Evaluation of Soy Oil Lutein Isotherms Obtained with Selected Adsorbents in Hexane Miscellas

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Bleaching of soy oil hexane/miscellas by adsorption of the lutein was examined. Quantitative differences in the adsorption behavior between a bleaching clay, alkaline rice hull ash and acid rice hull ash were measured by comparing the constants, K and n, of Freundlich isotherms. All the isotherms were dose-dependent with K being inversely related and n directly related, to adsorbent mass. Overall, the bleaching clay performed better than the ashes. Alkaline ash had a larger K value than acid ash, but the n value of acid ash was greater.

Equations of lutein adsorption were derived based on initial concentrations on lutein and the amount adsorbed per gram. Logarithmic plots produced constants, K^i and n^i, which were the intercept and slope, respectively. As adsorbent dose increased, K^i decreased and n^i increased for each adsorbent studied. These findings may have applications in the processing of dilute miscellas where low temperature, low viscosity oil refining is desired.

KEY WORDS: Bleaching clay, isotherms, predictive equations, rice hull ash, soy oil.

The commercial bleaching of soy oil is important in producing a light-colored vegetable oil which is acceptable to consumers. Bleaching is achieved by adsorption of oil pigments onto bleaching clay at 100°C under reduced pressure (1). A major pigment removed from soy oil is the xanthophyll, lutein.

Hassler and Hagberg (2) showed that this type of adsorption follows the Freundlich equation. The equation can be written as $x/m = Kc^n$, where x = amount of substance adsorbed, m = amount of adsorbent, and c = amount of residual substances after adsorption. The constants K and n provide valuable information regarding the adsorption. K describes the overall ability of the adsorbent to bind a solute, whereas n indicates the solute range where the adsorbent has greatest effect. As K increases, and n is constant, the adsorption is more efficient and less adsorbent is needed. As n increases, and K is constant, the adsorbent is more efficient at adsorbing pigments initially, but is less able to bleach an oil to low residual color (1,3). The relative merits of specific bleaching clays, or other adsorbents, can be found by plotting $\log x/m$ against $\log c$. This is referred to as a Freundlich isotherm, and describes the equation $\log x/m = \log K + n \log c$. The slope of the line is n and the y-intercept is K. Stout *et al.* (3) and Armstrong and Ireland (4) used such isotherms to compare bleaching clays.

Constants K and n have been derived for the bleaching of cottonseed oil/hexane miscellas by activated clay (5). Adsorption studies with soy oil miscellas showed that lutein is adsorbed by silicic acid (6) and inorganic rice hull ash (7), according to Freundlich isotherms. Rice hull ash is a waste product from rice milling which contains a large proportion of silica, as cristobolite (8). Acidification of the ash promotes adsorption of pigments (7). An increase in adsorbent dose results in a decrease in x/m which produces a different isotherm for each adsorbent dose. However, K and n were not calculated for these systems.

The objective of this paper is to compare the Freundlich constants of rice hull ash with those of bleaching clay in miscella systems, to better understand the adsorption behavior of these materials and the adsorption process in general.

MATERIALS AND METHODS

Oil, solvents and adsorbents. Crude soybean oil (Capital City Products, Columbus, OH) obtained by commercial extraction and stored at 4°C was used in this study. Miscellas were prepared by mixing oil with hexane. Official acid-activated bleaching clay (American Oil Chemists' Society, Champaign, IL) and rice hull ash, prepared by the method of Proctor and Palaniappan (9) were used in this study. Commercially available burnt rice hull ash (Riviana Foods, Houston, TX) was heated at 500°C for 10 hr in a muffle furnace. This material was referred to as alkaline ash. Acid ash was made by mixing alkaline ash with 20% sulfuric acid and subsequently washing the ash with an excess of water (9).

Isotherms. Lutein adsorption isotherms were generated for each of the adsorbents with 0.5 g, 1.0 g and 2.0 g of material in 100 mL of 10, 20, 30, and 40% soy oil in hexane according to the method of Proctor and Snyder (6). The lutein content of each miscella was found by absorbance at 445 nm before a known weight of adsorbent was added to the miscella. The miscella was agitated with a magnetic stirrer for 15 min at 22°C in a closed vessel. The residual lutein in the miscella was measured, and the adsorbed lutein was calculated by difference. Determinations were made in triplicate. Logarithmic plots of lutein adsorbed per g of adsorbent (x/m) versus residual μmolar lutein (c) were prepared. Using the data, equations were determined and values for K and n were obtained.

Equations based on initial lutein concentrations. Logarithmic plots were also made using the initial concentration of lutein (i) and lutein adsorbed per g (x/m).

RESULTS AND DISCUSSION

The isotherms and equations describing the adsorption of lutein from soy oil miscellas onto bleaching clay are in Figure 1. Different adsorbent dose-dependent isotherms were obtained, with smaller doses adsorbing most effi-

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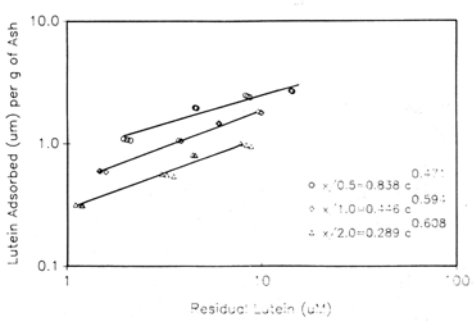

FIG. 1. Lutein isotherms were determined by incubating 100 mL of 10%, 20%, 30% and 40% crude soy oil/hexane miscella for 15 min at 22°C with variable amounts of bleaching clay. Lutein concentration was obtained by measuring absorbance at 445 nm. A Freundlich equation is presented for each adsorbent dose with K and n values.

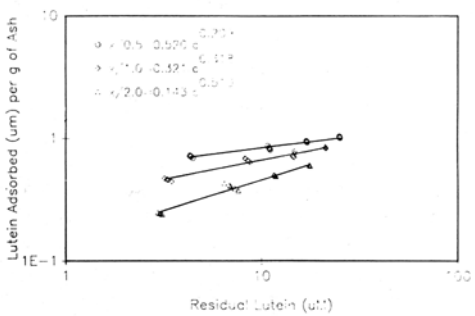

FIG. 2. Lutein isotherms were determined by incubating 100 mL of 10%, 20%, 30% and 40% crude soy oil/hexane miscella for 15 min at 22°C with variable amounts of alkaline rice hull ash. Lutein concentration was obtained by measuring absorbance at 445 nm. A Freundlich equation is presented for each adsorbent dose with K and n values.

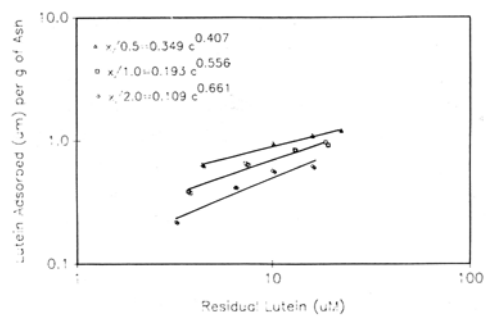

FIG. 3. Lutein isotherms were determined by incubating 100 mL of 10%, 20%, 30% and 40% crude soy oil/hexane miscella for 15 min at 22°C with variable amounts of acid rice hull ash. Lutein concentration was obtained by measuring absorbance at 445 nm. A Freundlich equation is presented for each adsorbent dose with K and n values.

ciently. This is reflected in the increase in K as the dose is decreased. In addition, n increases as the dose is increased. The data suggests that smaller doses are most efficient overall but are less able to bleach the miscella to a low residual lutein concentration. Larger amounts of adsorbent can more quickly bind pigment initially, as shown by the increasing value of n. These results would agree with the findings of the adsorption of soy lutein onto silicic acid, which occurs according to first order kinetics with respect to silicic acid (10) but smaller doses are more efficient at adsorption (6). This similarity is interesting because the mode of binding of the two adsorbents is probably different. Adsorption to bleaching clay is almost certainly irreversible chemisorption (11) whereas that of silicic acid is probably reversible H-bonding (10,11).

Freundlich plots obtained by earlier workers (3–5) used differing amounts of adsorbent as the variable. However, the approach in this paper follows that of Proctor and Snyder (6) where lutein concentration is the variable. Both methods produce linear log plots of the isotherms. However, the log plots using the earlier method produced isotherms with a steeper slope and therefore larger n and smaller K values than obtained by the method of Proctor and Snyder (6).

The greater available surface area obtained with the larger dose would explain the increase in n, but the inverse relationship of adsorbent mass with K is less obvious. An analogy between adsorption of solutes on a solid and liquid–liquid partition extraction has been suggested (Snyder, H.E., 1990 personal communication). Such an extraction is described by the equation:

$$x_n = x_o(KW/KW + L)^n$$

where x_n = the amount of solute remaining unextracted, x_o = the amount of solute originally present, K = the distribution coefficient, W = vol of original solvent, L = vol of extracting solvent and n = number of extractions. In such a system, using the same vol of extracting solvent, more solute is extracted using a number of smaller vols than with a single large vol. A similar phenomena is observed with dose-dependent isotherms. Snyder did indicate that the analogy was not totally adequate, in that K is a constant for liquid–liquid extractions but varies for adsorption on a solid.

The isotherms obtained with alkaline ash are in Figure 2. As with bleaching clay (Fig. 1), K values indicated that the bleaching efficiency is inversely proportional to the quantity of adsorbent used. Nevertheless, the n values showed that larger doses reduced the initial pigment concentration faster. Bleaching clay had larger K and n values than alkaline ash for each dose. Thus the bleaching clay was overall a better adsorbent of soy oil lutein, and decolorized the oil faster than alkaline ash. This conforms to earlier findings in which the same clay was more effective at decolorizing a 20% soy oil than the alkaline ash (7). The clay has a much smaller particle size than that of the ash (12) and would therefore have a much greater adsorptive capacity.

Isotherm data obtained with acid ash is in Figure 3. The same relationships between dose, K and n as described for clay and alkaline ash were found for acid ash. Overall bleaching efficiency, as shown by K values, was less than that of alkaline ash for any given dose. Data obtained previously (9) has shown acid ash to be the overall better adsorbent than alkaline ash. An explanation as to the conflict may be in the greater range

of the acid ash data points relative to the isotherms obtained with the other adsorbents. The points obtained with 20%, 30% and 40% miscellas are practically on the same line. The 10% miscellas points cause an increase in the slope of the curve and reduce the intercept value. However, n values of acid ash were greater than those of alkaline ash indicating this adsorbent was better at initially removing color and in bleaching miscella with a small pigment concentration. This may explain why acid ash was more effective than alkaline ash at adsorbing lutein from a 20% miscella (9).

Although K values of clay were larger than those of acid ash, n was greater for acid ash with 2.0 g doses. This may explain why there was little difference in soy lutein binding from miscellas in 20% oil, on 1 and 2 g of adsorbent (9).

Equations of the adsorptive capacities of the adsorbents using initial soy oil lutein concentrations were developed. Plots of x/m vs i (where i = initial concentration) on log scales were prepared to obtain the constants K_i (intercept) and n_i (slope); i.e. $x/m = K_i i^{n_i}$. Bleaching clay, alkaline ash and acid ash plots are in Figures 4a, 4b and 4c, respectively. The curves obtained are linear and similar to those obtained for Freundlich isotherms. The constants obtained by this method show the same trend as the constants derived from Freundlich isotherms.

Why the predictive equations should be linear is not immediately obvious. However, an explanation is offered by Snyder (personal communication 1989): for an adsorption, $I = A + R$, where I = initial solute concentration, A = amount of adsorbed solute, and R = residual solute concentration — substituting $I - A = R$; in $\log A = \log K + n \log R$; $\log A = \log K + n \log(I - A)$. It is possible that $\log(I - A)$ could approximate $\log(I)$ for a limited solute concentration range and the $\log A$ portion of $\log(I - A)$ would probably contribute to the term $\log K$.

Equations based on initial lutein concentrations may only be valid with dilute soy oil. However, they may be useful in bleaching systems where control of adsorption at low temperatures and low viscosity is desired i.e. an ambient temperature, continuous flow refining operation.

To summarize, a quantitative approach to Freundlich isotherm adsorption showed that constants K and n were dependent on the adsorbent dose. In the case of each of the adsorbents used, n increased and K decreased with adsorbent dose. Initial lutein concentration values were incorporated into predictive equations to measure the pigment binding capacity of adsorbents exposed to soy oil miscellas. These equations were also adsorbent dose-dependent.

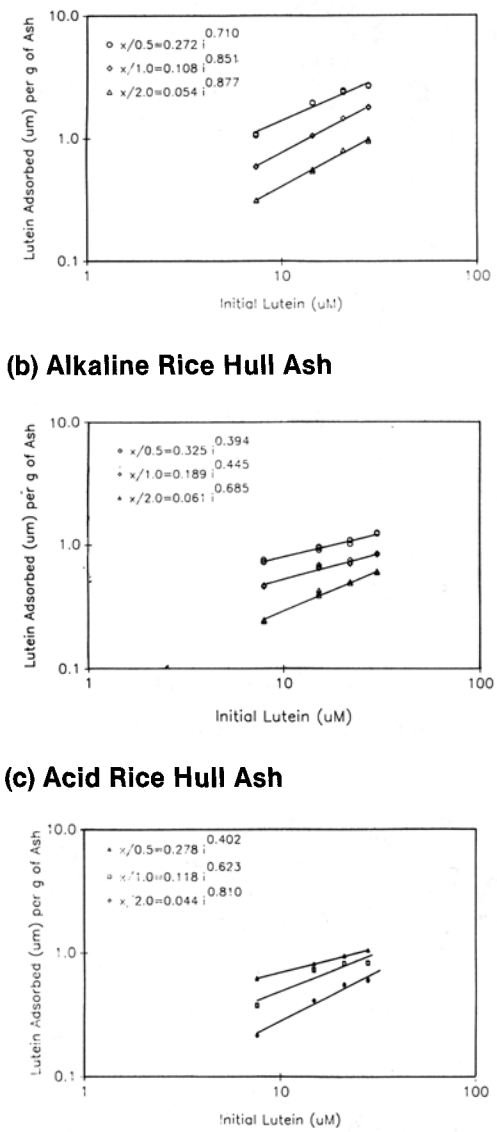

FIG. 4. Adsorption of lutein as a function of initial concentration of lutein determined by incubating 100 mL of 10%, 20%, 30% and 40% crude soy oil/hexane miscella for 15 min at 22°C with variable amounts of different adsorbents. Lutein concentration was obtained by measuring absorbance at 445 nm.

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