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The Adsorption Isotherms of the Bleaching of Sunflower-Seed Oil

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In this study, the absorbance measurements were taken for the bleaching of sunflower-seed oil with wt. 0.3, 0.5, 0.7 and 0.9 % of clay at 60, 70, 80 and 90°C. Bentonite EY-09 was used as the bleaching clay. Since the heat evolved during adsorption (0.33-1.07 kJ mol^{-1}) was less than 20 kJ mol^{-1}, the forces between the adsorbent and adsorbate appear to be van der Waals forces, and this type of adsorption is physical or van der Waals adsorption. Thus, it was seen that the Freundlich equation was more applicable than the Langmuir equation to the experimental adsorption isotherms for the bleaching of sunflower-seed oil with Bentonite EY-09.

Keywords: Adsorption isotherm, bleaching, Freundlich equation, Langmuir equation, sunflower-seed oil.

Introduction

The bleaching of vegetable oils with bleaching clays in industry has been reviewed by Norris[1] and Kaufmann and Mukherjee[2]. 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, adsorption of phospholipids and soaps and decomposition of oxidation products such as peroxides[3].

Two main types of adsorption may usually be distinguished on surfaces[4]. In the first type, the forces are of a physical nature and the adsorption is relatively weak. The forces in this type of adsorption are known as van der Waals forces and this type of adsorption is called van der Waals adsorption, physical adsorption or physisorption. The heat evolved during van der Waals adsorption is usually small, less than 20 kJ mol^{-1}.

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 occuring between bound atoms in molecules. The heat evolved during this type of adsorption, known as chemisorption, is usually comparable to that evolved during chemical bonding, namely, 300-500 kJ mol^{-1}.

Langmuir[5] considered adsorption to distribute molecules over the surface of the adsorbent in the form of a unimolecular layer and for the dynamic equilibrium between adsorbed and free molecules, he proposed the following relation:

$$\frac{P}{X/m} = \frac{1}{a} + \left(\frac{b}{a}\right) P \tag{1}$$

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

The mathematical expression relating adsorption to residual solute concentration was developed by Freundlich[6]:

$$\frac{X}{m} = KC^n \tag{2}$$

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

Since the absorbance measurements are taken in all experiments for the bleaching process, the relative amount of pigment adsorbed (X) and the residual relative amount at equilibrium (X_e) are obtained from Equations 3 and 4[7]:

$$X = \frac{A_0 - A_t}{A_0} \tag{3}$$

$$X_e = \frac{A_t}{A_0} = 1 - X \tag{4}$$

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 pressure P and the residual substance C, Equations 1 and 2 are rearranged as follows[8]:

$$\frac{X_e}{X/m} = \frac{1}{a} + \left(\frac{b}{a}\right) X_e \tag{5}$$

$$\frac{X}{m} = K\ X_e^n. \tag{6}$$

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 using the following modification of the Clausius-Clapeyron equation[9]:

$$\frac{d(\ln P)}{dT} = \frac{\Delta H_a}{RT^2}. \tag{7}$$

Integration of this equation gives

$$\ln P = -\frac{\Delta H_a}{RT} + c \tag{8}$$

where c is an integration constant.

For the bleaching process, Equation 8 can be written as

$$\ln X_e = -\frac{\Delta H_a}{RT} + c. \tag{9}$$

Boki et.al.[10] applied the Langmuir and Freundlich equations to the adsorption isotherms of β-carotene on montmorillonite, sepiolite and standard activated clay from alkali-refined rapeseed and soybean oils.

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

Experimental

Materials

Sunflower-seed oil. Crude sunflower-seed oil was supplied by Trakya Birlik Co., Edirne, Turkey.

Bleaching clay. Bentonite EY-09 was supplied by Bensan Co. Ltd., Edirne (Enez), Turkey. Its chemical composition is given in Table 1.

All the other chemicals were reagent-grade.

Table 1. Chemical composition of Bentonite EY-09

Compound	Amount %
SiO_2	70 ± 2.0
Al_2O_3	14 ± 1.0
Fe_2O_3	1.8 ± 0.2
CaO	0.7 ± 0.2
MgO	1.7 ± 0.2
K_2O	1.8 ± 0.2
Na_2O	0.4 ± 0.2

Method

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

The absorbance of the oil samples was measured by a UV spectrophotometer (Model Octagon 200 UV-160 A, Shimadzu Co., Tokyo, Japan) at 269 nm. During the measurement of the absorbance, the filtered oil was diluted to a concentration of 1.25 % (w/v) by adding hexane. The concentrations of the bleaching clay (Bentonite EY-09) were 0.3, 0.5, 0.7 and 0.9 % by weight. All the experiments were carried out at temperatures of 60, 70, 80 and 90°C.

Results and Discussions

The absorbance of unbleached (crude) sunflower-seed oil is 2.383 at 269 nm, and the values of absorbance are given in Table 2 for the bleaching process at concentrations of 0.3, 0.5, 0.7 and 0.9 % of Bentonite EY-09 at 60, 70, 80 and 90°C. As seen in Table 2, the bleaching efficiency increases as the temperature and the clay concentration increase.

Table 2. The values of absorbance at 269 nm for the bleaching of sunflower-seed oil with concentrations of 0.3, 0.5, 0.7 and 0.9 % of Bentonite EY-09 at various temperatures.

	Absorbance			
t(°C)	0.3 %	0.5 %	0.7 %	0.9 %
60	2.330	2.283	2.217	2.093
70	2.323	2.271	2.199	2.069
80	2.315	2.258	2.181	1.048
90	2.307	2.244	2.161	2.027

Since the absorbance decreases as the medium temperature and the concentration of clay increase (Table 2), the relative amount of pigment adsorbed (X) increases and the residual relative amount at equilibrium (X_e) decreases for the bleaching of sunflower-seed oil (Table 3).

Figure 1 shows the Langmuir isotherms for the bleaching of sunflower-seed oil with Bentonite EY-09 at various temperatures. Here, the slope gives $1/a$ and the intercept is equal to b/a in the plot of $X_e/(X/m)$ versus X_e. The Langmuir and Freundlich isotherm constants are listed in Table 4.

Table 3. The values of the relative amount of pigment adsorbed (X) and the residual relative amount at equilibrium (X_e) for the bleaching of sunflower-seed oil with concentrations of 0.3, 0.5, 0.7 and 0.9 % of 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
60	0.0222	0.9778	0.0420	0.9580	0.0697	0.9303	0.1217	0.8783
70	0.0252	0.9748	0.0470	0.9530	0.0772	0.9228	0.1318	0.8682
80	0.0285	0.9715	0.0525	0.9476	0.0848	0.9152	0.1406	0.8594
90	0.0319	0.9681	0.0583	0.9417	0.0932	0.9068	0.1494	0.8506

Table 4. Langmuir isotherm constants (a and b) and Freundlich isotherm constants (n and K) for the bleaching of sunflower-seed oil with concentrations of 0.3, 0.5, 0.7 and 0.9 % of Bentonite EY-09 at various temperatures.

	Langmuir constants		Freundlich constants	
t(°C)	a	b	n	K
60	-0.0193	-1.2766	-5.5787	0.0659
70	-0.0250	-1.3181	-4.7979	0.0746
80	-0.0328	-1.3697	-4.0559	0.0845
90	-0.0423	-1.4266	-3.4500	0.0950

By taking the logarithm of Equation 6, if $\log(X/m)$ against $\log X_e$ is plotted, the constants may be evaluated from the slope n and the intercept $\log K$ (Figure 2). K is a general measure of the activity or decolorizing power of the adsorbent, whereas n is an indication of its characteristic manner of adsorption[11]. It is seen that Bentonite EY-09 has a higher activity or decolorizing power at higher temperatures (Table 4).

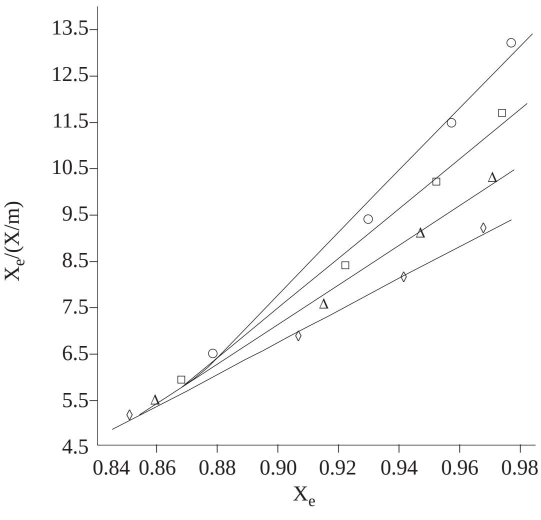

Figure 1. Langmuir isotherms for the bleaching of sunflower-seed oil with Bentonite EY-09 at temperatures of ○ : 60° C, □ : 70° C, Δ : 80° C, and ◇ : 90° C.

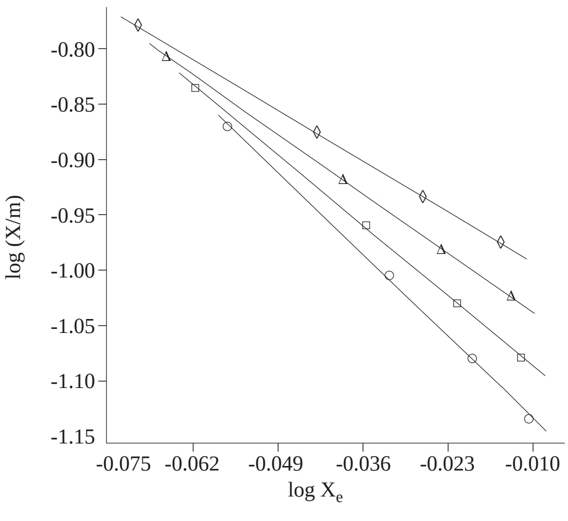

Figure 2. Langmuir isotherms for the bleaching of sunflower-seed oil with Bentonite EY-09 at temperatures of ○ : 60° C, □ : 70° C, Δ : 80° C, and ◇ : 90° C.

The heats of adsorption, ΔH_a, which were obtained from the slope of the linear plots of $\ln X_e$ versus $1/T$ (Figure 3), are given in Table 5. The negative values of heat of adsorption indicate that the adsorption is exothermic in nature because a given amount of heat is evolved during the bleaching process. Since the heat evolved is less than 20 kJ mol^{-1}, the forces between Bentonite EY-09 and the pigments in sunflower-seed oil are weak, like van der Waals forces.

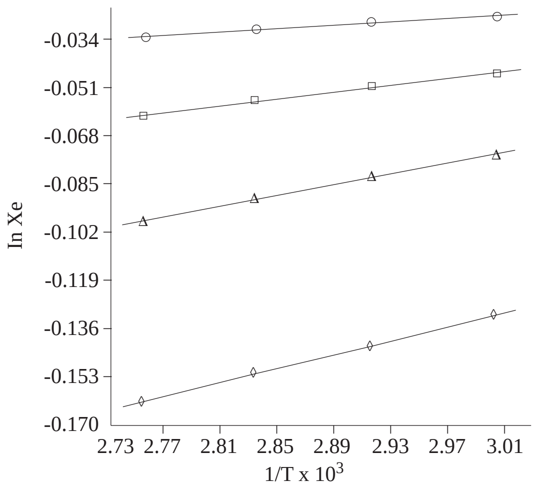

Figure 3. The plot of $\ln X_e$ vs. $1/T(K^{-1})$ at concentrations of 0.3 %, 0.5 %, 0.7 %, and 0.9 % of Bentonite EY-90.

Table 5. The values of the heat of adsorption, ΔH_a, for the bleaching of sunflower-seed oil with concentrations of 0.3, 0.5, 0.7 and 0.9 % of Bentonite EY-90 at various temperatures.

Bentonite (%)	ΔH_a (kJ mol^{-1})
0.3	-0.33
0.5	-0.58
0.7	-0.85
0.9	-1.07

Rich[12] showed that the bond of attraction between the adsorbent and te color body (pigment) was relatively weak as shown by the fact that the coloring matter can be readily removed from the clay used in laboratory bleaching by extraction with acetone, isopropyl alcohol, or benzene at room temperature.

As shown in Figure 1, all points of the Langmuir isotherm plot were present randomly on the line, whereas a better fit with a straight line was obtained in the Freundlich isotherm plot (Figure 2). Figures 1 and 2 were plotted by a computer program (grapher). This program gives the best linear fit and regression values together with a line equation for a straight line. The error (%) values between experimental and calculated values (from the line equation) are given in Table 6.

Since the error (%) values in Figure 2 for the Langmuir isotherm are less than in Figure 1 for the Freundlich isotherm, it can be seen that the Freundlich equation is more applicable than the Langmuir equation to the adsorption isotherms in the case of bleaching of sunflower-seed oil with Bentonite EY-09. The magnitude of heat evolved during adsorption confirms this conclusion.

Table 6. The values of error, %, related to the Langmuir (Lang.) and Freundlich (Freund.) isotherms for the bleaching of sunflower-seed oil with concentrations 0.3, 0.5, 0.7 and 0.9 % of Bentonite EY 09 at various temperatures.

	Errors, %							
	0.3 %		0.5 %		0.7 %		0.9 %	
t(°C)	Langm.	Freund.	Langm.	Freund.	Langm.	Freund.	Langm.	Freund.
60	2.5815	0.3714	1.3740	0.1673	4.1165	0.4192	3.2362	0.1611
70	1.8630	0.1302	1.0021	0.0390	3.3607	0.2715	2.6465	0.1558
80	1.3817	0.0196	0.6848	0.0511	2.3614	0.0436	1.7996	0.0124
90	1.0468	0.0514	0.5250	0.0964	1.9405	0.0228	1.5183	0.0128

Conclusion

The heat evolved during adsorption was recorded as 0.33-1.07 kJ mol^{-1} during the bleaching of sunflower-seed oil at concentrations of 0.3, 0.5, 0.7 and 0.9 % of Bentonite EY 09. Since this value is less than 20 kJ mol^{-1}, it shows that there are van der Waals forces between the adsorbent and adsorbate.

The experimental data show the Freundlich adsorption equation to be applicable in the bleaching of sunflower-seed oil. The magnitude of heat evolved during adsorption confirms the applicability of the Freundlich isotherm in the decolorization of sunflower-seed oil.

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