Applicability of the Freundlich and Langmuir Adsorption Isotherms in the Bleaching of Rubber and Melon Seed Oils

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The applicability of Freundlich and Langmuir adsorption isotherms to guide bleaching of vegetable oils was examined using rubber [*Hevea brasiliensis* (Willd. ex Adr. Juss) Muell. Arg.] and melon [*Colocynthis vulgaris* (Schrad)] seed oils at temperatures of 30, 55 and 80 C. Fuller's earth, activated charcoal and a mixture thereof (1:1 ratio) were used as the decolorizing agents (adsorbents). The degree of bleaching was monitored spectrophotometrically.

Plots of log(x/m) versus log X_e (for Freundlich) and (X_e/x/m) versus X_e (for Langmuir) were made; where x is the amount of coloring matter removed per unit mass of the adsorbent, m, and X_e is the equilibrium concentration of the coloring matter. The results obtained show good agreement with Freundlich and Langmuir isotherms, indicating that the adsorption of the coloring matter from the oils proceeds by monolayer formation on the surface of the adsorbent. The specific adsorption (x/m) and the Freundlich and Langmuir 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.

Bleaching or decolorization of vegetable oils is an adsorption process, a surface phenomenon involving the removal of the coloring matter (the adsorbate) by means of an activated earth, a carbon or another chemical agent (the adsorbent). The nature of the attractive forces holding the molecules on the surface of the adsorbent has been used to classify adsorption into physical adsorption (physiosorption) and chemisorption.

In physical adsorption the attractive forces are the weak van der Waals forces. The magnitude of heat evolved is on the order of the heat of vaporization or condensation of gases (less than 40 kJ mole^{-1}) (1). Physical sorption is a fast, reversible process, being influenced by temperature and concentration of the adsorbate. It is possible for additional layers of the adsorbate to be formed on the first, leading to multilayer formation. In chemisorption, however, the adsorbate is chemically bound to the adsorbent. The process is not easily reversible and is temperature dependent, with the heat of adsorption being comparable to that of a chemical reaction (80 kJ mole^{-1}) (1). Only a monomolecular layer is produced in chemisorption, whereas multilayer formation is possible in physiosorption.

Generally, the temperature dependence of adsorption is such that at low temperatures chemisorption may be so slow that only physical adsorption is observed. However, chemisorption increases with temperature increases, and at high temperatures only chemisorption is exhibited. Though physiosorption and chemisorption may occur simultaneously at intermediate temperatures, they are easily distinguishable at extreme temperatures.

In the adsorptive bleaching of fats and oils, physiosorption is believed to predominate because a large portion of the coloring matter adsorbed by a bleaching earth can be eluted with 95% alcohol. For the adsorbent/adsorbate systems studied here, we have demonstrated the predominance of physiosorption by measuring the enthalpy of adsorption (2).

Phenomenologically, adsorption is generally described by a graphic representation of the distribution ratios of adsorbate adsorbed per unit mass of the adsorbent and the concentration of the unadsorbed adsorbate at constant temperature. This graphic representation is known as the adsorption isotherm. Several types of adsorption isotherms have been reported in the literature, but the most widely used are the Freundlich and the Langmuir isotherms. The former is purely empirical and the latter is a theoretical expression obtained by assuming a uniform monolayer adsorption of the adsorbate molecules. The mathematical forms of the two isotherms for adsorption from solution are given by equations [1] and [2], respectively.

$$x/m = KX_e^{1/n} \quad [1]$$

$$X_e/(x/m) = 1/a.b + X_e/a \quad [2]$$

where x and X_e are the amounts of adsorbed and unadsorbed coloring matter at equilibrium, respectively; m is the weight of the adsorbent; K is a constant which represents a measure of the surface area of the adsorbent (3); 1/n is an irrational fraction that varies between 0.1 and 1 and is a measure of intensity of adsorption (3); a and b are constants which give a measure of the surface area of the adsorbent and the intensity of adsorption, respectively.

Some reports in the literature on the applicability of these isotherms to the adsorption of coloring matter from oil and other solutions show varying agreement. For instance, the application of the Freundlich isotherm to the data obtained in the bleaching of sunflower oil (4,5) was reported to show deviations in the lower and higher concentrations of the oil, which were attributed to partial involvement of chemisorption. However, a more recent work in which refined olive oil (6) was bleached with activated charcoal and diatomaceous earth shows the Freundlich isotherm to be applicable. The Langmuir isotherm has been reported to be applicable to the adsorption process involving the removal of β-carotene from solution by activated earths (7,8); these studies indicate that both physiosorption and chemisorption are involved, the latter arising from protonization of the polyenic chain (the colorant) by the polysilicic acids present in the activated earths.

We have examined in part in an earlier study the applicability of the Freundlich isotherm in the decolorization of the oils of rubber [*Hevea brasiliensis* (Willd. ex Adr. Juss. Arg.], melon [*Colocynthis vulgaris* (Shrad)] and oilbean [*Pentaclethra*

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macrophylla (Benth.)] seeds at 80 C using Fuller's earth (FE), activated charcoal (AC) and a FE/AC mixture (2). In this study, a fixed amount of the oil was bleached with varying amounts of the bleaching agents. The Freundlich isotherm was found to be generally applicable with deviations observed in the bleaching of melon seed oil and oilbean seed oil with FE/AC and AC, respectively. The above study was quite restrictive in temperature, and the experimental approach was different from the normal isotherm study procedure, namely, keeping the amount of the bleaching agent constant while varying the amount of oil (and hence the coloring matter).

The present work adopts the normal isotherm procedure and widens the scope of our previous work. The objectives are to elucidate the mechanism of coloring matter removal from vegetable oils with bleaching earths and to obtain values for the fundamental constants in the Freundlich and Langmuir expressions, which are useful in the design of adsorption process equipment.

MATERIALS

Fuller's earth. This was a product of Fulmont Ltd., England, and was donated by Lever Brothers (Nigeria) Ltd., Aba.

Activated charcoal. The sample was a product of Hoechst Chemical Co., Frankfurt, W. Germany.

Rubber seed oil. The oil was extracted from rubber seeds supplied by the Agricultural Development Corp., Nekede, Owerri, Nigeria; Acid value was 44.40; iodine value, 136-142; saponification value, 186-196.

Melon seed oil. The oil was extracted from melon seeds bought from the Nsukka urban market. Acid value was 2.00; iodine value, 100-115; saponification value, 166-176.

PROCEDURE FOR ISOTHERM STUDIES

Five g of each of the bleaching agents (FE, AC and FE/AC mixture) were mixed thoroughly with varying amounts of the oil in a two-necked flask. The flask with its content was immersed in an oil bath maintained at a constant temperature (30, 55 or 80 C) by means of a thermo heater. The mixture was kept under vacuum and stirred continuously with a magnetic stirrer during the bleaching, which lasted 40 min. After bleaching, the oil was filtered with a Whatman Grade 1 filter paper, and the absorbance of the neat oil was determined in a Pye Unicam 500 series spectrophotometer at maximum excitation wavelength, λ_{max}, of 400 nm.

RESULTS AND DISCUSSION

The absorbance values of the unbleached oil (A_o) and those of the bleached oil (A_x) are given in Table 1 (rubber seed oil) and Table 2 (melon seed oil) for temperatures 30, 55 and 80 C and for bleaching agents FE, AC and FE/AC mixture. Values of the relative amount of coloring matter adsorbed, x (in equations [1] and [2]) were obtained by multiplying the fractional degree of bleaching, $(A_o - A_x)/A_o$ by the amount of oil used; while values of X_e (the relative amount of unadsorbed coloring matter at equilibrium) were given by the fractional unadsorbed coloring matter times the amount of oil used.

Effects of oil concentration and temperature on adsorption isotherm curves. Plots of the logarithm of specific adsorption (x/m) vs the logarithm of the equilibrium concentration of the coloring matter X_e at the three temperatures are given for rubber seed oil by the (a) curves in Figures 1-3 for FE, AC and FE/AC, respectively. Similar plots for melon seed oil are given by the (a) curves in Figures 4-6. These plots indicate a rise in (x/m) values with increase in oil concentration, probably as a result of an increase in the collision

TABLE 1

Absorbance Values of Bleached Rubber Seed Oil

Temperature (°C)	Wt of oil (g)	Absorbance (A_x) FE	AC	FE/AC
30	20	1.222	0.903	1.155
	25	1.367	0.996	1.387
	30	1.398	1.022	1.456
	35	1.409	1.108	1.523
	40	1.432	1.155	1.620
	45	1.699	1.260	1.723
	Unbleached oil (A_o)	2.301	2.301	2.398
55	20	0.700	0.827	0.921
	25	0.824	0.921	1.097
	30	0.854	1.022	1.131
	35	0.854	1.046	1.155
	40	0.921	1.131	1.222
	45	1.046	1.215	1.317
	Unbleached oil (A_o)	2.301	2.301	2.301
80	20	0.420	0.460	0.823
	25	0.489	0.495	0.939
	30	0.509	0.638	1.066
	35	0.553	0.638	1.097
	40	0.595	0.668	1.102
	45	0.699	0.770	1.155
	Unbleached oil (A_o)	2.398	2.398	2.301

TABLE 2

Absorbance Values of Bleached Melon Seed Oil

Temperature (°C)	Wt of oil (g)	Absorbance (A_x) FE	AC	FE/AC
30	20	0.164	0.117	0.166
	25	0.171	0.128	0.195
	30	0.182	0.149	0.208
	35	0.182	0.155	0.219
	40	0.184	0.215	0.222
	45	0.206	0.268	0.237
	Unbleached oil (A_o)	0.509	0.498	0.498
55	20	0.110	0.113	0.152
	25	0.118	0.135	0.160
	30	0.122	0.158	0.170
	35	0.140	0.161	0.174
	40	0.145	0.179	0.210
	45	0.170	0.210	0.220
	Unbleached oil (A_o)	0.498	0.565	0.565
80	20	0.102	0.097	0.125
	25	0.119	0.108	0.131
	30	0.131	0.109	0.137
	35	0.131	0.119	0.143
	40	0.143	0.125	0.155
	45	0.171	0.131	0.161
	Unbleached oil (A_o)	0.565	0.309	0.498

frequency between the molecules of the coloring matter (the adsorbate) and the particles of the bleaching agent (the adsorbent). However, this concentration effect does reach a maximum (the saturation point) beyond which decrease in specific adsorption is observed. The decrease is probably due to increased adsorption of the oil (solvent) molecules in preference to the molecules of the coloring matter.

The log (x/m) vs log X_e plots also reveal significant effects of temperature on specific adsorption. For each oil and each of the three bleaching agents, substantial increases in specific adsorption are observed as the temperature is increased from 30 to 80 C. This could be attributed to activation of more adsorption sites on the adsorbents through increased porosity and total pore volume at higher temperatures. It is also possible that the observed rise in specific adsorption may derive partly from the destruction of temperature-sensitive coloring matter such as carotenoids at the increased temperatures used. However, this factor appears to be much less significant than the influence of temperature on the morphology of the adsorbent because the observed temperature effect on specific adsorption appears to be dependent on the nature of the bleaching agent.

For instance, for rubber seed oil the variation in specific adsorption among 30, 55 and 80 C is much wider with FE as bleaching agent (Fig. 1, set a) than with AC (Fig. 2, set a), in which the specific adsorptions at 30 and 55 C are essentially the same. The use of the FE/AC mixture (Fig. 3, set a) produces an intermediate variation in specific adsorption with temperature. Thus, the nature of the bleaching agent appears to determine to a significant degree the temperature effect on specific adsorption.

With melon seed oil, the effect of temperature on the specific adsorption is not as dramatic as with rubber seed oil. Also, the influence of the nature of the bleaching agent on the observed temperature effect appears less pronounced. For instance, at 55 and 80 C, the observed specific adsorption values are comparable for FE, AC and FE/AC as shown in Figures 4a, 5a and 6a, while the specific adsorption figures at 30 C are generally moderately lower. These bleaching results show that, on the whole, melon seed oil is more readily bleached at lower temperature than rubber seed oil.

The foregoing temperature effects are also manifest in the plots of $X_e/(x/m)$ vs Xe [the (b) curves] as the Xe/(x/m) ratios are highest at 30 C.

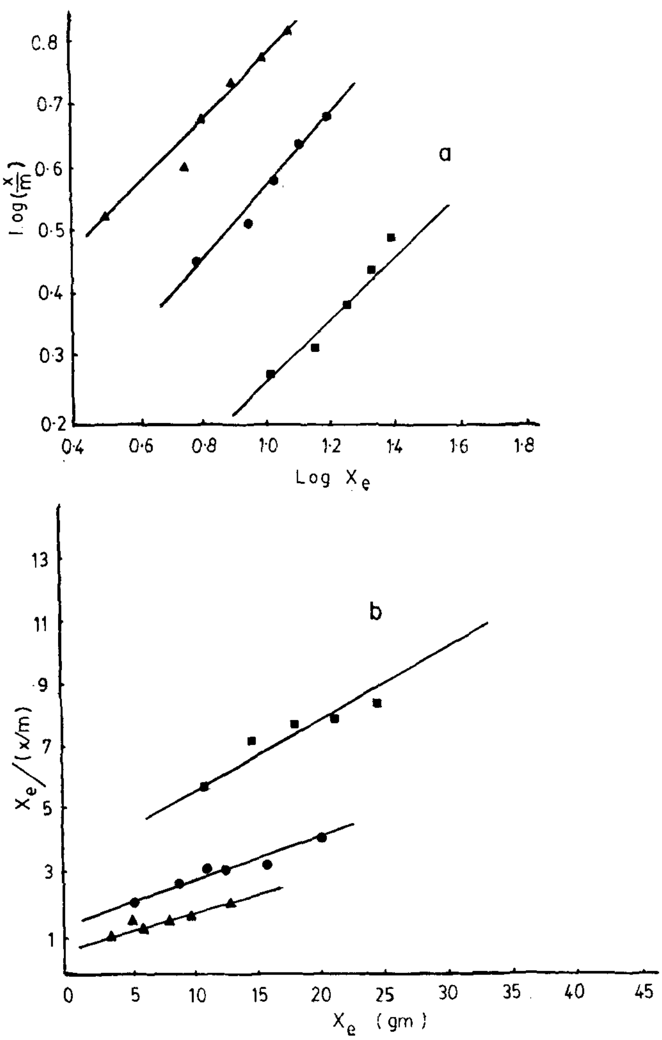

FIG. 1. Freundlich (a) and Langmuir (b) adsorption isotherms for the bleaching of rubber seed oil with Fuller's earth. ■, 30 C; ●, 55 C; ▲, 80 C.

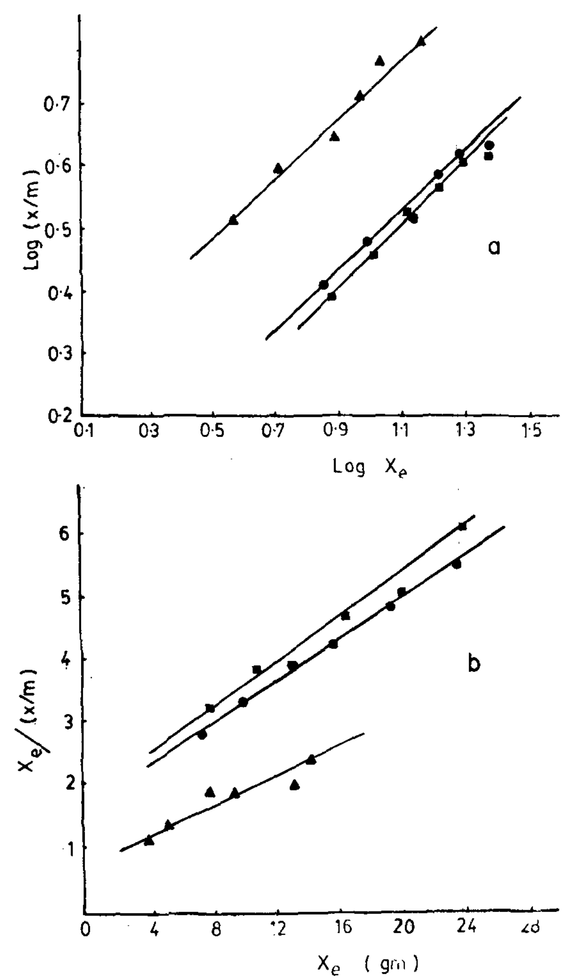

FIG. 2. Freundlich (a) and Langmuir (b) adsorption isotherms for the bleaching of rubber seed oil with activated charcoal. ■, 30 C; ●, 55 C; ▲, 80 C.

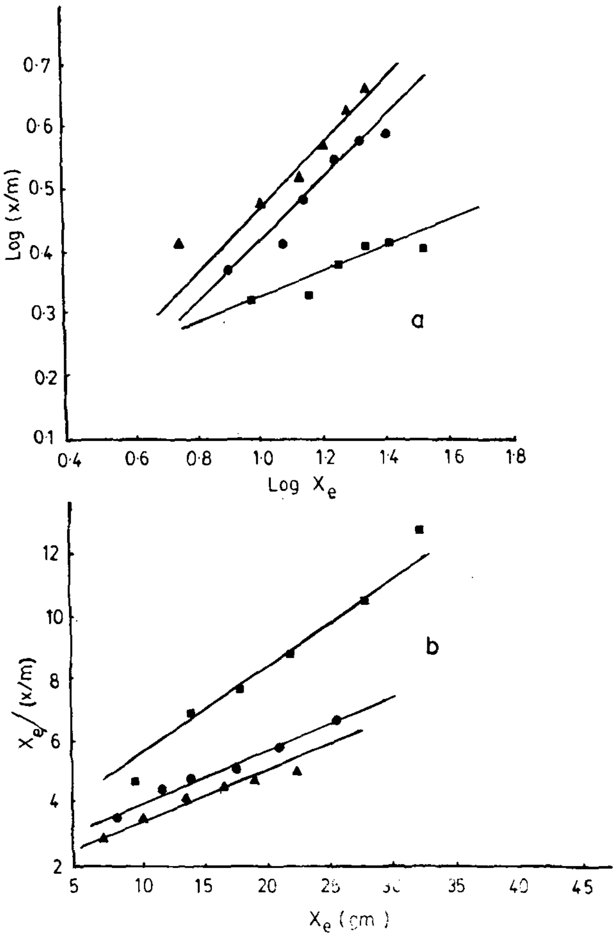

FIG. 3. Freundlich (a) and Langmuir (b) adsorption isotherms for the bleaching of rubber seed oil with FE/AC mixture. ■, 30 C; ●, 55 C; ▲, 80 C.

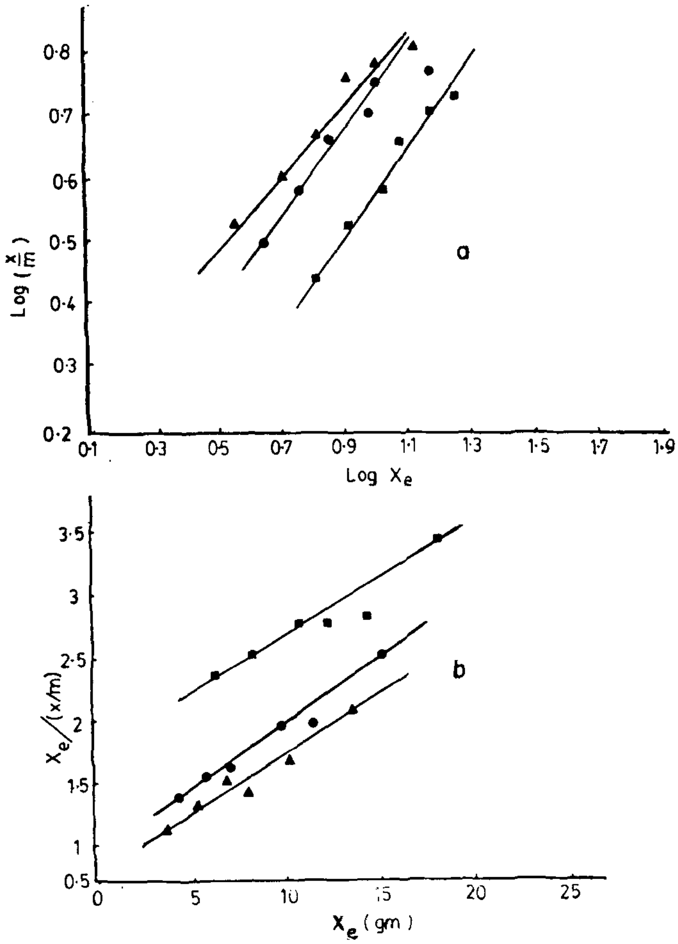

FIG. 4. Freundlich (a) and Langmuir (b) adsorption isotherms for the bleaching of melon seed oil with Fuller's earth. ■, 30 C; ●, 55 C; ▲, 80 C.

THE FREUNDLICH ISOTHERM

The applicability of the Freundlich isotherm (equation [1]) to the decolorization of rubber and melon seed oils can be examined by considering the plots of log(x/m) vs log X_e, given by the (a) curves in Figures 1-3 (for rubber seed oil) and Figures 4-6 (for melon seed oil). Generally, the linearity of the logarithmic plot (i.e., log (x/m) vs log X_e) is an indication that the Freundlich isotherm is obeyed by the system in question. Thus, it can be concluded from the foregoing plots that the Freundlich isotherm is applicable to the bleaching of rubber and melon seed oils when FE, AC and FE/AC are used as bleaching agents. The deviations observed at high oil concentrations for the rubber seed oil/AC system (at 30 and 50 C) and the melon seed oil/AC system (at 30 and 50 C) occur outside the adsorption saturation point where desorption due to oil molecule interference has become significant, and the Freundlich isotherm can no longer apply.

Values for the constants 1/n and K in the Freundlich equation are given in Table 3. The 1/n values, obtained from the slope of the log plot, are within the range of 0.1-1.0 generally reported in the literature. The 1/n values show varying temperature dependence, depending on the bleaching agent used: with FE, there is a fall in 1/n with rise in temperature while the reverse is true for the FE/AC mixture. However, with pure AC, there is no clear trend. The observed fall in 1/n and hence increase in n value with rise in temperature corroborates the observed effect of temperature on specific adsorption and thus is in keeping with the significance of n as a measure of the intensity of adsorption (3). The reason for the trend obtained with FE/AC is not clear, although it may stem from the observed moderate effects of temperature on specific adsorption with this bleaching agent, as indicated earlier.

The K values in Table 3 are obtained from the intercepts in the Freundlich adsorption isotherms (Figs. 1a-6a). K is a rough measure of the surface area of the adsorbent (3). The observed increase in K value with rise in temperature in bleaching of rubber and melon seed oil with FE and AC supports the above meaning of K and hence corroborates the earlier observation that temperature rise seems to create more adsorption sites. The case of FE/AC is, however, slightly different, with no significant changes in the K value with rise in temperature; again, the reason for this is not clear.

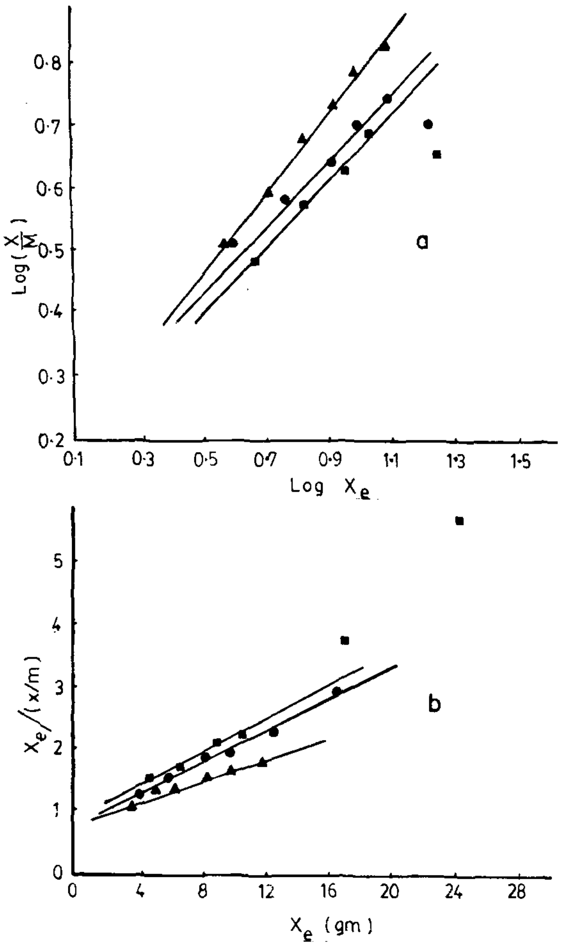

FIG. 5. Freundlich (a) and Langmuir (b) adsorption isotherms for the bleaching of melon seed oil with activated charcoal. ■, 30 C; ●, 55 C; ▲, 80 C.

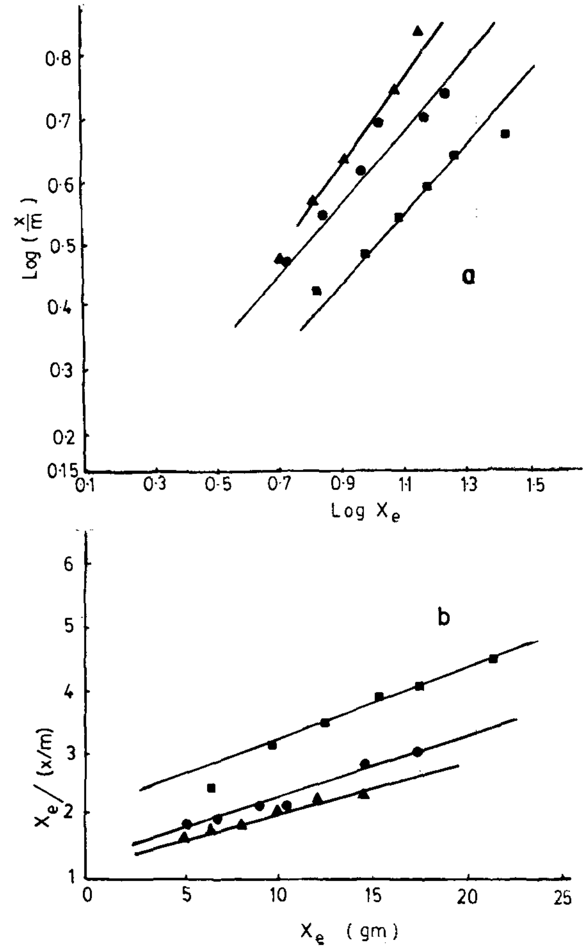

FIG. 6. Freundlich (a) and Langmuir (b) adsorption isotherms for the bleaching of melon seed oil with FE/AC mixture. ■, 30 C; ●, 55 C; ▲, 80 C.

TABLE 3

Freundlich Isotherm Constants for Rubber and Melon Seed Oils

Bleaching agent	Temperature (°C)	Rubber 1/n	Rubber K	Melon 1/n	Melon K
FE	30	0.73	1.02	0.74	1.02
	55	0.55	1.66	0.70	1.36
	80	0.41	2.88	0.57	1.79
AC	30	0.50	1.10	0.54	1.51
	55	0.48	1.20	0.53	1.60
	80	0.47	1.95	0.63	1.64
FE/AC	30	0.21	1.58	0.58	1.05
	55	0.50	1.32	0.47	1.26
	80	0.56	1.38	0.69	1.26

TABLE 4

Langmuir Isotherm Constants for Rubber and Melon Seed Oils

Bleaching agent	Temperature (°C)	Rubber 1/a	Rubber 1/ab	Melon 1/a	Melon 1/a.b
FE	30	0.22	3.2	0.09	1.75
	35	0.14	1.4	0.10	0.80
	80	0.10	0.7	0.09	0.55
AC	30	0.18	1.29	0.13	0.90
	55	0.13	0.16	0.13	0.75
	80	0.11	0.70	0.09	0.75
FE/AC	30	0.29	3.9	0.11	2.00
	55	0.17	3.0	0.10	1.30
	80	0.15	2.50	0.08	1.20

THE LANGMUIR ISOTHERM

The applicability of the Langmuir Isotherm (Equation [2]) to the data obtained by bleaching rubber and melon seed oils with FE, AC and FE/AC can be examined from the plots of $X_e/(x/m)$ vs X_e (Figs. 1b-6b). The Langmuir isotherm is considered to apply if the plot of $X_e/(x/m)$ vs X_e is linear. The observed linearity in Figures 1b-6b therefore suggests the applicability of the Langmuir isotherm to the systems studied here. This implies that the adsorption of the colored matter from the oils proceeds by monolayer formation with minimal competition from the oil molecules, provided the 'saturation point' is not reached. The deviations observed in the Langmuir isotherms at 30 C for the systems rubber seed oil/FE (Fig. 1b) and melon seed oil/AC (Fig. 5b) occur outside the optimum adsorption (or saturation point) where the Langmuir isotherm no longer applies due to desorption.

The Langmuir isotherm constants 1/a and 1/a.b for rubber and melon seed oils are given in Table 4. The values of 1/a for both oils decrease with a rise in temperature for the three bleaching agents. This means an increase in the value of a as temperature increases; this observation agrees with the physical meaning of a as a measure of the active surface area of the adsorbent, which, as observed earlier, seems to increase with temperature.

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