Competitive Adsorption Among Sesame Oil Components in a Concentrated Miscella System

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ABSTRACT: Competitive adsorption of free fatty acids and carotenoids adsorption from sesame oil miscellas on vegetable carbon was studied by regression analysis. The equations obtained indicated that unsaturated carbonyls, free fatty acids (FFA_0), and carotenoids interacted to determine fatty acid and carotenoid adsorption. The driving force for carotenoid adsorption, the carotenoid concentration (C_0), was affected by a quadratic function of free fatty acid concentration [i.e., $(FFA_0/C_0)^2$]. As FFA_0/C_0 increased, carotenoid adsorption efficiency was reduced, possibly because the accessible adsorption sites for carotenoids were occupied by fatty acids. Unsaturated carbonyls promoted free fatty acid adsorption, probably in the pores that were readily accessible for fatty acids. However, when the carbonyl concentration increased in the oil miscella, carbonyls were adsorbed instead of fatty acids. The results indicated how different oil molecules interact and affect adsorption (i.e., free fatty acids and carotenoids). Therefore, the adsorption process of vegetable oils (i.e., bleaching) has to be considered a multicomponent adsorption system.

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Free fatty acids, carotenoids, phospholipids, carbonyl compounds, and peroxides are removed from crude oil to produce a refined oil with desirable organoleptic characteristics and acceptable shelf life. The longer these compounds remain in the oil, the greater their negative effect on oil quality and the lower the efficiency of their removal during oil refining. Therefore, it is desirable to refine the oil on extraction for optimum efficiency and oil yield. Continuous miscella refining is the best option to attain these goals because oil refining is performed immediately after the extraction process. The main advantages of continuous miscella vegetable oil refining, compared to continuous conventional refining, are the lower refining losses, the possibility of dewaxing, winterizing, and hydrogenation on continuous operation after miscella refining, and the lower degree of oil oxidation, color fixation, and flavor reversion in the refined oil (1).

Conventional and miscella oil refining are achieved through physical and chemical processing. The two methods differ in the process of free fatty acid elimination (i.e., steam refining vs. alkali refining); nevertheless, the adsorption bleaching process is common to both procedures. Although adsorption bleaching was designed for pigment removal during vegetable oil refining, this process involves a combination of catalytic (i.e., peroxide production and decomposition) and adsorption events (i.e., chlorophyll, carotenoid, and free fatty acid adsorption) (2–4). Thus, bleaching is more than removing colored compounds and is an important step in edible oil processing (3–12).

Most studies on the adsorption of oil components have been performed with dilute miscellas (i.e., <40% oil in the solvent) with reports of Freundlich-type isotherms (9–12). Under these conditions, oxidation and viscosity effects on adsorption equilibrium are negligible. However, in the modern practice of miscella oil refining, the concentrations are 40–80% oil (1). At these concentrations, kinetic and diffusional factors (i.e., oil oxidation and viscosity) may limit the achievement of thermodynamic adsorption equilibrium. Chatzopoulos *et al.* (13) showed that, even under vigorous stirring, the rate of adsorption is significantly affected by the mass transfer resistance of the fluid (i.e., viscosity). Additionally, research in our laboratory with concentrated sesame oil miscellas (i.e., >40% of oil in the solvent) in a batch adsorption system with carbon as adsorbent showed that, at miscella concentrations of greater than 60%, the adsorbent catalytic effect and the miscella viscosity significantly affect adsorption of oil components. Thus, the isotherm models of Langmuir, BET, and Freundlich did not appropriately fit the adsorption data for free fatty acids, unsaturated carbonyls, carotenoids, and peroxides (3). Under these circumstances, the adsorption (adsorbate bound per mass of adsorbent, Q) at a given miscella oil concentration was described by the linear regression of Q on the respective initial adsorbate concentration in the miscella. Although some of the results suggested competitive adsorption among oil components, competitive adsorption was not properly addressed in that work.

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Most of the research performed in the area of competing adsorption of oil components has utilized the approach of either (i) adding a compound to the oil with potential to compete with an oil component for adsorption sites on the adsorbent, or (ii) addition of compounds to the adsorbent to occupy the adsorption sites on the adsorbent before adsorption (9,12). The effect of the "competing" compounds on the adsorption efficiency of a particular oil component is measured by comparison with the respective adsorption efficiency achieved in a control experiment without added competitors. Although these methodologies provide valuable information, they do not measure competition between the natural oil compounds that actually determine adsorption efficiency.

The objective of this paper was to develop equations that describe the competitive adsorption among the oil components in unrefined sesame oil that determine the adsorption efficiency of free fatty acids and carotenoids. The adsorption system utilized was miscella with oil concentrations similar to those used in miscella oil refining (i.e., 40% and 60%). Under such conditions, the miscella viscosity might affect the adsorption efficiency. Therefore, the viscosity of different oil miscella concentrations was measured. Additional adsorption conditions were 50°C, 5% of vegetable carbon as adsorbent, and 100 min of time. Adsorption studies at 50°C with sesame oil and other vegetable oils indicated that most of the oil components achieved equilibrium after 60–90 min (3); additionally, carbon concentrations above 2.5% are needed to limit oil oxidation while favoring peroxide decomposition and carbonyl adsorption during the bleaching process (2,3).

EXPERIMENTAL PROCEDURES

Materials. Eight batches of unrefined sesame oil were obtained (Aceitera San Juan, Salvatierra, Gto., Mexico). The oils represented common batches derived from sesame oil extraction with 4 d of storage and long-term storage periods of up to 4 mon. Free fatty acid (14), peroxide (14), unsaturated carbonyl (15), and carotenoid (16) analyses of the oils were made for each batch in duplicate.

Fresh and stored sesame oil batches were blended in various proportions (50:50, 60:40, 70:30, 75:25, 80:20, 90:10, w/w) to obtain a wide range of oxidation product, free fatty acid, and carotenoid concentrations. The oils were stored in the dark under nitrogen at 4°C.

The adsorbent was vegetable carbon (Carbones Mexicanos S.A., Guadalajara, Jal., Mexico). The same lot of adsorbent was utilized in all experiments after been sieved (U.S. standard, −14 ± 24), washed (mixed for 24 h in 2 vol of deionized water), filtered, and dried (100°C for 24 h).

Adsorption system. Each oil blend was randomly chosen and diluted with *n*-hexane at either 40% or 60% (w/w). After thoroughly mixing, the miscella was analyzed in duplicate for free fatty acids (FFA_0, mg of oleic acid/g of miscella), peroxides (P_0, μEq/g of miscella), carotenoids (C_0, μg/g of miscella), and unsaturated carbonyls (UC_0, μmoles/g of miscella).

The adsorption experiments were carried out in a closed-system mixer, described previously (3). The miscella (380 g) was weighed, and the mixing system was assembled to gently stir the miscella until it reached a temperature of 50°C (about 5–10 min). Twenty grams of adsorbent (5% w/w) was added directly to the miscella without stopping the mixing, and the mixing speed was increased to just below the vortex formation speed. After 100 min of constant agitation, an aliquot of the mixture (approx. 30 g) was weighed in a polycarbonate centrifuge tube, and 10% (w/w) of an aqueous solution of 10% (w/w) sodium pyrophosphate was added to precipitate the carbon (17). The mixture was gently mixed and then centrifuged (5000 rpm/15 min). After centrifugation, the miscellar phase was analyzed, and the adsorbed amount per mass of carbon was calculated for carotenoids (Q_c, μg/g of adsorbent) and free fatty acids (Q_{FFA}, mg of oleic acid/g of adsorbent). Due to the addition of sodium pyrophosphate and solvent evaporation during centrifugation, appropriate gravimetric considerations were made in the calculations.

Viscosity measurements. The apparent viscosities (in centipoises) of miscellas with different oil concentrations (i.e., 40–100%) were determined at 30°C with a Brookfield DV-II viscosimeter (Brookfield Co., Stoughton, MA) at 6 and 12 rpm with spindle 1 of the LV type. A 600-mL beaker with 400 mL of miscella was used in all determinations. Temperature control was achieved with a water bath.

Statistical analysis. This was basically an observational experiment in which the only controlled variable was oil concentration in the miscella (i.e., 40% or 60%), thus the chemical characteristics of the oils were considered random variables. Nevertheless, for the same oil, the component ratios (i.e., FFA_0/C_0, FFA_0/UC_0, FFA_0/P_0, etc.) were statistically identical and independent of oil miscella concentration (e.g., 40% or 60%). Accordingly, the oil miscellas were characterized through quantitative variables, associated with their particular component ratios and the initial adsorbate concentration (i.e., FFA_0, C_0, UC_0, P_0). Thus, the statistical analysis considered the miscellas obtained from each oil as independent experimental units. Therefore, no true replication existed.

Multiple regression analysis was used to develop equations that describe the Q_{FFA} and Q_c variability among the different oil miscellas investigated. The regression analyses utilize FFA_0, C_0, UC_0, P_0, as explanatory (i.e., independent) variables, their quadratic effects, their linear and quadratic interactions, as well as the linear and quadratic effects of the respective component ratios. The variable selection for the multiple regression modeling was performed with the "forward" methodology available in the multiple regressional procedures in the STATISTICA program (StatSoft, Tulsa, OK) (18). The "no intercept" option was utilized; that is, the models developed satisfied the assumption that, at zero initial adsorbate concentration, no adsorption was achieved. The criteria utilized for model selection were the residual analysis (e.g., outliers and normal distribution), the magnitude of the determination coefficient ($R^2 > 0.85$), as well as the magnitude of the "tolerances" (TOL) for the estimated ß-regression coefficients of the explanatory variables in the equation (2,18,19).

RESULTS AND DISCUSSION

Figure 1 shows that miscellas at oil concentrations used in miscella refining (i.e, 40–80%) (1) had significantly lower viscosities than crude oil. Viscosity was inversely proportional to oil concentration, reaching a plateau below 60% of oil in the miscella (Fig. 1). Similar results have been reported (3). Miscella viscosities were determined at 30°C because some solvent evaporation occurred at 50°C. Although the magnitude of the miscella viscosities would be lower at 50°C than at 30°C, a relatively similar viscosity profile would be obtained. The lower viscosity of oil miscellas in contrast with crude oil seems to be associated with the higher adsorption efficiency of oil components achieved when miscellas instead of oil are used in adsorption systems (3).

All adsorption data were expressed according to common isotherm models (i.e., Langmuir, BET, Freundlich). However, appropriate fits were not obtained. Figure 2 shows the Freundlich isotherms for free fatty acids and carotenoids that included all adsorption data. No improvement in isotherm fitness was achieved when a separated analysis of the adsorption data for the 40% and 60% oil miscella concentration was performed. No significant differences in viscosity were observed between the 40% (4.51 cps at 12 rpm) and 60% (5.51 cps at 12 rpm) miscellas (Fig. 1). Therefore, the lack of fitness of Q_{FFA} and Q_C with the isotherm models utilized could not be attributed to differences in mass-transfer resistance among the oil miscellas. Although the addition of 10% sodium pyrophosphate (pH = 9.66) to separate the carbon from the miscella extracted a small amount of free fatty acids in the aqueous phase, its effect on the magnitude of Q_{FFA} was negligible (<1.0 mg of oleic acid/g of carbon).

In the dilution method for isotherm determination, a given batch of oil is diluted with solvent to different levels, and the same amount of adsorbent is added to each dilution. This methodology provides different initial adsorbate concentrations without affecting the original ratio among the oil components (i.e., an adsorption isotherm is obtained for a given batch of oil). In this investigation, the hexane dilution of a given oil provided two miscellas with different initial adsorbate concentrations but with the same ratio of oil components (data not shown). Within the wide interval of FFA_0 and C_0 achieved with all the oil miscella systems developed (Fig. 2), just one isotherm should fit Q, unless the effect of the driving force for adsorption (e.g., the gradient concentration of the adsorbate between the fluid phase and the adsorbent surface) was different among the oils investigated. Some of the factors that might affect the magnitude of the driven force for free fatty acid or carotenoid adsorption include interactions of the adsorbent surface with other lipids, as well as interaction of free fatty acids or carotenoids with other oil components in the liquid phase and on the adsorbent surface. In the Langmuir, BET, and Freundlich isotherm models, the effect of component interactions on adsorption is not considered.

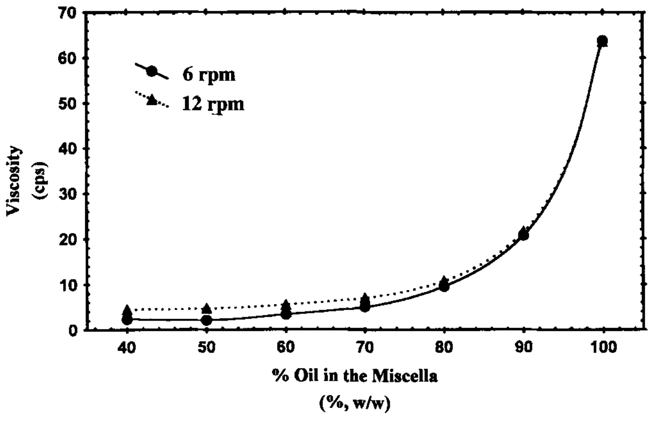

FIG. 1. Viscosity profile, at 6 and 12 rpm, of sesame oil miscellas in *n*-hexane.

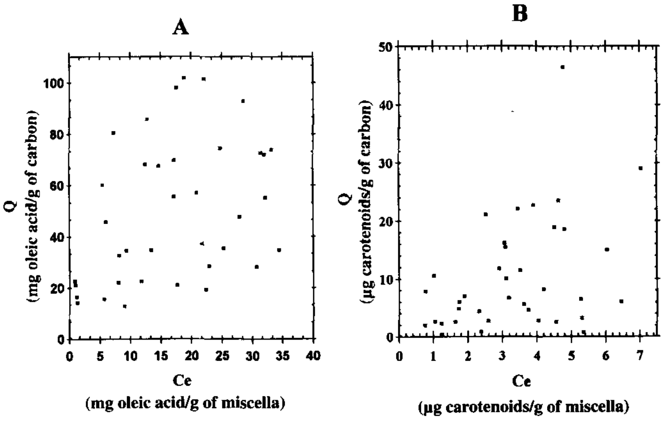

FIG. 2. Freundlich isotherms for free fatty acids (A) and carotenoids (B). The Q values represent the respective adsorbed amount after 100 min of adsorption with 5% vegetable carbon at 50°C. Ce is the concentration of adsorbate remaining in the miscella after adsorption.

The multiple regression analysis allowed us to evaluate the effect of the initial adsorbate concentrations (i.e., the driving force for adsorption) at different native component ratios (i.e., different batches of sesame oil) on the magnitude of Q_{FFA} and Q_C. The best isotherm model obtained for Q_{FFA} ($R^2 = 0.90$) was the following:

$$Q_{FFA} = 2.143(FFA_0) + 30.226(UC_0) - 16.669(UC_0)^2 + 0.996(FFA_0)(UC_0) - 0.035(FFA_0)^2 \quad [1]$$

The standard error of the estimates obtained through this equation was 14.41 mg of oleic acid/g of carbon (n = 68). In the same way, the best model for Q_C ($R^2 = 0.86$) was:

$$Q_C = 4.589(C_0) - 0.014(FFA_0)^2 + 0.012(FFA_0/C_0)^2 \quad [2]$$

The corresponding standard error of the estimate calculated with this equation was 3.77 μg of carotenoid/g of carbon ($n = 66$).

None of the variables that included peroxide concentration showed a significant effect on Q_{FFA} or Q_C. However, the magnitude of the determination coefficients (R^2) indicated that additional variables should be considered in the equations to improve their predictive power. Nevertheless, these were the equations with the highest values of R^2 and the highest independence among the explanatory variables (i.e., the variables included in the equation were not redundant). Moreover, all the equation coefficients (e.g., ß regression coefficients) were significant ($P < 0.06$). Other important sesame oil components, such as sterols, tocopherols and lignans, might be involved in determining the extent of free fatty acid and carotenoid adsorption. However, their effect was not evaluated in this investigation.

The equation for Q_{FFA} indicated that free fatty acid adsorption was mainly affected by the concentration of unsaturated carbonyls (i.e., FFA_0/UC_0). Likewise, the equation for Q_C indicated that the driving force for carotenoid adsorption was affected by a quadratic function of free fatty acid concentration [i.e., $(FFA_0/C_0)^2$]. These equations were utilized to estimate Q_{FFA} and Q_C values at different FFA_0/UC_0 and FFA_0/C_0 ratios, respectively. As already mentioned, these ratios remained constant for the same oil, regardless of the oil dilution. Therefore, from the practical point of view, different FFA_0/UC_0 and FFA_0/C_0 ratios actually represented different concentrated sesame oil miscellas to be utilized in miscella refining. Thus, Figures 3 and 4 show the adsorption isotherms that define Q_{FFA} and Q_C behavior in oil miscellas that have the same magnitude of FFA_0/UC_0 and FFA_0/C_0. The magnitudes of initial concentration of free fatty acids, unsaturated carbonyls, and carotenoids that were used in the determination of Q_{FFA} and Q_C values (Figs. 3 and 4) were within the interval of experimental values observed in the oil miscellas.

Based on the variables included in the equations, the unsaturated carbonyls in solution affected free fatty acid adsorption. Likewise, free fatty acids in solution affected carotenoid adsorption; however, the concentration of carotenoids in the miscella did not show a significant effect on fatty acid adsorption. Although typical free fatty acid adsorption isotherms were obtained at all values of FFA_0/UC_0 (Fig. 3), a particular increase in free fatty acid adsorption was observed at each of the FFA_0/UC_0 ratios. A greater free fatty acid adsorption was observed when the oil miscella showed an increased concentration of unsaturated carbonyls (e.g., $FFA_0/UC_0 = 66.22$ vs. 27.94). However, this effect was less pronounced as the FFA_0/UC_0 ratio decreased to values below 27.94. In fact, an antagonist effect of unsaturated carbonyls on free fatty acid adsorption was observed at $FFA_0/UC_0 = 12.23$ and even more pronounced at $FFA_0/UC_0 = 5.95$ (Fig. 3). The behavior of the adsorption isotherms suggested that unsaturated carbonyls promoted free fatty acid adsorption, mainly in the pores that were readily accessible for fatty acids. However, when the carbonyl concentration increased in the oil miscella, the less accessible adsorbent pores were occupied by carbonyls instead of fatty acids. Actually, some free fatty acid desorption was observed at the highest carbonyl levels in the oil miscella. Thus, highly oxidized oils would show a decreased adsorption efficiency for fatty acids due to the competing effect of carbonyls.

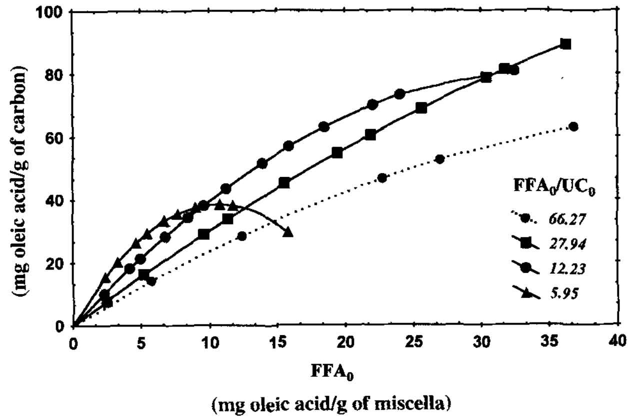

FIG. 3. Free fatty acid adsorption isotherms (Q) as a function of different FFA_0/UC_0 ratios. The Q values were calculated with the respective equation for free fatty acids. The carbonyl concentrations utilized were within 0.087 and 2.65 μM/g of miscella.

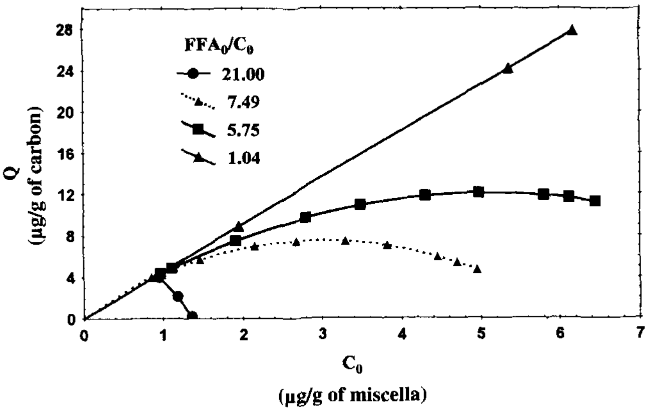

FIG. 4. Carotenoid adsorption isotherms (Q) as a function of different FFA_0/C_0 ratios. The Q values were calculated with the respective equation for carotenoids. The free fatty acid concentrations were within 2.03 and 37.08 mg of oleic acid/g of miscella.

In a similar adsorption system, ethanol decreased the adsorption efficiency for free fatty acid (3). Likewise, Adhikari *et al.* (20) showed that isopropanol and oleic acid interact through hydrogen bonding; they observed that the extent of oleic acid adsorption on silica was affected by its interaction with isopropanol in solution and the amount of isopropanol adsorbed. Although alcohols and carbonyls present different functional groups, these results indicate how different molecules interact in complex systems, affecting the particular absorbability of the adsorbate of interest (i.e., free fatty acid). As Suzuki has pointed out (21), when two or more adsorbable components can occupy the same adsorption sites, the interpretation of adsorption isotherms becomes complex.

Figure 4 shows the inhibition of free fatty acids on carotenoid adsorption. As the FFA_0/C_0 increased in the oil miscella, carotenoid adsorption efficiency was reduced. Although chemical structures such as carotenoids have a high affinity to carbon-type adsorbents (22), Q_C was substantially reduced by free fatty acids, even producing carotenoid desorption at high fatty acid concentration (Fig. 4). Similar results for protoporphyrin IX and fatty acid adsorption competing on acid-activated clay have been reported (23). These results pointed out the need to limit oil lipolysis, refining vegetable oils as soon as they are extracted, and to avoid tissue damage prior to oil extraction. These events significantly increase free fatty acid concentration in vegetable oils (24). The fact that carotenoids did not show a significant effect on Q_{FFA} confirms previous results that indicated that carotenoids do not compete for adsorption sites with fatty acid molecules (3). It has been suggested that, in oil miscella systems, carotenoids are in a colloidal state (25,26), thus needing pore diameters in the 50–100 Å region to be adsorbed.

In similar previous studies, within a narrow interval of FFA_0 and C_0, a significant linear regression of Q_{FFA} and Q_C on the respective initial adsorbate concentration in the miscella was found (3). The positive slope of this regression (i.e., K_p) was different for fatty acids and carotenoids, and its magnitude was associated to the relative sensitivity of Q to the initial adsorbate concentration in the miscella. In this study, a wider interval of FFA_0 and C_0 was used, and oil component interactions were considered in the development of the isotherm model. Nevertheless, the meaning of K_p did not change. Its magnitude was obtained from the coefficients associated to the FFA_0 and C_0 variables in the respective equations. Thus, after considering the effect of component interactions on adsorption, free fatty acids ($K_p = 2.143$) showed an affinity for carbon more independent of their initial concentration than carotenoids ($K_p = 4.589$). Additionally, unsaturated carbonyls indirectly affect carotenoid adsorption through their effect on fatty acid adsorption. Basically, as the concentration of FFA_0 increased in the miscella, a higher fatty acid adsorption was achieved (Fig. 3), and, as a result, carotenoid adsorption decreased (Fig. 4). However, in oxidized oils, the increase in fatty acid adsorption was higher because of the synergistic effect of carbonyls on fatty acid adsorption (Fig. 3), probably on the adsorption sites accessible to carotenoids. In conclusion, oxidized oil miscellas would have a low bleaching efficiency. In contrast, good-quality oil miscellas would achieve both excellent bleaching efficiency and good free fatty acid removal during the adsorption process.

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