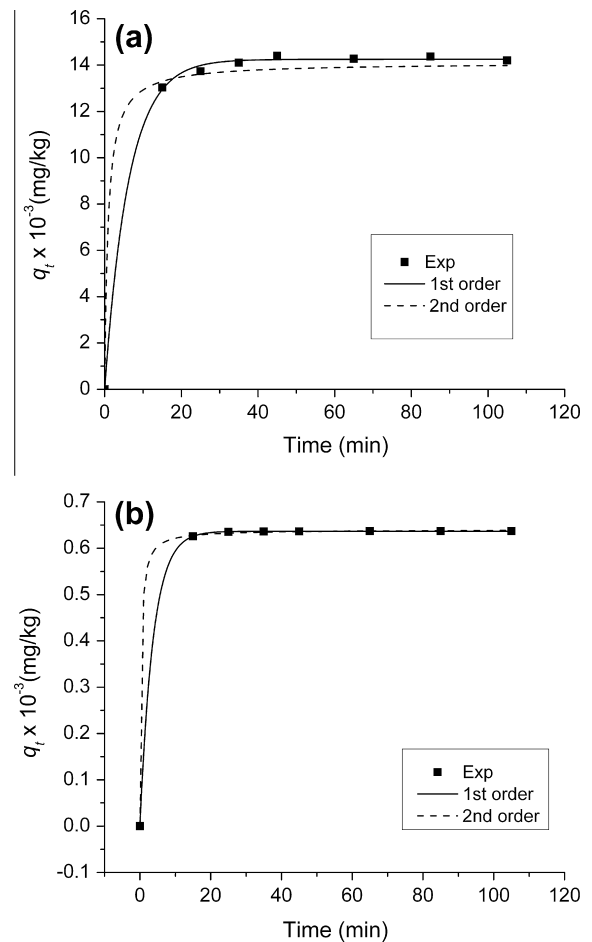
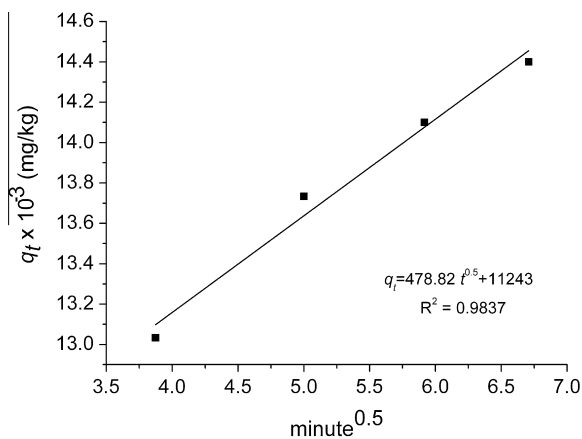


Fig. 1. Adsorption kinetics of Carotenes (A) and phosphorus (B) onto acid activated bleaching earth at 105 °C and using 3.0 wt% of bleaching earth. (Initial concentration: carotenes  $454 \pm 5.5 \text{ mg/kg}$  and phosphorus  $19.1 \pm 0.02 \text{ mg/kg}$ ).

**Table 2**

Fitting kinetics and mechanism parameters of adsorption of carotene and phosphorus onto Tonsil OPT 210 FF according to pseudo-first-order, pseudo-second-order and intra-particle diffusion at 105 °C.

	$q_{exp} \times 10^{-3}$ (mg/kg)	Carotenes 14.30 ± 0.10	t-Value
Pseudo-first-order	$q_e \times 10^{-3}$ (mg/kg)	14.25 ± 0.06	113
	$K_1$ (min <sup>-1</sup> )	0.16 ± 0.01	20
	$R^2$	0.9992	
	F-test	11,187	
	P-value	<0.0001	
Pseudo-second-order	$q_e \times 10^{-3}$ (mg/kg)	14.10 ± 0.27	205
	$K_2 \times 10^3$ (kg/mg min <sup>-1</sup> )	0.08 ± 0.01	17
	$R^2$	0.9948	
	F-test	4587	
	P-value	<0.0001	
Intra-particle diffusion	$K_{id} \times 10^{-3}$ (mg/kg min <sup>0.5</sup> )	0.4788 ± 0.044	47
	$C_i$	11.24 ± 0.23	11
	$R^2$	0.9837	
	F-test	120	
	P-value	0.0083	



**Fig. 2.** Intra-particle diffusion plots for the adsorption of  $\beta$ -carotenes onto acid activated bleaching earth at 105 °C and using 3.0 wt% of bleaching earth.

with experimental data ( $14.40 \times 10^3$  mg/kg). These data suggests that both kinetic models are suitable to describe carotene adsorption data. The curve-fitting plot of intra-particle model presented

high  $R^2$ , ( $q_t = 478.82 \cdot t^{0.5} + 11,243$ ,  $R^2 = 0.9837$ ), for carotenes, but it did not pass through the origin (Fig. 2). This result indicates that, even though intra-particle diffusion is involved in the adsorption process, it is not the sole rate limiting step (Alkan et al., 2007). Liquid film resistance may be also involved in the process. Phosphorus adsorption was faster than carotenes and it reached equilibrium in less than 25 min of contact time. For this reason, a lack of concentration data occurred to calculate the kinetic parameters. In fact, bleaching earth adsorbs preferentially cationic and polar molecules, such as phospholipids (Zschau, 2001).

### 3.2. Isotherm studies

Adsorption equilibria information is important to understand, to design and to implement the process. The temperature affects adsorption capacity of adsorbents. Thus, isotherms can provide the relation between the amount of a solute adsorbed at a constant temperature and its concentration in the equilibrium solution (Yousef et al., 2011). In this work, four adsorption isotherms were applied to evaluate adsorption of carotenes and phosphorus onto bleaching earth: Langmuir, Freundlich, Temkin and multi component Freundlich.

#### 3.2.1. Langmuir

The Langmuir model was the first model presenting a coherent theory of adsorption. It assumes that the adsorbent surface is homogenous, adsorption is localized in specific sites, which can adsorb only one adsorbate molecule (Do, 1998). It is generally expressed as:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (6)$$

where  $q_e$  (mg/kg) is the amount of adsorbate per unit mass of adsorbent,  $C_e$  (mg/kg) is the equilibrium concentration of adsorbate in solution,  $q_{max}$  (mg/kg) and  $K_L$  (mg/kg)<sup>-1</sup> are Langmuir constants related to the adsorption capacity and rate of adsorption, respectively.

#### 3.2.2. Freundlich

The Freundlich model is an empirical one (Do, 1998), assuming a heterogeneous surface energy, i.e. stronger binding sites are occupied first and the binding strength decreases with an increasing degree of site occupation (Yousef et al., 2011). It is described as in the following equation:

$$q_e = K_F C_e^n \quad (7)$$

**Table 3**

Removal of carotenes and phosphorus from crude palm oil onto acid activated bleaching earth at 90, 105 and 115 °C.

BE (%)	90 °C			105 °C			115 °C		
	$C_e$ (mg/kg)	$q_e \times 10^{-3}$ (mg/kg)	% removal	$C_e$ (mg/kg)	$q_e \times 10^{-3}$ (mg/kg)	% removal	$C_e$ (mg/kg)	$q_e \times 10^{-3}$ (mg/kg)	% removal
<b>Carotenes</b>									
0	399			454			399		
0.5	233	33	42	258	42	43	96	43	76
0.7	177	32	56	178	41	61	52	39	87
0.9	135	29	66	128	38	72	47	35	88
1.0	121	28	70	93	37	80	21	25	95
2.0	74	16	81	40	21	91	15	19	96
3.0	44	12	89	16	15	96	10	13	97
<b>Phosphorus</b>									
0	19.1	3.3		19.1			19.1		
0.5	2.9	2.4	85	2.7	3.3	86	3.4	3.2	82
0.7	2.3	1.9	88	2.3	2.4	88	2.5	2.4	87
0.9	1.8	1.8	91	1.8	1.9	91	1.9	1.9	90
1.0	1.3	1.2	93	1.3	1.8	93	1.5	1.8	92
2.0	0.4	0.6	98	0.4	0.9	98	0.3	0.9	98
3.0	0.3	0.6	98	0.2	0.6	99	0.1	0.6	99

**Table 4**  
Isotherms constants for carotenes and phosphorus adsorption onto acid activated bleaching earth at 90 °C, 105 °C and 115 °C.

Model	Equation	Parameters			Carotenes						Phosphorus									
		90 °C	105 °C	115 °C	t-Value	90 °C	105 °C	115 °C	t-Value	90 °C	105 °C	115 °C	t-Value	90 °C	105 °C	115 °C	t-Value			
Langmuir	$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e}$	$q_{max} \times 10^{-3}$ (mg/kg)	59.21 ± 11.15	5.3	50.53 ± 2.73	18.5	57.05 ± 2.99	19.3	5.23 ± 1.39	3.8	5.18 ± 1.70	3.1	3.93 ± 1.05	3.7	5.23 ± 1.39	3.8	5.18 ± 1.70	3.1	3.93 ± 1.05	3.7
		$K_L$ (mg/kg) <sup>-1</sup>	0.0063 ± 0.0023	2.8	0.0228 ± 0.0034	5.7	0.0349 ± 0.0047	7.4	0.4326 ± 0.14	3.1	0.4517 ± 0.17	2.7	0.70 ± 0.28	2.5	0.4326 ± 0.14	3.1	0.4517 ± 0.17	2.7	0.70 ± 0.28	2.5
		$R^2$	0.9453		0.9691		0.9917		0.9267		0.9019		0.8532		0.9267		0.9019		0.8532	
		F-test	388		878		1428		179		132		92		92		132		92	
		P-value (95%)	<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001	
Freundlich	$q_e = K_T C_e^n$	$K_T \times 10^{-3}$ ((mg/kg)(mg/kg) <sup>-n</sup> )	1.572 ± 0.8644	1.8	6.838 ± 1.860	3.7	5.978 ± 1.494	4.0	1.53 ± 0.10	15.3	1.57 ± 0.12	13.5	1.59 ± 0.10	15.1	1.53 ± 0.10	15.3	1.57 ± 0.12	13.5	1.59 ± 0.10	15.1
		n	0.575 ± 0.1091	5.3	0.340 ± 0.055	6.1	0.448 ± 0.063	7.1	0.64 ± 0.08	8.2	0.62 ± 0.10	6.7	0.48 ± 0.07	7.0	0.64 ± 0.08	8.2	0.62 ± 0.10	6.7	0.48 ± 0.07	7.0
		$R^2$	0.9048		0.9106		0.9260		0.9533		0.9390		0.9469		0.9533		0.9390		0.9469	
		F-test	222		312		272		283		213		258		283		213		258	
		P-value (95%)	<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001	
Temkin	$q_e = B \ln(K_T C_e)$	$K_T$ (mg/kg) <sup>-1</sup>	0.051 ± 0.011	8.9	0.241 ± 0.078	9.7	0.277 ± 0.036	7.7	6.01 ± 1.65	3.6	8.88 ± 3.73	2.38	25.25 ± 16.92	1.5	6.01 ± 1.65	3.6	8.88 ± 3.73	2.38	25.25 ± 16.92	1.5
		$B \times 10^{-3}$ (mg/kg)	14.227 ± 1.591	4.8	10.772 ± 1.102	3.1	13.717 ± 0.791	17.3	0.97 ± 0.13	7.2	0.83 ± 0.15	5.48	0.57 ± 0.12	4.9	0.97 ± 0.13	7.2	0.83 ± 0.15	5.48	0.57 ± 0.12	4.9
		$R^2$	0.9524		0.9523		0.9830		0.9121		0.9121		0.8297		0.9121		0.8571		0.8297	
		F-test	446		577		1252		79		89		79		89		79		89	
		P-value (95%)	<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001	
Freundlich	$q_i = K_i (\sum_{j=1}^k a_{ij} C_j)^{n_i-1}$	$K_i \times 10^{-3}$ ((mg/kg)(mg/kg) <sup>-n</sup> )	1.57 ± 0.70	2.2	6.90 ± 1.47	4.7	5.98 ± 1.22	4.9	1.56 ± 1.30	1.2	1.57 ± 1.04	1.2	1.53 ± 1.61	0.9	1.56 ± 1.30	1.2	1.57 ± 1.04	1.2	1.53 ± 1.61	0.9
		$n_i$	<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001	
		$a_{ij}$ (mg/kg) <sup>-1</sup>	0.57 ± 0.09	6.5	0.34 ± 0.04	7.8	0.45 ± 0.05	8.7	0.61 ± 1.00	0.6	0.62 ± 1.04	0.6	0.53 ± 1.04	0.5	0.61 ± 1.00	0.6	0.62 ± 1.04	0.6	0.53 ± 1.04	0.5
		$R^2$	0.9607		0.9738		0.9735		0.9607		0.9738		0.9735		0.9607		0.9738		0.9735	

where  $K_F$  ((mg/kg)·(mg/kg)<sup>-n</sup>) is defined as the adsorption capacity of the adsorbent. The  $n$  values range from zero to one, reflecting the adsorption intensity or surface heterogeneity.

3.2.3. Temkin

The Temkin model is also an empirical one and does not assume a saturation limit. It takes into account indirect interactions between adsorbate and adsorbent and is expressed as follow:

$$q_e = \frac{TR}{b} \ln(K_T C_e) \tag{8}$$

$$B = \frac{TR}{b} \tag{9}$$

where  $R$  is the ideal gas constant (8.134 J/mol K),  $T$  is the temperature in Kelvin,  $K_T$  (mg/kg)<sup>-1</sup> is the equilibrium binding constant corresponding to the maximum binding energy and  $B$  (mg/kg) is related to the heat of adsorption (Do, 1998; Yousef et al., 2011).

3.2.4. Multi component isotherms

A Freundlich based isotherm was chosen to study multi component adsorption of carotenes and phosphorus onto acid activated bleaching earth, as Freundlich model correlated well both mono-component experimental data. It is written in the form (Eq. (10)) (Sheindorf et al., 1982):

$$q_i = K_i C_i (\sum_{j=1}^k a_{ij} C_j)^{n_i-1} \tag{10}$$

where  $a_{ij}$  (kg/mg) describes the inhibition to the adsorption of component  $i$  by component  $j$ , and can be determined from thermodynamic data, or more likely, from experimental data of bicomponent systems. The equation is based on the assumption that each component individually obeys the Freundlich isotherm and that for each component in a multicomponent adsorption there is an exponential distribution of adsorption energy sites (Sheindorf et al., 1982).

Table 3 presents the carotenes and phosphorus removal from crude palm oil by acid activated bleaching earth. For both adsorbents, there is a greater removal when using more bleaching earth, as expected. Concerning to the temperature influence, Table 3 shows that for carotenes there is a clear trend of improving removal with higher temperatures. In case of Phosphorus adsorption, the influence of temperature on the percentage of removal is less important, with similar removal values in the entire range of temperatures investigated. In the conditions tested, it was possible to reach a removal up to 99% of both compounds.

Langmuir, Freundlich and Temkin parameters were determined from non-linear fitting for both carotenes and phosphorus and are presented in Table 4. For carotenes adsorption at 90 °C, the Temkin model presented the highest  $R^2$  (0.9524). At 105 °C and 115 °C, the Langmuir model described the experimental data in a better way ( $R^2 = 0.9691$  and  $R^2 = 0.9917$ , respectively). Our results are in accordance with previous works found in the literature. (Low et al., 1998) studied the decolorization of CPO using acid activated spent bleaching clay, and the Langmuir model presented a better adjustment to experimental data, but Freundlich still allowed a good description of experimental data. The same results was observed by (Ahmad et al., 2009) in the adsorption of  $\beta$ -carotene from a n-hexane solution onto a silica-based adsorbent. On the other hand, in the study performed by (Boki et al., 1992), Freundlich isotherm presented a better agreement with pigments adsorption. However, it should be highlighted that, this study used different kinds of oil (rapeseed, soybean, wheat germ, safflower, corn, cottonseed and sunflower) in which  $\beta$ -carotene is not the most important pigment. The calculated isotherms are plotted in Fig. 3. It is interesting to note that better agreements between experimental and theoretical data were observed at higher temperatures,

according to the higher  $R^2$  values. The  $T$ -test shows a low accuracy in parameter estimation by Langmuir model at 90 °C. For all other models and temperatures,  $T$ -test shows a high accuracy, i.e.  $t$ -values  $>$  than standard deviation. The lowest  $q_{max}$ , i.e. maximum adsorption capacity and the complete coverage of adsorbent surface by adsorbate, was obtained at 105 °C. The highest value was obtained at 90 °C. However, as previously discussed, Langmuir model did not present a good accuracy at this temperature. The Langmuir parameter  $K_L$  presented a positive correlation with temperature, i.e. increasing the temperature the affinity between adsorbent and adsorbate also increases.

Phosphorus adsorption was described more accurately by the Freundlich model, presenting  $R^2$  higher for all tested temperatures ( $R^2 = 0.9533, 0.9390$  and  $0.9469$  for 90 °C, 105 °C and 115 °C, respectively, Table 4). The  $T$ -test shows a high accuracy in parameter estimation of all models tested for phosphorus.  $K_F$  values, a measure of adsorption capacity, increases slightly with temperature for phosphorus adsorption. (Gutfinger and Letan, 1978) observed that the Freundlich isotherm described the adsorption of phospholipids from soybean oil onto silica gel, which is an empirical model that takes into account different energy of interactions between adsorbent and adsorbate. The same result was observed by (Brown and Snyder, 1985). In both studies,  $n$  values were lower than 1, as in our work. Considering that Langmuir model was the best to describe the carotenes adsorption, it can be inferred that heterogeneity is due to the adsorbate. In fact, phosphorus occurs in vegetable oils as phospholipids, a lipid class which can have different properties depending on its organic chain.

Calculated isotherms for phosphorus are plotted in Fig. 4. The fit accuracy of Freundlich model can be observed for the entire concentration range. The Temkin model presented the highest devia-

tions from experimental data at lower concentration, which is confirmed by low  $R^2$  values.

Parameters for multi component Freundlich type isotherm are shown in Table 4. The competition coefficients  $a_{ij}$  presented low values, lower than 0.0001 kg/mg, so that the multi component Freundlich type isotherm assumes the same form as the monocomponent Freundlich model. It is interesting to highlight that the coefficients  $K_i$  and  $n_i$  obtained for the mono and multi component Freundlich equations are quite similar, differing, in the worst case, in the magnitude of the second decimal. For that reason, it can be concluded that under the tested conditions, i.e. bleaching conditions and initial adsorbates' concentrations, the competitive effects of carotenes on phosphorus adsorption and vice versa are not important.

### 3.2.5. Estimation of thermodynamic parameters

Thermodynamic parameters can provide useful information to design an adsorption process. For instance, they indicate if the process is spontaneous or not and if it is exo- or endothermic. Thermodynamic parameters are calculated using the variation of equilibrium constants  $K_0$  (or the solute coefficient of distribution between the solid and liquid phases at equilibrium) which changes with temperature (Khan and Singh, 1987; Zuim et al., 2011).

$$K_0 = \lim_{q_e \rightarrow 0} \frac{q_e}{C_e} \quad (11)$$

The standard free energy ( $\Delta G_{ads}^0$ ) was calculated by Eq.s 12 and 13 (Calvet, 1989; Khan and Singh, 1987; Zuim et al., 2011). The standard Enthalpy ( $\Delta H_{ads}^0$ ) and standard entropy ( $\Delta S_{ads}^0$ ) were calculated by Van't Hoff equation.

$$\Delta G_{ads}^0 = -RT \ln(K_0) \quad (12)$$

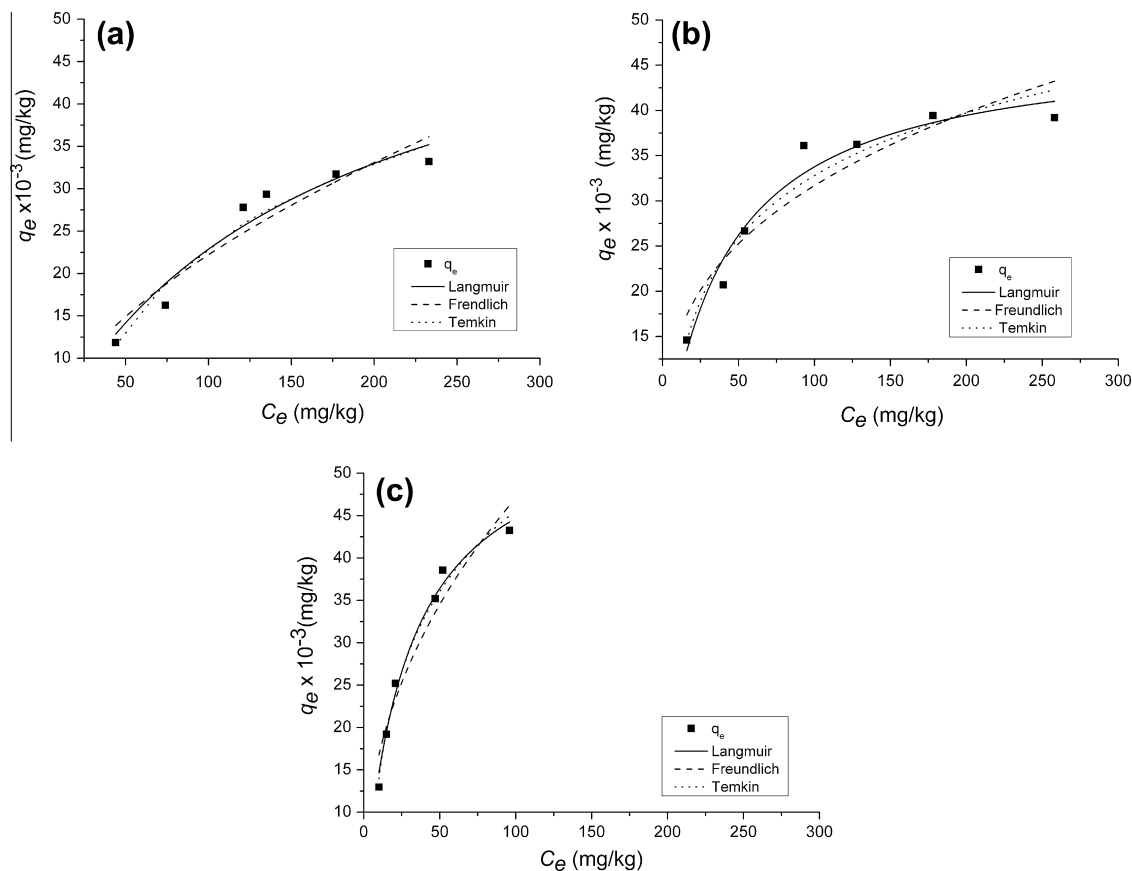


Fig. 3. Adsorption isotherm plots for carotenes onto acid activated bleaching earth at (A) 90 °C, (B) 105 °C and (C) 115 °C.

$$\ln(K_0) = -\frac{\Delta G_{ads}^0}{RT} = \frac{\Delta S_{ads}^0}{R} - \frac{\Delta H_{ads}^0}{RT} \quad (13)$$

where  $R$  (8.134 J/mol K) is the universal gas constant, and  $T$  (K) is the absolute solution temperature. The thermodynamic parameters are presented in Table 5. Both carotenes and phosphorus presented negative values for Gibbs Free Energy, indicating that the adsorption process of the studied compounds onto Tonsil OPT 210 FF is feasible and spontaneous (Srivastava et al., 2006). The magnitude of the Gibbs Free Energy increases with temperature, showing that adsorption is more spontaneous at higher temperatures. The phosphorus adsorption presented higher absolute values for Gibbs Free Energy, suggesting that this process is more spontaneous than  $\beta$ -carotene adsorption, which is in accordance with the kinetic results found in this work (Section 3.1).

On the other hand,  $\Delta H_{ads}^0$  was positive for both compounds at all temperatures, indicating an endothermic process, i.e. an increase in temperature improves adsorption. It is also indicative for a chemical adsorption process, as physisorption is always exothermic (Erbil, 2006). Those results are in agreement with (Sarier and Guler, 1988) stating that  $\beta$ -carotenes are chemisorbed onto acid activated bleaching earth. (Ahmad et al., 2009) also found that  $\beta$ -carotene adsorption from hexane solutions onto silica gel was an endothermic process.

$\Delta S_{ads}^0$  was positive indicating that the randomness at solid/liquid interface increased during the adsorption process (Srivastava et al., 2006; Zuim et al., 2011), i.e. the molecules are in a less ordered state than in solution, as a result of redistribution of energy

between the adsorbate and the adsorbent (Ahmad et al., 2009). Positive values for entropy during  $\beta$ -carotene adsorption onto silica gel (Ahmad et al., 2009) and sepiolite (Sabah et al., 2007) were also observed in previous studies.

The positive values of  $\Delta H_{ads}^0$  and  $\Delta S_{ads}^0$  indicate that both carotene and phosphorus adsorption onto acid activated bleaching earth is entropy-driven rather than energy driven. The reason of this gain in entropy may be related to a release of compounds and other species originally present in the adsorbent surface (Bouhamed et al., 2007; de Reese and Plank, 2011). For instance, in the present case it is possible that water molecules originally present in the adsorbent due to its natural humidity be released as a consequence of the adsorption process. Moreover, knowing the relative portion of enthalpic and entropic contributions allows the adsorption optimization by modifying the process conditions, for instance, the adsorption temperature.

### 3.2.6. Isotheric heat

The heat of adsorption depends on the adsorbent fraction covered. The heat of adsorption at a constant surface area, denominated isosteric heat of adsorption, can be calculated by the following equations (Do, 1998; Erto et al., 2010):

$$\left(\frac{d \ln C_e}{dt}\right) = -\frac{\Delta H_{st,a}}{RT^2} \quad (14)$$

$$\Delta H_{st,a} = R \left. \frac{d \ln C_e}{d(1/T)} \right|_{q_e} \quad (15)$$

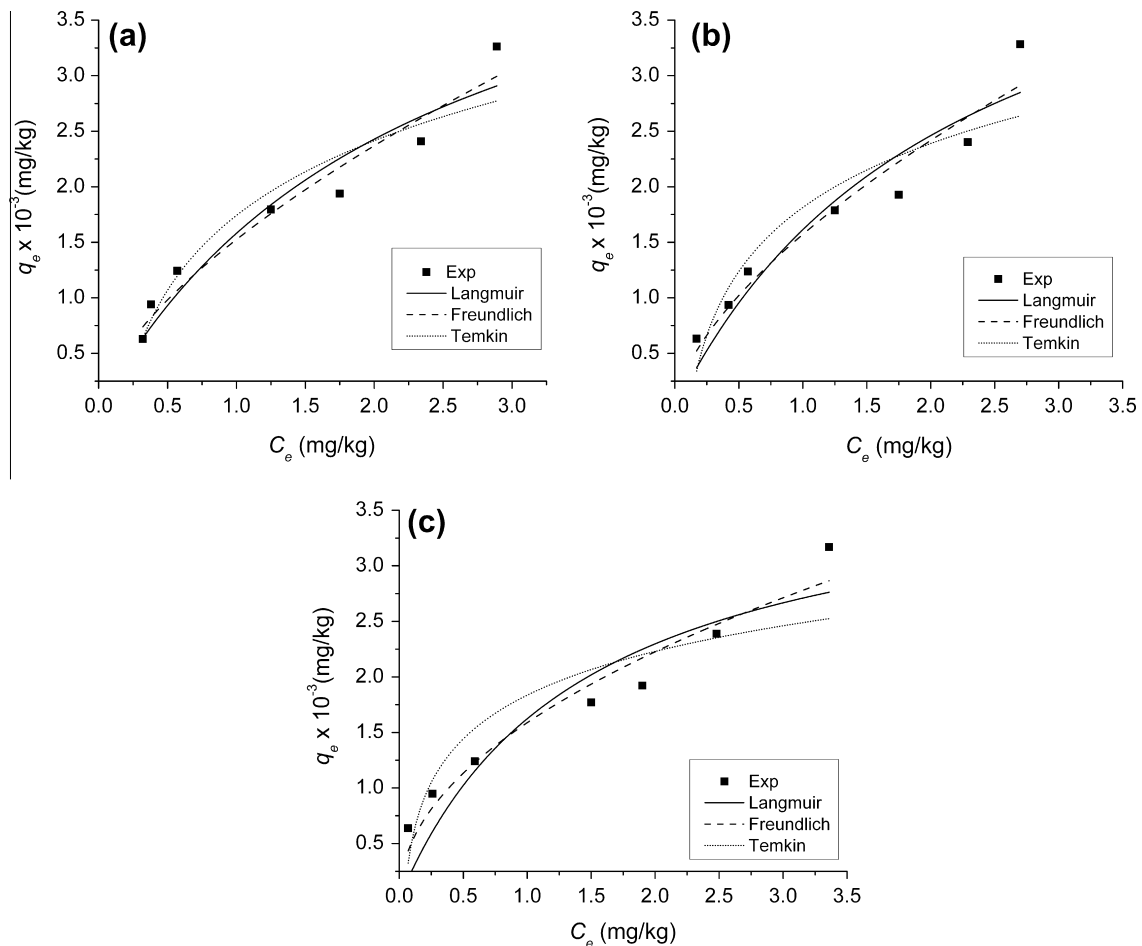
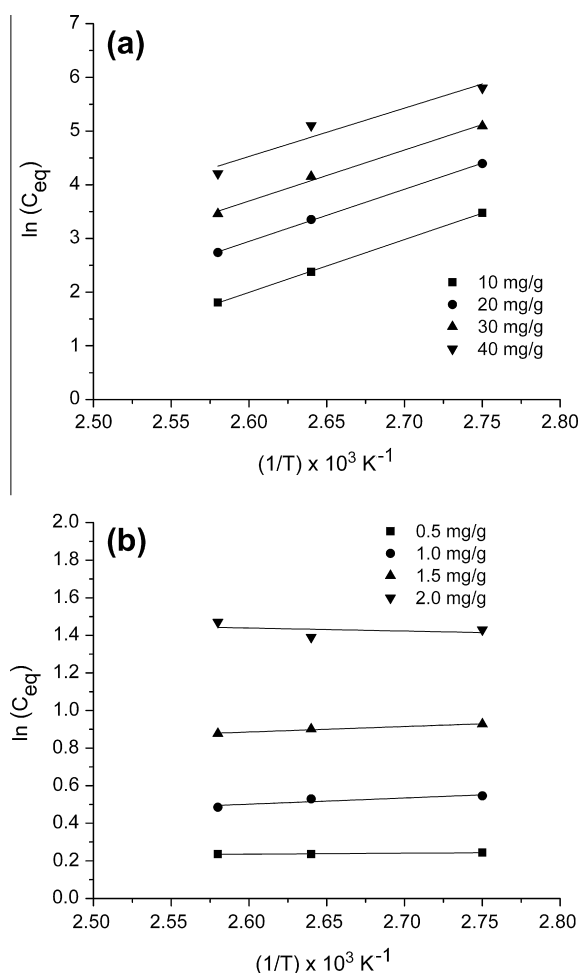


Fig. 4. Adsorption isotherm plots for phosphorus onto acid activated bleaching earth at (A) 90 °C, (B) 105 °C and (C) 115 °C.

**Table 5**

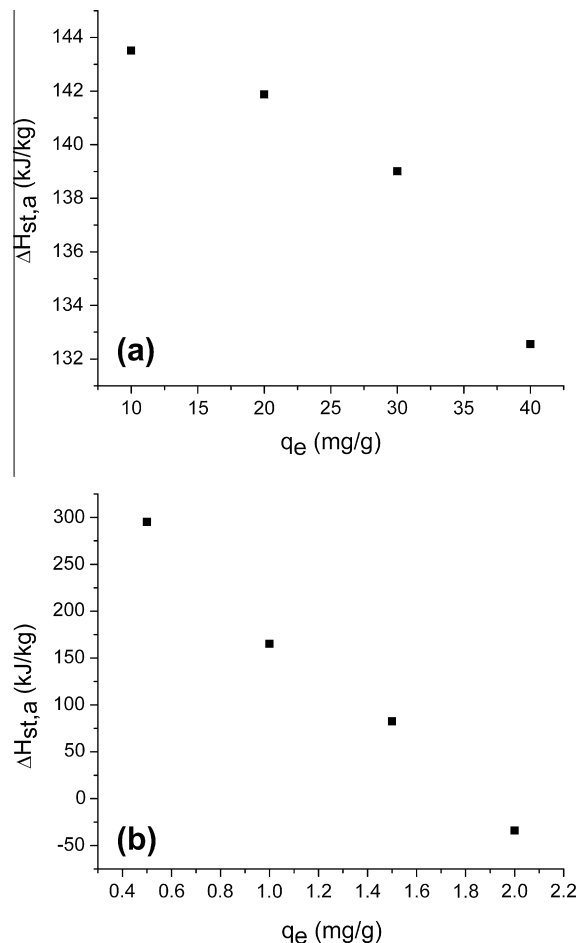
Equilibrium constants, standard Gibbs Free Energy, enthalpy and entropy of carotenes and phosphorus adsorption from crude palm oil onto acid activated bleaching earth at 90 °C, 105 °C and 115 °C.

°C	Carotenes				Phosphorus			
	$K_0$	$\Delta G_{ads}^0$ (kJ/mol)	$\Delta H_{ads}^0$ (kJ/mol)	$\Delta S_{ads}^0$ (kJ/mol K)	$K_0$	$\Delta G_{ads}^0$ (kJ/mol)	$\Delta H_{ads}^0$ (kJ/mol)	$\Delta S_{ads}^0$ (kJ/mol K)
90	333	-17.15	126.65	0.40	2731	-23.37	46.17	0.19
105	1944	-23.29			3516	-25.11		
115	5210	-27.02			7947	-28.35		



**Fig. 5.** Adsorption isotherms used to determine the isotheric heat of carotenes (A) and phosphorus (B).

Carotenes and phosphorus equilibrium concentrations at a constant amount of adsorbed compounds were determined through Langmuir isotherms. The isotheric heat of adsorption was obtained from the slope of the plot of  $\ln(C_e)$  versus  $(1/T)$  for different amounts of adsorbed adsorbates (Fig. 5). The  $\Delta H_{st,a}$  vary with surface loading for both carotenes and phosphorus (Fig. 6), indicating that interaction between Tonsil OPT 210 FF and the studied compounds are energetically heterogeneous. In fact, when the adsorbent surface has different energetic sites, molecules will adsorb preferentially at sites with the highest energy of adsorption and progressively go to lower energetic ones, resulting in a decrease of the heat of adsorption with the loading (Do, 1998). This can be due to differences in adsorbent surface or difference in adsorbed molecules. In fact, crude palm oil has different carotenoids, mostly  $\alpha$ - and  $\beta$ - (Gee, 2007) and phospholipids (Goh et al., 1984b), which



**Fig. 6.**  $\Delta H_{st,a}$  as a function of the amount adsorbed of carotenes (A) and phosphorus (B).

in this work are all expressed as  $\beta$ -carotenes and phosphorus, respectively. Positive values of  $\Delta H_{st,a}$  confirm that the adsorption is endothermic (Do, 1998; Srivastava et al., 2006).

#### 4. Conclusion

Results presented in this work suggest that adsorption of carotenes and phosphorus increases with temperature. It was possible to reach a removal up to 99% of both compounds at tested conditions. Both the pseudo-first-order and the pseudo-second-order kinetic models describe the  $\beta$ -carotene experimental data accurately. Intra-particle diffusion is involved in  $\beta$ -carotene adsorption process, although it is not the sole rate limiting step in the adsorption onto Tonsil OPT 210 FF. The equilibrium data are described more accurately by Langmuir and Freundlich models, for  $\beta$ -carotene and phosphorus, respectively. A thermodynamic study demonstrated that  $\beta$ -carotene and phosphorus adsorption is spontaneous, endothermic and an entropy-driven process. Isotheric heat values suggest that interaction between adsorbate and adsorbent are heterogeneous. High temperatures are better for adsorptive removal of carotenes and phosphorus. However, industrially it should be taken into account other factors, as unwanted side reactions, to establish the optimum bleaching temperature.

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