The Freundlich Isotherm in Studying Adsorption in Oil Processing

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ABSTRACT: The objective of this review is to discuss the history of the use of the Freundlich isotherm in investigating adsorption processing of vegetable oils and to evaluate its current value in adsorption studies. The Freundlich isotherm was originally developed to explain the adsorption of a single solute from solution. However, a similar adsorption pattern has been observed when studying a more complex system of adsorption of vegetable oil pigments onto bleaching clay during commercial bleaching of vegetable oils. The Freundlich isotherm has been useful for decades in finding the commercial value of adsorbents as long as a narrow experimental interval of adsorbate is used. More recent studies have shown that a complex series of interactions controls the adsorption process. While the isotherm summarizes these interactions, investigating them is vital to understand the physicochemical factors involved during adsorption. Statistical modeling and spectroscopy are useful in understanding the vegetable oil bleaching/refining process as a multiple-component adsorption system.

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Adsorption involves the separation of a substance from a liquid or gas phase, and its accumulation on the adsorbent surface. Adsorption bleaching of vegetable oils was originally designed to remove chlorophyll and carotenoid pigments. However, it is now used to adsorb a number of other components that adversely affect oil quality and stability. These include free fatty acids, phospholipids (PL), peroxides, and carbonyl compounds. Bleaching, the only adsorption operation used in vegetable oil refining, greatly improves oil quality.

The Freundlich isotherm has been used for almost 50 years to describe the adsorption of pigments onto adsorbents in vegetable oil bleaching. During this time, understanding of the mechanisms and physical chemistry of the adsorption bleaching process has significantly increased. However, there are still limitations in explaining the adsorption of other components, e.g., fatty acids and PL, from a relatively complex multicomponent system such as vegetable oil. The objectives of this paper are to review the history of the use of the Freundlich isotherm in studying adsorption bleaching and to evaluate the current value of the Freundlich isotherm in studying vegetable oil lipid adsorption.

The Freundlich isotherm. Adsorption is a physical chemical process that involves the mass transport of an adsorbate from the solution phase (i.e., bulk solution, film and intraparticle transportation) to the adsorbent surface where adsorption occurs. When the thermodynamic equilibrium of the adsorbate concentration is established between solution and adsorbent, no further net adsorption occurs (1). This equilibrium is defined by the concentrations of adsorbent and adsorbate in the system, and conditions of temperature, viscosity, and pH. Adsorption equilibrium is the most fundamental property of the adsorbate–adsorbent interaction. Therefore, the theoretical and empirical models that describe reversible adsorption have been developed on the basis of a thermodynamic equilibrium.

Several equilibrium models have been developed to describe adsorption isotherm relationships (Table 1). However, no single model has been found to be generally descriptive of the process. Thus, Langmuir and Brunauer–Emmet–Teller (BET) isotherm models often fail to describe experimental data in vegetable oil systems, despite their sound theoretical

TABLE 1
Common Isotherm Adsorption Models Based on Thermodynamic Equilibrium

Adsorption isotherm	Equation[a]
Freundlich	$Q_e = k_f C_e^{(1/nf)}$; also used as $Q_e = k_f C_e^n$; used by oil processors as $x/m = KC^n$
Brunauer–Emmet–Teller (BET)	$Q_e = (BC_eQ)/(C_e–C_s)[1 + (B - 1)(C_e/C_s)]$
Langmuir	$Q_e = (QbC_e)/(1 + bC_e)$
Linear	$Q_e = K_pC_e$

[a]Legend: $Q_e = x/m$, the amount of substance adsorbed per mass of adsorbent at equilibrium; $C_e = C$, residual adsorbate concentration in solution at equilibrium; x, amount adsorbed per mass of adsorbent; m, amount of adsorbent; $K = k_f$, intercept and $n = 1/n_f$, slope of Freundlich isotherm when expressed as $\log (x/m) = \log K + n \log (C)$; Q, adsorbate surface concentration when all available adsorption sites are occupied; b, adsorption equilibrium constant (ratio of adsorption and desorption rates); C_s, adsorbate concentration to saturate the solvent (solubility limit); B, energy adsorption constant; K_p, the partition coefficient of the adsorbate.

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basis. Although the Freundlich equation is an empirical model, it is widely used to describe vegetable oil adsorption bleaching (2–7).

Freundlich (8), in 1924, described the adsorption of a single adsorbate in an aqueous solution as a reversible equilibrium, when the equilibrium was established in a few seconds or minutes at a fixed temperature. The Freundlich equation (Table 1) states that, at a constant temperature, the amount of adsorbate bound per unit weight of adsorbent, Q_e (adsorption efficiency of the adsorbent) is a logarithmic function of the residual concentration in the fluid phase at equilibrium, C_e. At low solute concentrations, the amount of adsorbate adsorbed increases greatly with an increase in solution concentration. However, at larger concentrations of adsorbate, the amount adsorbed approaches a constant value (Fig. 1). Thus, the gradient of the curve is greatest at low solute concentrations and decreases with solute concentration. An important limitation of the Freundlich equation is that it does not allow for a limit in adsorption capacity; theoretically, the amount adsorbed may be infinite as solute concentration increases (9) (Fig. 1). In addition, it is paradoxical that the Freundlich isotherm has been successfully used to describe adsorption bleaching of oils to bleaching clays because the equation describes reversible adsorption, whereas adsorption bleaching itself is irreversible.

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 (9), a condition commonly found in adsorption systems. In contrast,

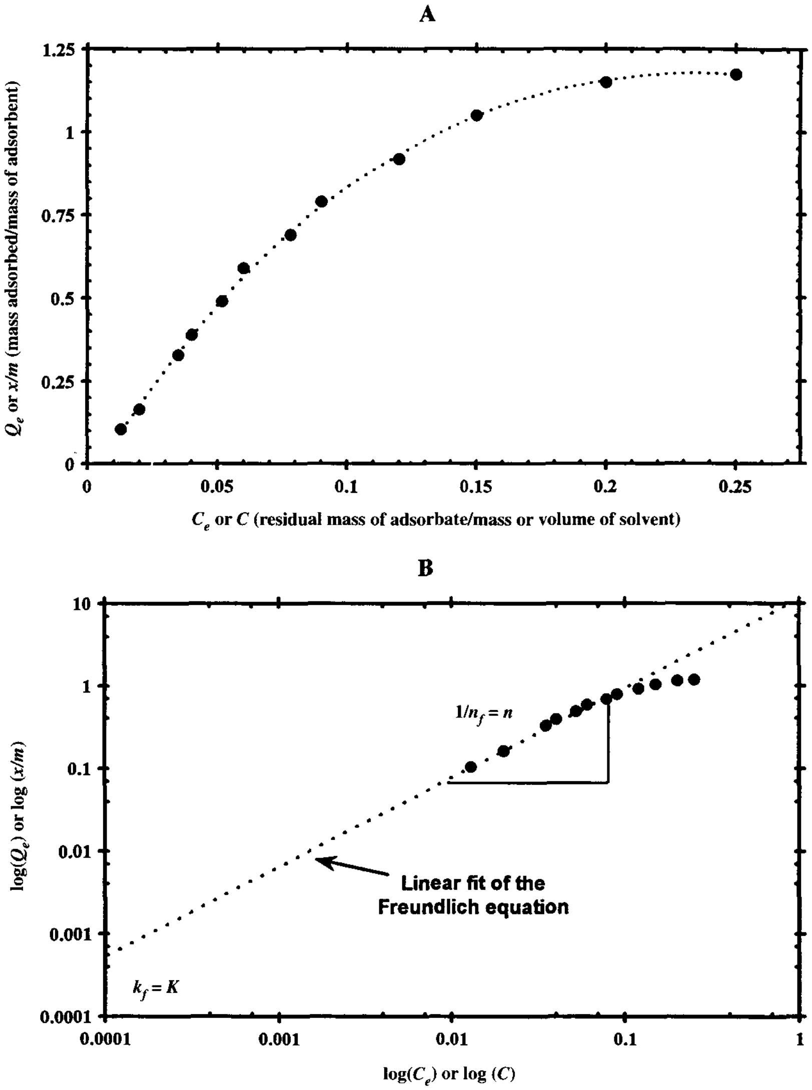

FIG. 1. Freundlich isotherm in its logarithmic (A) and linear (B) form. The isotherm is shown for two different nomenclatures, $Q_e = k_f C_e^{(1/nf)}$ and $x/m = KC^n$.

the Langmuir and BET models are based on the assumption that adsorption takes place on energetically uniform adsorption sites, which seldom occurs in oil bleaching systems.

Although the Freundlich model (Table 1) is based on empirical concepts, the parameters of the equation, k_f (or K) and $1/n_f$ (or n), are relative indicators of adsorption capacity and energy of adsorption, respectively (1,5,9). The values k_f (or K) and $1/n_f$ (or n), obtained from fitting the experimental data into the logarithmic form of the equation [i.e., $\log(Q_e) = \log(k_f) + 1/n_f \log(C_e)$ or $\log(x/m) = \log(K) + n \log(C)$, Fig. 1], depend also on factors other than the concentration of the adsorbate, namely temperature, nature of the adsorbent, adsorbate, solvent characteristics, and liquid phase viscosity (5,10). The oil processing industry uses the Freundlich equation with a different nomenclature (Table 1); the relationship between the nomenclatures is shown in Table 1 and Figure 1.

Conventional adsorption bleaching. Hassler and Hagberg (11) pioneered the application of the Freundlich isotherm to describe adsorption bleaching. The work describes industrial adsorption of cottonseed oil color bodies by Fuller's earth and active carbon by measuring Lovibond units before and after adsorption. The adsorption isotherm in a log/log plot showed linear behavior that allowed comparison between the adsorbents. The authors indicated that the slope of the log/log isotherm (i.e., n or $1/n_f$) was a useful index of the adsorption efficiency of adsorbents. The steeper the slope, the greater the adsorption efficiency of the adsorbent (11). This work was important in establishing the potential of the Freundlich isotherm as a mean of evaluating adsorbents and distinguishing between them. However, the Freundlich isotherm model was developed in a single adsorbate system in which the residual adsorbate concentration was measured, whereas the Hassler and Hagberg system (11) was a multicomponent lipid system and used subjective Lovibond color measurements. Nevertheless, by assuming that oil Lovibond color is proportional to pigment concentration, the adsorption data resembled a Freundlich isotherm (11). This work indicated that, because the isotherm represents a concentration equilibrium for the adsorbate, an adsorbent in contact with a lightly colored oil will have reserve adsorptive capacity for additional pigment from darker oils. Hence, a countercurrent procedure, whereby fresh oil is first contacted with partly exhausted adsorbent that can no longer take up pigment (or other oil compounds) from partly treated oil, can still adsorb a significant amount of pigments from an unbleached oil (11). This was later used to explain the so-called "press bleaching effect," a phenomenon observed during continuous filtration of the oil–adsorbent mixture during bleaching, which results in a substantial cake build-up on the filter cake. This filter press cake acts as a fixed-bed adsorption column, and if the adsorbent has additional adsorption capacity, additional pigment binding by the adsorbent occurs during filtration of the oil (7,12).

In 1946, Hinners *et al.* (13) used different bleaching earths to bleach soybean oil and showed that the adsorptive capacity of the adsorbents cannot be adequately evaluated by measuring Lovibond color. The color of oils is mostly the result of a mixture of different pigments, and Lovibond color is unable to provide a satisfactory oil color match that directly represents the concentration of each particular pigment. Furthermore, the ratio of various pigments changes after bleaching as a function of adsorbent concentration and type of adsorbent. Thus, Lovibond measurements are insufficient to explain differences in pigment adsorptive capacity among adsorbents (13). In general, the technique of color measurement to evaluate bleaching efficiency must represent the relative proportion of each color to the overall color of the oil. Additionally, color intensity must be proportional to pigment concentration (13). In fact, the authors used spectrophotometry to determine chlorophyll to evaluate the adsorption capacity of different bleaching earths by means of the Freundlich isotherm (13). The isotherm equations obtained for the different bleaching earths indicated that the slope n was the same, suggesting that the nature of the adsorption sites was probably similar (Fig. 2). Analysis of the equations and the respective log/log plots indicated that constant K in the Freundlich equation was directly proportional to the bleaching capacity of the earth for chlorophyll (Fig. 2). In general, a large K value for an adsorbent is always desirable because it indicates the ability to bleach oils to a low residual pigment concentration. Thus, according to Hinners *et al.* (13), K is the number of color units that each gram of earth would hold if the oil was reduced to one color unit. A large n value is also beneficial because it indicates the ability to efficiently bind pigment from highly colored oils (e.g., n indicates the interval over which the adsorbent is most effective for color reduction). However, a high n value should not be at the expense of K. Within this framework, the Freundlich equation and its constants allowed the prediction of the earth doses and earth types necessary to produce an oil of a desired color (13).

Stout *et al.* (14), in 1949, used the log/log plot technique to survey a large number of clays and silicates to estimate their relative effectiveness to decolorize cottonseed and soy oils. King and Wharton (15) noted that reactions other than adsorption may be occurring during industrial adsorption bleaching, which may affect pigment binding. Atmospheric adsorption bleaching produced Freundlich log/log plots with K and n lower than that obtained with the same adsorbent in vacuum bleaching. They proposed that, in atmospheric bleaching, oil oxidation catalyzed by the adsorbent was responsible for darkening the oil and affected the Freundlich constants. As with previous studies (11), subjective Lovibond values were used as units of pigment concentration, and the study could not distinguish between natural oil pigments and pigments produced by oxidation during bleaching.

Gutfinger and Letan (16), in 1978, used Freundlich log/log plots to measure PL and pigment binding by adsorbent clays from phosphoric acid-degummed soybean oil. PL concentration was measured at the level of µg/g of oil with a specific technique, but pigment was reported as Lovibond color. PL binding by Tonsil adsorbents and Fuller's earth conformed to a Freundlich isotherm. However, for pigment binding, as evaluated by Lovibond color, only the Tonsil adsorbent fol-

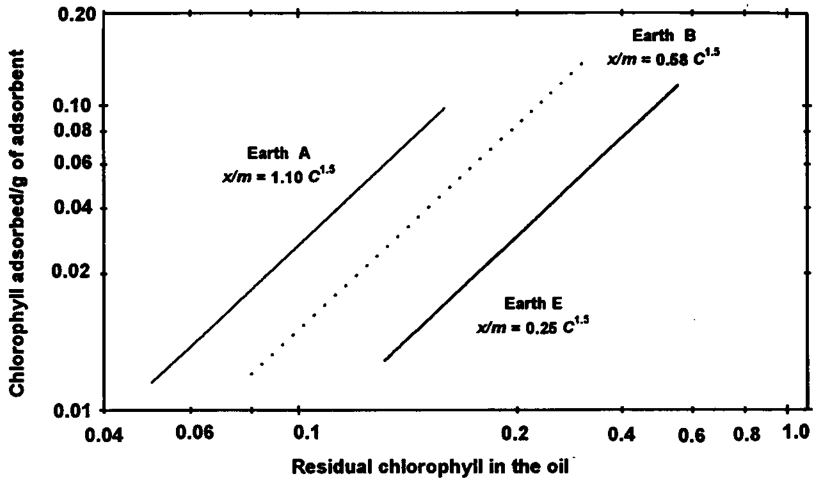

FIG. 2. Chlorophyll adsorption isotherms obtained by bleaching soybean oil (30 min at 110°C *in vacuo*) with different commercial bleaching earths (A, B, and E) at adsorbent concentrations from 1.0 to 6.0%. The Freundlich equations that fit the experimental data are shown for each particular earth by using the format $x/m = KC^n$. From Hinners *et al.* (Ref. 13).

lowed the Freundlich isotherm. This was explained as being due to an increase in oil color due to oxidation by Fuller's earth, as previously mentioned by King and Wharton (15). Unfortunately, the data were fitted to the logarithmic form of the Freundlich equation with only three experimental data points. With such a small number of data points in a narrow experimental interval, a high correlation coefficient might be obtained by random chance alone. In this work, the Freundlich isotherm was used for its mathematical simplicity and significance of its empirical constants. Nevertheless, there was little attempt to understand why the Freundlich equation was effective in describing adsorption in a multicomponent oil system, which is prone to oxidation and catalysis. These are very different conditions from those described in Freundlich's original work with a single stable solute. The significance of oil adsorption studies was to show the empirical value of the Freundlich isotherm and to allow comparisons between bleaching clays and other potential adsorbents used for commercial oil bleaching. More recent studies have used the Freundlich isotherm to evaluate bleaching of novel oils (17), evaluate adsorbents and the effect of temperature on the isotherm to increase maximum adsorption (17,18).

Dilute miscella processing. Miscella vegetable oil refining has been successful in industrial operations for over 35 years. The main advantages of continuous miscella refining, compared with continuous conventional refining of vegetable oils, are the lower refining losses; the possibility of dewaxing, winterizing and hydrogenating in continuous operation right after miscella refining; and the lower degree of oil oxidation, color fixation, and flavor reversion in the refined oil because miscella refining is performed right after the extraction process (19). Particularly, oil miscella (i.e., mixtures of oil and organic solvent) bleaching is used to avoid the use of high temperature to reduce oil viscosity (20–22), thus favoring film and intraparticle transportation of the adsorbate to the interior surface of porous adsorbent where adsorption takes place. Thus, effective bleaching is possible at lower temperatures and avoids oxidation problems experienced at high temperatures, such as the production of new pigments.

Feuge and Janssen (20), in 1951, studied the reduction in Lovibond red values in cottonseed oil in hexane solution by adsorption with a commercial-grade activated clay. In general, the color of refined oil was reduced more by miscella oil bleaching (i.e., 30% oil miscella concentration at 25°C) than by conventional adsorption (i.e., oil bleaching at 25 or 110°C), independent of the clay dosage utilized (0.5–8.0%). The authors also showed that bleaching efficiency decreased linearly when the concentration of oil in the miscella increased from 10 to 100%. In this work, the Freundlich equation was used to compare the different adsorption procedures; thus, bleaching oil with activated clay at 25°C, with and without hexane, produced similar n values (5.10 and 4.55, respectively), but processing in hexane solution furnished a greater K value (0.002 and 0.0006, respectively). These results indicated that the presence of solvent did not significantly change the mechanism of adsorption (i.e., similar n value) but did significantly increase maximum pigment adsorption by approximately 3.3 times (i.e., ratio between the respective K values). Under conventional bleaching conditions at 110°C, a larger K value (0.07) was obtained, showing a greater decolorizing power in contrast with miscella bleaching; nevertheless, a significant lower n value (2.39) was achieved, which indicated that miscella bleaching was more effective in removing the first portion of color than conventional bleaching. On the basis of these results, the authors proposed a countercurrent bleaching procedure with 30% oil miscellas (20).

Proctor and Snyder, in 1987 (23), used miscella refining to investigate the nature of the Freundlich isotherm and how it could be used to better understand the theoretical aspects of pigment adsorption from vegetable oils. The introduction of polar species into the soy oil/hexane miscella (e.g., isopropanol) and water deactivation of the silicic acid adsorbent reduced the maximum amount of pigment binding. They proposed that lutein, the major soy oil carotenoid, did not occupy all available adsorption sites because the pigment was competing for adsorption sites with isopropanol or with oil components that were present in larger concentrations than lutein (i.e., triglycerides). This hypothesis was further tested in adsorption studies with lutein-rich low-triglyceride mixtures in hexane, prepared from crude soybean oil. In this case, the majority of the pigment was bound, to produce a straight-line isotherm close to the vertical axis (Fig. 3). Pure lutein in hexane was totally bound by silicic acid; therefore, triglyceride and other substances in the miscella limited pigment binding. Competitive adsorption was proposed as an important factor in controlling the Freundlich isotherm in miscellas, and it probably plays an important role in oil systems (23).

Earlier, in 1985, Brown and Snyder (2) showed that PL was adsorbed from a soy oil/hexane miscella according to a Freundlich isotherm. Because the Freundlich isotherm is a reversible process, the reversibility of PL was examined by incubating silicic acid with two soy oil/hexane miscellas, the second miscella with a lower PL concentration than the first. However, the second incubation resulted in additional binding of PL, and not PL desorption as would be expected if the adsorption was irreversible. PL is a polar/ionic lipid molecule which could be an important competitor of soy oil pigment for adsorption sites. "Irreversible" adsorption may be caused by the polar/ionic PL being thermodynamically more stable as a bound complex than in nonpolar solution; the ionic portion of the molecule may be involved at the adsorption site (24). Hence, in addition to thermodynamics, chemical equilibria of the molecular species involved may affect the nature of the isotherm in a soy oil/hexane system. In this system, maximum PL adsorption was enhanced by addition of a polar solvent (i.e., isopropanol) to the soy oil/hexane miscella. Later research showed that the enhanced PL adsorption could be due to disruption of PL miscellas by isopropanol, enabling individual PL molecules to adsorb more freely (25). This is in contrast to the reduction in lutein binding from soybean oil by the same polar solvent. However, the incomplete adsorption of PL has been associated with competition of triglycerides for adsorption sites (25), as was also proposed for soy oil pigments (18). Although triglyceride is not so polar as PL, it is present in vastly greater concentration, which in turn results in a higher thermodynamic drive for adsorption. Similar findings have been reported for rice hull ash in adsorbing soy oil pigment (4,26) and PL (27) from soy oil hexane miscellas.

Chapman and Pfannkoch (28) used single-component isotherms and the ideal dilute solution theory (IDST) to study the co-adsorption of protoporphyrin IX dimethyl ester, fatty acids (i.e., stearic and linolenic acid), and triglycerides (i.e., tripalmitin and trilinolein) on acid-activated bleaching clay with dichloromethane as solvent. IDST predicts two-solute adsorption from single-solute adsorption data, providing that the solutions are diluted (29). The experimental relative affinities to bleaching clay from single-component isotherms were: protoporphyrin >> fatty acids and triglycerides. The isotherms for binary mixtures of low protoporphyrin concentrations with higher concentrations of triglycerides or fatty acids were calculated from single-component isotherm data by using IDST. The resulting isotherm showed dramatically the ability of the lipids to suppress protoporphyrin adsorption. This investigation pointed out the importance of competitive adsorption in determining the performance of adsorbents in oil bleaching.

Concentrated miscella processing. Investigations based on the Freundlich isotherm equation have been performed mostly with dilute miscellas of vegetable oils (i.e., <40% of oil in solvent) and short contact times (i.e., <20 min) while

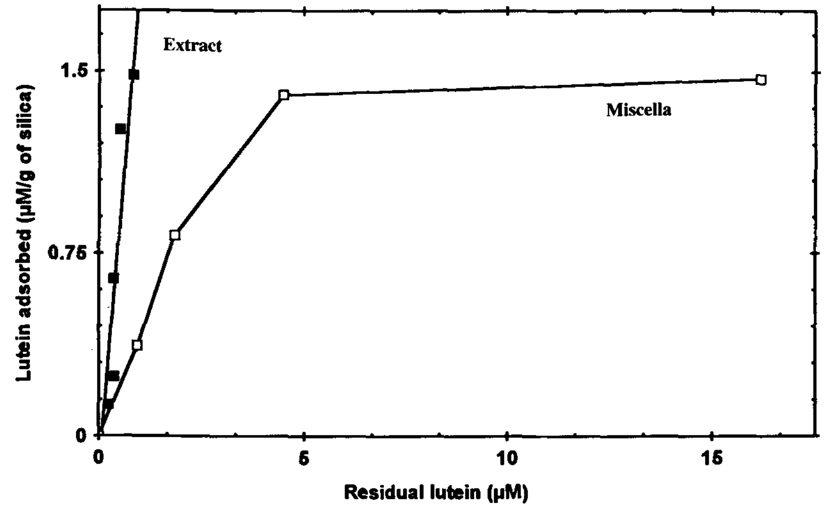

FIG. 3. Adsorption of lutein from a miscella of soybean oil in hexane (Miscella) and an extract of lutein-rich low-triglyceride mixture in hexane prepared from crude soybean oil (Extract). From Proctor and Snyder (Ref. 23).

assuming thermodynamic adsorption equilibrium. However, in miscella oil refining, the functional oil concentration utilized is within 40 to 80% (19). At such miscella oil concentrations, additional kinetic and diffusion factors (i.e., oil oxidation and viscosity) might limit the achievement of a real thermodynamic adsorption equilibrium (21,22). Furthermore, oil miscellas are mixtures of compounds with a great diversity in physicochemical properties, chemical reactivity, molecular structure, and concentrations. In consequence, each organic component has a different degree of adsorption on the adsorbent. Thus, the adsorption process during miscella oil bleaching/refining must be considered as an adsorption process of mixtures of organic compounds, i.e., a multicomponent adsorption system. Consequently, the adsorption profile of a given oil component depends on the level of adsorption of other components and their adsorption mechanisms, which are both affected by the respective concentrations of the different oil components in solution as well as on the adsorbent. Through infrared spectroscopy Adhikari *et al.* (24) have shown that isopropanol, a potential oil solvent for industrial use, reduced free oleic acid adsorption (i.e., free fatty acids) on silicic acid. This effect was explained by a combination of competitive adsorption of isopropanol, as well as an interaction between isopropanol and oleic acid in solution. Toro-Vazquez and Rocha-Uribe (21) demonstrated the complex nature of interactions among different oil components in determining the adsorption isotherm behavior. The authors used a split-plot experimental design to evaluate the effect of oil miscella concentration (60–100% oil in hexane) and the presence of different levels of ethanol (0, 5, and 25%) on vegetable carbon adsorption at 50°C of peroxides, unsaturated carbonyls, free fatty acids, and carotenoids from sesame oil miscellas. In general, adsorption was promoted as solvent concentration increased in the miscella (i.e., lower viscosity), and a prooxidant effect of ethanol was observed. Furthermore, Toro-Vazquez and Mendez-Montealvo (22), by using multiple regression analysis, studied competitive adsorption on vegetable carbon among free fatty acids, carotenoids, and unsaturated carbonyls. This study utilized different sesame oil batches at oil miscella concentrations normally found in industrial miscella refining (40 and 60%). The adsorption isotherms suggested that unsaturated carbonyls promoted free fatty acids adsorption, mainly in the pores that were readily accessible for fatty acids. However, in the presence of high concentrations of carbonyls, the less accessible adsorbent pores were occupied by carbonyls and fatty acid adsorption decreased. It was concluded that highly oxidized oils would decrease the adsorption efficiency for fatty acids due to the competing effect of carbonyls (22). In contrast, carotenoid adsorption was substantially reduced by free fatty acids. This is in agreement with the results of protoporphyrin IX and fatty acid competitive adsorption studies obtained by Chapman and Pfannkoch (28). The Freundlich isotherm failed to fit the experimental data. However, in the mathematical expression of the Freundlich isotherm, the effect of component interactions on adsorption efficiency is not considered.

When two or more adsorbable components can occupy the same adsorption sites, the interpretation of adsorption isotherms becomes complex (9,22). Equations that deal with the isotherm adsorption of a mixture of compounds have been shown by Suzuki (9). Some of these isotherms are mathematical extensions of the Freundlich and Langmuir equations with relatively large numbers of empirical parameters and a lack of thermodynamic background (9). To the authors' knowledge, these equations have not been used in oil bleaching studies.

The Freundlich isotherm was originally presented to explain the adsorption of a single solute from solution. However, a similar adsorption pattern has been observed when studying the much more complex system of adsorption of vegetable oil pigments onto bleaching clay during commercial bleaching of vegetable oils. The Freundlich isotherm has been useful to compare the commercial value of adsorbents as long as a narrow experimental interval of adsorbate is utilized. More recent studies have shown that a complex series of interactions controls the adsorption process; and while the isotherm summarizes this process, investigating these interactions is vital to better understand the physicochemical factors involved during adsorption. Approaches that are proving effective are statistical modeling and experimental design to evaluate vegetable oil bleaching/refining as a multiple-component adsorption system (21,22). Furthermore, the use of physical chemical techniques to elucidate the nature of the solute–adsorbent complex and solute–solvent interactions has provided the basis to understand the interactions that contribute to adsorption (24,30,31). These techniques will support the development of new isotherm models that are applicable to oil bleaching/refining. However, isotherm studies based on the Freundlich model will continue to have value in summarizing the main factors that control adsorption of vegetable oil in conventional and miscella systems.

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