Adsorption Isotherms in Bleaching Hazelnut Oil

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ABSTRACT: Adsorption isotherms in bleaching hazelnut oil were determined to investigate the applicability of the Langmuir and Freundlich equations and to elucidate the adsorption characteristics of oil on bentonite EY-09 (Bensan Co. Ltd., Edirne, Turkey). The degree of bleaching was monitored spectrophotometrically. Absorbance measurements were carried out to investigate the adsorption force of clay during bleaching of hazelnut oil with 0.3, 0.5, 0.7, and 0.9 wt% clay at 50, 60, 70, 80, and 90°C. Bentonite EY-09 was used as the bleaching clay (adsorbent). Plots of log(x/m) vs. log X_e (for the Freundlich isotherm) and $X_e/(x/m)$ vs. X_e (for the Langmuir isomtherm) were made (where x is the amount of pigment removed per unit mass of the adsorbent, m, and X_e is the equilibrium concentration of the pigment). The Freundlich constants were found to increase with temperature for a given oil/bleaching agent ratio, showing the formation of more active sites on the adsorbent with a rise in temperature. Since the heat evolved during adsorption (0.32–1.03 kJ mol^{-1}) was less than 20 kJ mol^{-1}, the forces between the adsorbent and adsorbate appeared to be van der Waals forces. This type of adsorption is defined as physical or van der Waals adsorption. The results obtained show good agreement with the Freundlich isotherm, indicating that the adsorption of the pigment from the oil proceeds by monolayer formation on the surface of the adsorbent.

Paper no. J10528 in *JAOCS 80,* 1143–1146 (November 2003).

KEY WORDS: Adsorption isotherm, bleaching, Freundlich equation, hazelnut oil, Langmuir equation.

Crude oil is processed by degumming, alkali refining, bleaching, and deodorizing. Bleaching reduces chlorophylls, carotenoids, and peroxides by adsorbing pigments onto the bleaching medium (1,2).

Many investigations have been conducted into the bleaching of vegetable oils with bleaching clays in industry (3,4). Nonmontmorillonite minerals (such as kaolinites and micas), synthetic minerals (such as zirconium phosphate), or types of three-layered aluminosilicates (1) are reportedly ineffective or inferior adsorbents. Although at present montmorillonite does seem to be the most effective adsorbent clay available in industry, evaluations of alternative cheaper sources have attracted great attention in recent years. The most important adsorbent used in bleaching fats and oils is bleaching earth or clay. Bleaching clay performs not only color removal but also the removal of trace metals, the adsorption of phospholipids and soaps, and the decomposition of oxidation products such as peroxides (1, 5–7).

Two main types of adsorption on surfaces can usually be distinguished (7). In the first type, the forces are of a physical nature and the adsorption is relatively weak. The forces involved in this type of adsorption are known as van der Waals forces, and the adsorption is called van der Waals adsorption, physical adsorption, or physiosorption. The quantity of heat evolved during van der Waals adsorption is usually small—less than 20 kJ mol^{-1}. This type of adsorption is less important in catalysis, except for certain special types of reactions involving free atoms or radicals.

In the second type of adsorption, first considered in 1916 by Langmuir, the adsorbed molecules are held to the surface by covalent forces of the same general type as those occurring between the bound atoms in molecules. The heat evolved per mole for this type of adsorption, known as chemisorption, is usually comparable to that evolved in chemical bonding, namely, 100–500 kJ mol^{-1}.

Langmuir considered adsorption to distribute molecules over the surface of the adsorbent in the form of a unimolecular layer and for a dynamic equilibrium to occur between adsorbed and free molecules. He proposed the following relationship (8):

$$\frac{P}{x/m} = \frac{1}{a} + \left(\frac{b}{a}\right)P \qquad [1]$$

where P is the equilibrium pressure for a given amount of substance adsorbed, x is the amount of substance adsorbed, m is the amount of adsorbent, and a and b are constants.

The Freundlich isotherm can be derived by modifying the Langmuir assumptions to allow for several kinds of adsorption sites on the solid, each having a different heat of adsorption (8). The Freundlich isotherm is not valid at very high pressures but is frequently more accurate than the Langmuir isotherm for intermediate pressures.

The mathematical expression relating adsorption to residual solute concentration was developed by Freundlich (9):

$$\frac{x}{m} = KC^n \qquad [2]$$

where C is the amount of residual substance, and K and n are constants.

Since absorbance measurements are taken in all experiments for the bleaching process, the amount of pigment adsorbed (x) and the residual amount at equilibrium (X_e) can be obtained from Equations 3 and 4 (10):

$$x = \frac{A_0 - A_t}{A_0} \qquad [3]$$

$$X_e = \frac{A_t}{A_0} = 1 - x \qquad [4]$$

where A_0 is the absorbance of unbleached (crude) oil and A_t is the absorbance of bleached oil at time t. Thus, by means of Equations 3 and 4, by writing X_e instead of equilibrium

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pressure, P, and the residual substance, C, Equations 1 and 2 can be rearranged as follows (11):

$$\frac{X_e}{x/m} = \frac{1}{a} + \left(\frac{b}{a}\right) X_e \quad [5]$$

$$\frac{x}{m} = K X_e^n \quad [6]$$

Although the Freundlich equation is an empirical model, it is widely used to describe adsorption in vegetable oil bleaching (12,13). The widespread use of the Freundlich equation for oil bleaching and other industrial processes can be justified for three reasons: (i) For practical purposes, the equation is adequate to describe nonlinear adsorption in a narrow range of adsorbate concentrations; (ii) the mathematical simplicity of the equation enables it to be used easily; and (iii) the Freundlich model describes adsorption processes on surface adsorption sites that are energetically heterogeneous (14), a condition commonly found in adsorption systems. In contrast, the Langmuir model is based on the assumption that adsorption takes place on energetically uniform adsorption sites, which in practice rarely occurs in oil bleaching systems.

The heat of adsorption, ΔH_a, may be calculated in a manner similar to that used to calculate the heat of vaporization of a liquid by using the following modification of the Clausius–Clapeyron equation:

$$\frac{d(\ell n P)}{dT} = \frac{\Delta H_a}{RT^2} \quad [7]$$

where T is temperature (K), and R is the universal gas constant. Integration of this equation gives

$$\ell n P = -\frac{\Delta H_a}{RT} + C \quad [8]$$

where C is an integration constant.

For the bleaching process, Equation 8 can be written as

$$\ell n X_e = -\frac{\Delta H_a}{RT} + C \quad [9]$$

The applicability of the Freundlich and Langmuir adsorption isotherms to the bleaching of vegetable oils has been examined using rubber and melon seed oils at temperatures of 30, 55, and 80°C; the Freundlich and Langmuir constants have been found to increase with temperature for a given oil/bleaching agent ratio, showing the formation of more active sites on the adsorbent with a rise in temperature (11).

The purpose of this study was to determine the applicability of the Langmuir and Freundlich equations to the adsorption isotherms for bleaching crude hazelnut oil with bentonite EY-09 and to elucidate the forces between the adsorbent and the adsorbate by calculating the heat evolved during adsorption.

EXPERIMENTAL PROCEDURES

Materials. Crude hazelnut oil was supplied by Fiskobirlik Co. (Trabzon, Turkey), and bentonite EY-09 was supplied by Bensan Co. Ltd. (Edirne, Turkey). All other chemicals were of reagent grade.

Method. The bleaching vessel was a 500-mL Pyrex glass flask with a magnetic stirrer. The vessel was immersed in a thermostat-controlled glycerol bath. Crude hazelnut oil (200 g) was heated to the desired temperature before adding the bleaching clay. The mixture continued to be heated and stirred for 2 h at the desired temperature. A vacuum of 700 mm Hg was maintained throughout all experiments. The hot oil and clay mixture was filtered before measuring the absorbance.

Absorbances of the oil samples were measured by a UV spectrophotometer (UV-1601 Visible; Shimadzu Co., Tokyo, Japan) at 269 nm. During the measurement of absorbance, the filtered oil was diluted to a concentration of 1.25% (wt/vol) by adding hexane. The concentrations of bleaching clay (bentonite EY-09) were 0.3, 0.5, 0.7, and 0.9% by weight. Bleaching was carried out at 50, 60, 70, 80, and 90°C.

RESULTS AND DISCUSSION

The absorbance of unbleached (crude) hazelnut oil was 2.431 at 269 nm; the absorbance values are given in Table 1 for oil bleached at 0.3, 0.5, 0.7, and 0.9% bentonite EY-09 at 60, 70, 80, and 90°C. The bleaching efficiency increased as the temperature and clay concentration increased. Since absorbance decreased as the temperature and clay concentration increased (Table 1), the amount of pigment adsorbed (x) increased and the residual amount at equilibrium (X_e) decreased (Table 2).

The applicability of the Langmuir isotherm (Eq. 1) to the data obtained by bleaching hazelnut oil with bentonite EY-09 at various temperatures can be examined from the plots of $X_e/(x/m)$ vs. X_e (Fig. 1). The Langmuir isotherm is considered to apply if the plot of $X_e/(x/m)$ vs. X_e is linear. The constants in the Langmuir and Freundlich equations are useful in designing adsorption process equipment (11). The Langmuir isotherm constants decreased with a rise in temperature for the bleaching agents (Table 3). The slope gives $1/a$, and the intercept is equal to b/a in the plot of $X_e/(x/m)$ vs. X_e. The Langmuir isotherm constants are listed in Table 3.

The applicability of the Freundlich isotherm (Eq. 2) to the bleaching of hazelnut oil can be examined by considering the plots of log(x/m) vs. log X_e, given in Figure 2. Generally, the linearity of the logarithmic plot [i.e., log(x/m) vs. log X_e] is an indication that the Freundlich isotherm is being obeyed by the system in question. Thus, it can be concluded from the

TABLE 1
Absorbance Values at 269 nm for the Bleaching of Hazelnut Oil with Concentrations of 0.3, 0.5, 0.7, and 0.9% Bentonite EY-09 at Various Temperatures

	Absorbance (nm)			
T (°C)	0.3%	0.5%	0.7%	0.9%
50	2.292	2.252	2.192	2.073
60	2.284	2.238	2.172	2.052
70	2.278	2.227	2.156	2.028
80	2.270	2.214	2.138	2.008
90	2.262	2.200	2.119	1.987

TABLE 2
Values of the Amount of Pigment Adsorbed (x) and the Residual Amount at Equilibrium (X_e) in Bleaching Hazelnut Oil with Concentrations of 0.3, 0.5, 0.7, and 0.9% Bentonite EY-09 at Various Temperatures

	0.3%		0.5%		0.7%		0.9%	
T (°C)	x	X_e	x	X_e	x	X_e	x	X_e
50	0.0189	0.9811	0.0364	0.9636	0.0618	0.9382	0.1135	0.8865
60	0.0221	0.9779	0.0419	0.9581	0.0697	0.9303	0.1223	0.8777
70	0.0254	0.9746	0.0473	0.9527	0.0775	0.9225	0.1315	0.8685
80	0.0286	0.9714	0.0528	0.9472	0.0853	0.9447	0.1408	0.8592
90	0.0319	0.9681	0.0582	0.9418	0.0931	0.9069	0.1500	0.8500

TABLE 3
Langmuir Isotherm Constants (a and b) and Freundlich Isotherm Constants (n and K) in Bleaching Hazelnut Oil at Various Temperatures

	Langmuir constants		Freundlich constants	
T (°C)	a	b	n	K
50	−0.01400	−1.23380	−6.78249	0.05622
60	−0.01909	−1.27472	−5.59643	0.06521
70	−0.02546	−1.32125	−4.76657	0.07489
80	−0.03300	−1.37058	−4.03864	0.08484
90	−0.04222	−1.42606	−3.46605	0.09482

foregoing plots that the Freundlich isotherm is applicable to the bleaching of hazelnut oil when bentonite EY-09 is used as a bleaching agent.

The n and K values in Table 3 were obtained from the intercept in the Freundlich adsorption isotherm (Fig. 2). K is a constant that represents a measure of the surface area of the adsorbent, whereas n is an indication of its characteristic manner of adsorption (15). The values of n and K depend on a temperature increase. This observation agrees with the physical meaning of a measure of the active surface area of the adsorbent, which seems to increase with temperature. Bentonite EY-09 had higher activity or decolorizing power at higher temperatures (Table 3).

The differential molar enthalpies of adsorption, ΔH_a, which were obtained from the slope of the linear plots of ln X_e vs. $1/T$ (Fig. 3), are as follows [bentonite EY-09 (%), ΔH_a (kJ mol^{-1})]: 0.3, −0.3244; 0.5, −0.5572; 0.7, −0.8253; 0.9, −1.0359. The negative values for the heat of adsorption indicate that the adsorption was exothermic. The reason enthalpies of adsorption must be negative is that the adsorption process inevitably involves a decrease in entropy. This is because a molecule in the gas phase or in solution has more freedom of motion than one attached to a surface. Therefore, for $\Delta G = \Delta H - T\Delta S$ to be negative, ΔH must be negative (that is, the process is exothermic). The heat of adsorption decreases with the amount of adsorbent. Since the heat evolved was less than 20 kJ mol^{-1}, the forces between bentonite EY-09 and the pigments in hazelnut oil were weak, characteristic of van der Waals forces. It was determined that the bond of attraction between the adsorbent and the color body (pigment) was relatively weak, as shown by the fact that the pigment could be readily removed from the clay with acetone, isopropyl alcohol, or benzene at room temperature (16,17).

The enthalpy of adsorption depends on the extent of surface coverage, mainly because the adsorbate particles interact. If the particles repel each other, the adsorption becomes less exothermic (the enthalpy of adsorption is less negative) as coverage increases.

Adsorption isotherms of pigments from hazelnut oil on bentonite EY-09 at 50, 60, 70, 80, and 90°C are shown in Figures 1 and 2, respectively. A substantial increase in the relative amount adsorbed was observed as the temperature was increased from

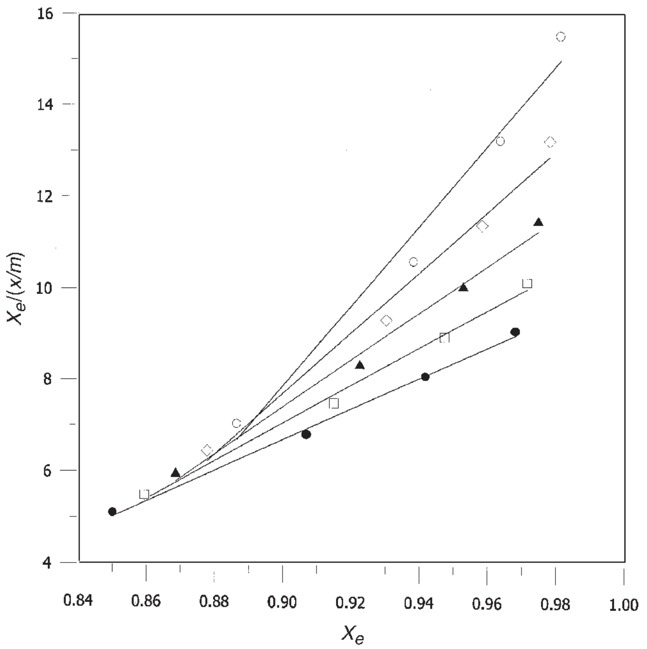

FIG. 1. Langmuir isotherms for bleaching hazelnut oil with bentonite EY-09 (Bensan Co. Ltd., Edirne, Turkey) at temperatures of: (○) 50°C, (◇) 60°C, (▲) 70°C, (□) 80°C, and (●) 90°C.

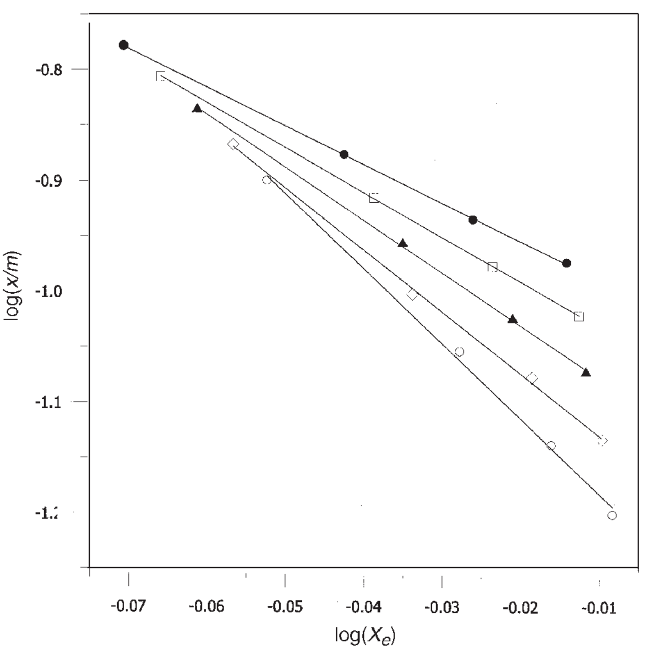

FIG. 2. Freundlich isotherms for bleaching hazelnut oil with bentonite EY-09 at temperatures of: (○) 50°C, (◇) 60°C, (▲) 70°C, (□) 80°C, and (●) 90°C. See Figure 1 for the supplier of bentonite.

TABLE 4
Error Value[a] (%) Related to the Langmuir (Lang.) and Freundlich (Freund.) Isotherms in Bleaching Hazelnut Oil with Concentrations of 0.3, 0.5, 0.7, and 0.9% Bentonite EY-09 at Various Temperatures

	0.3%		0.5%		0.7%		0.9%	
T (°C)	Langm.	Freund.	Langm.	Freund.	Langm.	Freund.	Langm.	Freund.
50	2.9310	0.4028	1.5809	0.1362	4.7096	0.5329	3.7261	0.2281
60	2.5309	0.3641	1.3471	0.1640	4.0358	0.4109	3.1728	0.1579
70	1.8265	0.1277	0.9825	0.0382	3.2948	0.2662	2.5946	0.1528
80	1.3546	0.0192	0.6714	0.0501	2.3151	0.0428	1.7643	0.0122
90	1.0263	0.0504	0.5147	0.0945	1.9025	0.0224	1.4885	0.0126

[a]Standard error (%) values between experimental and calculated values.

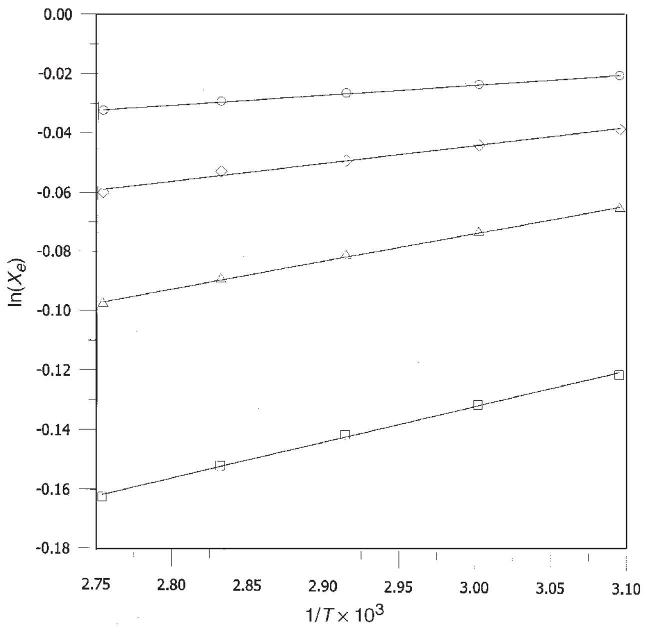

FIG. 3. The plot of ln X_e vs. $1/T \times 10^3$ at concentrations of 0.3, 0.5, 0.7, and 0.9% bentonite EY-09. (○) 50°C, (◇) 60°C, (△) 70°C, (□) 80°C. See Figure 1 for the supplier of bentonite.

50 to 90°C (Table 2). This can be indicated by a decrease in the residual amount of pigment at equilibrium. The isosteric heat of adsorption was calculated to elucidate the adsorption nature of pigments on the clays by applying a Clausius–Clapeyron equation. The effect of temperature on specific adsorption was also dependent on the nature of the bleaching agent (2).

All points in the Langmuir isotherm plot (Fig. 1) fell randomly on the line, whereas a better fit with a straight line was obtained in the Freundlich isotherm plot (Fig. 2). Error (%) values between experimental and calculated values (from the line equation) are given in Table 4; these were greater for the Langmuir isotherm (Fig. 1) than for the Freundlich isotherm (Fig. 2).

The heat evolved during adsorption was recorded as 0.32–1.03 kJ mol^{-1} during the bleaching of hazelnut oil at different concentrations of bentonite EY-09. Since this value was less than 20 kJ mol^{-1}, it shows the effect of van der Waals forces between the adsorbent and adsorbate. The experimental data show that the Freundlich adsorption equation is applicable in bleaching hazelnut oil.

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[Received December 23, 2002; accepted August 25, 2003]