

Mode of Oleic Acid Adsorption on Rice Hull Ash Cristobalite

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ABSTRACT: Fourier transform infrared spectroscopy was used to investigate the adsorption of oleic acid (OA) onto dry rice hull ash (RHA) silica. Adsorption partially occurred by surface hydrogen bonding of the carboxylic acid. There was also formation of carboxylate ions by reaction of OA with residual potassium oxide. These ions were strongly bound by the ash. Isopropanol inhibited OA adsorption by H-bonding and encouraged desorption of H-bonded OA, but without itself being significantly bound. RHA with 40% moisture also adsorbed a small amount of OA by H-bonding and reacted with OA to form and adsorb carboxylate ions.

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Bleaching by adsorption is an important step in refining vegetable oil. This is done with montmorillonite aluminosilicate clays at 100°C under low pressures to adsorb carotenoid oil pigments and residues of previous refining steps such as phospholipids and fatty acids (1). Synthetic silica gels are now added in many bleaching operations because they have a high affinity for phospholipids and, therefore, reduce competition between phospholipids and pigments for clay binding sites.

There is interest in examining materials as alternatives to conventional adsorbents. For example, the Okija clay of Nigeria, where montmorillonite is unavailable, was found to be an effective alternative to traditional adsorbents (2). Rice hulls are a biological source of silica (3) common in many developing countries and may have potential as a pigment adsorbent in oil processing. Rice hulls are burnt by some cereal processors, and the resulting ash consists of 55% silica with a carbon residue (3). This ash was further burnt in the laboratory at 500°C to yield 97% silica and 2% potassium oxide (4). X-ray crystallography indicated that the silica was in the form of amorphous cristobalite (4). Isotherm studies showed adsorption of carotenoid pigments (3), free fatty acids (5), and phospholipids (6) from soy oil hexane miscellas.

A recent study reported that a rice hull ash (RHA), prepared by heating rice hulls between 200 and 800°C, was capable of only a small reduction in carotene pigment concentration of palm oil miscella (7). The investigators claimed that

RHA was not capable of true adsorption and that residual acid on the surface was responsible for catalyzing solute changes. These findings show the importance of demonstrating the nature of the lipid/silica interactions, rather than just measuring solute concentrations before and after exposure to RHA.

Diffuse reflectance Fourier transform infrared spectroscopy (FTIR) has been used to observe the mode of adsorption of oleic acid (OA) (8), triglyceride (9), and phospholipid (10) on silicic acid (SA) from hexane solution by polar (8–10) and/or ionic (10) interactions. In addition, FTIR should be useful in determining if lipid adsorption does occur on the surface of RHA and how the activity of this novel surface may differ from that of SA.

The objective of this study was to use FTIR to demonstrate OA adsorption onto RHA cristobalite from hexane solution and to describe the nature of binding. OA was chosen because it is a simple lipid whose adsorption by H-bonding onto synthetic SA is understood (8). Furthermore, RHA is reported to adsorb fatty acids from soy oil miscellas (5).

MATERIALS AND METHODS

Lipid, solvents, and adsorbent. OA (Sigma Chemical Co., St. Louis, MO), hexane and isopropanol (IPA) [high-performance liquid chromatography (HPLC)] were used. A laboratory-prepared RHA was made according to the method of Proctor and Palaniappan (3). The RHA was stored in a desiccator after heating, unless stated otherwise. The X-ray diffraction pattern of the laboratory-prepared RHA was obtained (4) and found to be similar to ash described by Proctor (4). This was the only form of RHA used in this study.

FTIR spectra. The FTIR spectra were obtained with a Nicolet Model 205 FTIR instrument (Nicolet, Madison, WI) with a diffuse reflectance unit 0300–002 (Barnes Analytical, Stamford, CT) having a resolution of 4 cm⁻¹ according to the method of Adhikari *et al.* (8–10). Spectra were obtained by co-adding 100 interferograms before transformation to spectra. These conditions were used throughout.

Control experiment. An FTIR spectrum of the RHA was obtained prior to adsorption to examine the nature of the material and to produce an adsorbent baseline spectrum, which was subtracted from subsequent spectra after lipid adsorption.

OA adsorption. OA adsorption from hexane solution was performed according to the method of Adhikari *et al.* (8).

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RHA (0.5 g) was stirred with 100 mL of 0.05M OA in hexane for 15 min before recovering and air-drying. FTIR analysis was then performed. The experiment was repeated with 100 mL of 0.05M IPA in hexane.

OA desorption. RHA, obtained from adsorption in pure hexane, was washed with 100 mL hexane for 15 min, and then examined by FTIR. The experiment was repeated by washing with 0.05M IPA in hexane.

FTIR analysis was also performed with RHA with adsorbed OA from 0.05M IPA in hexane and subsequently washed in 100 mL hexane. This experiment was repeated but by desorbing OA with 0.05M IPA in hexane.

Effect of moisture content on OA adsorption. To investigate the effect of bound moisture, RHA was equilibrated to 40% moisture, and FTIR data were obtained before adsorption. The OA adsorption procedure was then repeated in hexane, and the RHA FTIR spectra were observed. The spectral data were interpreted by examining the literature values of IR adsorption (11,12).

RESULTS AND DISCUSSION

Control experiment. Figure 1 shows the FTIR spectrum of dry RHA. The spectrum is similar in many ways to that of SA (8). However, the nonhydrogen-bonded silanol stretch around 3747 cm^{-1} is shown as a sharp peak. This differs from the broad band of SA found in this region due to bound water. The peak at 1359 cm^{-1} is the siloxane (Si-O-Si) peak of the silica "skeleton," whereas 1633 cm^{-1} is the OH bending vibration. Both of these peaks were more intense in the SA spectra.

OA adsorption. The FTIR spectrum of RHA after incubation with 0.05M OA in hexane is given in Figure 2. The carbonyl stretch of bound OA, at 1715 cm^{-1} , was slightly shifted relative to that of free OA at 1712 cm^{-1} (8), indicating OA adsorption by hydrogen bonding of the carboxyl and/or the acid OH group. The surface group hydrogen-bonding to OA is the free surface silanol group, whose IR band at 3747 cm^{-1}

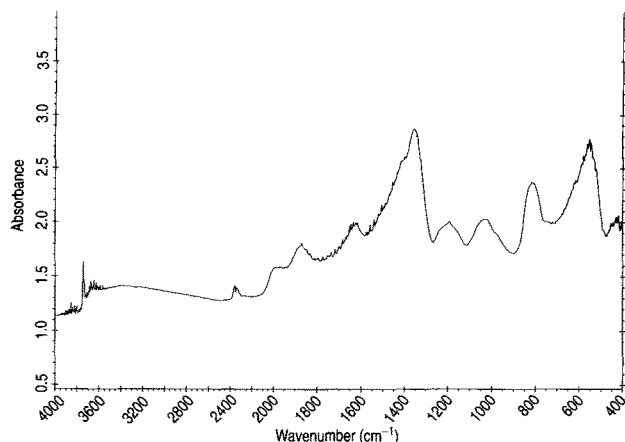


FIG. 1. The Fourier transform infrared spectra of dry laboratory-prepared rice hull ash.

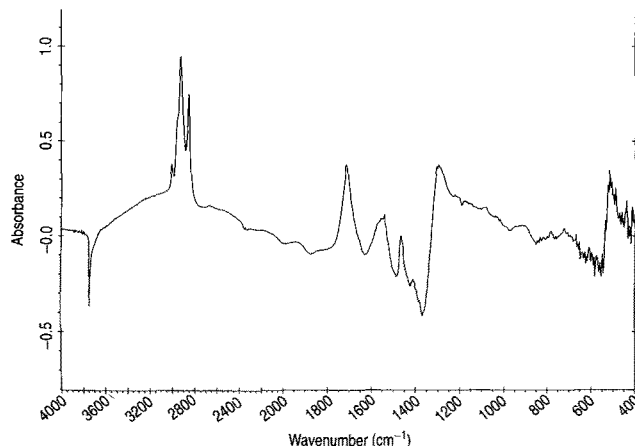
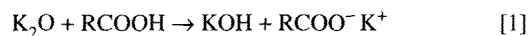


FIG. 2. The Fourier transform infrared spectra of rice hull ash (RHA) incubated for 15 min with 100 mL of 0.05M oleic acid in hexane. The spectrum of RHA has been subtracted.

in Figure 1 has disappeared in Figure 2. The spectra allow some conclusions to be drawn about the RHA surface relative to SA. The carbonyl band of OA was shifted more (to 1721 cm^{-1}) on SA and was broader adsorbed on SA than on RHA. This indicates a stronger interaction and a more heterogeneous surface for SA than for RHA. One interesting feature of the adsorption on SA was that some of the adsorbed OA had a considerably reduced intensity of the asymmetric CH_2 stretch at 2921 cm^{-1} relative to the symmetric stretch, as well as an unperturbed carbonyl stretch. This leads to the conclusion that this fraction of the adsorbed OA was laying down parallel to the surface (8). Because Figure 2 shows the relative intensities of the asymmetric and symmetric CH_2 to be just like those of free OA, it is concluded that the RHA surface does not have surface sites like those of SA that produced the laying down orientation of OA.

The peak at 1550 cm^{-1} corresponds to a carboxylate ion (RCOO^-) (11,12), most likely formed by the removal of a hydrogen ion from OA by metal oxides (4). Thus, there was very strong carboxylate ion binding to both silanol groups and metal. This work supports the findings of Proctor and Palaniappan (5) who found that alkaline RHA, which had not been acid washed, was more effective in binding free fatty acids from crude soy oil/hexane miscellas than acid-washed RHA. Furthermore, Proctor (4) reported potassium oxide in alkaline ash, which was removed on acid washing. This supposition is further supported by the fact that potassium oxide is a strong base. This leads to the following acid-base reaction occurring on the surface.



On a pure silica surface, adsorption of organic acids does not lead to the formation of carboxylate ions.

Figure 3 shows the FTIR spectrum of OA adsorbed on RHA in the presence of 0.05M IPA in hexane. The carbonyl stretch and the CH stretching intensities were reduced relative to that of Figure 2. This may have been due to IPA/OA

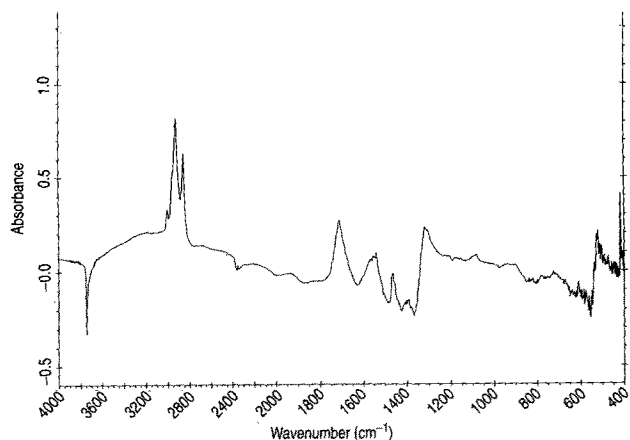


FIG. 3. The Fourier transform infrared spectra of rice hull ash (RHA) incubated for 15 min with 100 mL of 0.05M oleic acid and 0.05M isopropanol in hexane. The spectrum of RHA has been subtracted.



FIG. 5. The Fourier transform infrared spectra of rice hull ash (RHA) incubated for 15 min with 100 mL of 0.05M oleic acid in hexane and subsequently washed with 100 mL of 0.05M isopropanol in hexane. The spectrum of RHA has been subtracted.

hydrogen-bonded complexes in solution (8). However, there was no sign of IPA adsorption, such as the IPA C-H stretch at 2975 cm^{-1} , as was found with SA in the same system (8). IPA did not bind to RHA.

OA desorption. Figure 4 shows the FTIR spectrum of OA adsorbed on RHA in hexane after washing in hexane. The carbonyl peak intensity (1715 cm^{-1}) was considerably reduced relative to Figure 2. This suggests the desorption of weakly bound OA leaving intermediate-strength hydrogen-bonded OA and tightly held carboxylate ions (1550 cm^{-1}). Little OA was desorbed from SA in this solvent system (8).

Figure 5 shows the FTIR spectrum of OA adsorbed on RHA in hexane after washing in 0.05M IPA/hexane. The reduction in carbonyl intensity relative to that in Figure 4 means that IPA desorbed more OA than did hexane alone. OA was probably removed from silanol sites by disruption of weak and intermediate-strength H-bonds, while some intermediate-strength OA H-bonds and strongly bound carboxylates re-

mained adsorbed. However, there is no sign of IPA binding. IPA was also effective in removing OA from SA, but this was by competitive adsorption, with IPA being bound at the expense of OA (8). This behavior may again be promoted by OA/IPA interaction in solution.

Figure 6 shows the FTIR spectrum of OA adsorbed on RHA in 0.05M IPA in hexane after washing in hexane. The intensity of the carbonyl peak (1715 cm^{-1}) was less than that in Figure 4 but with no change in the carboxylate ion stretch (1550 cm^{-1}). The data show that hexane removed weak and intermediate-strength H-bonding. Carboxylate ion adsorption occurred independently of IPA. Thus, IPA does not interact with the basic potassium oxide sites.

Figure 7 is the FTIR spectrum of OA adsorbed on RHA in 0.05M IPA and then washed again in the same solvent system. The carbonyl stretch was almost negligible, showing that the small amount of OA bound with IPA was removed by further exposure to the same solvent system. As in Figure 6, the

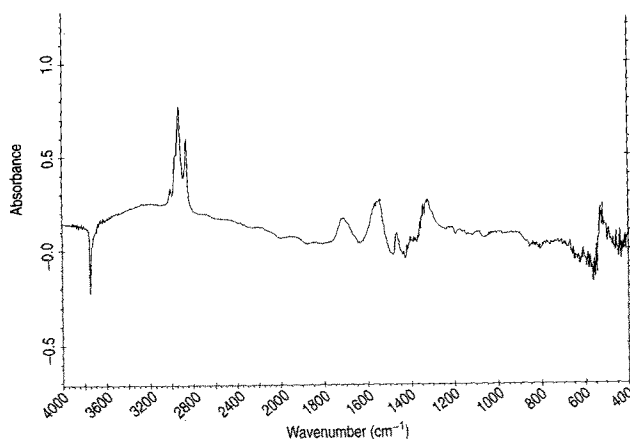


FIG. 4. The Fourier transform infrared spectra of rice hull ash (RHA) incubated for 15 min with 100 mL of 0.05M oleic acid in hexane and subsequently washed with 100 mL hexane. The spectrum of RHA has been subtracted.



FIG. 6. The Fourier transform infrared spectra of rice hull ash (RHA) incubated for 15 min with 100 mL of 0.05M oleic acid and 0.05M isopropanol in hexane and subsequently washed with 100 mL hexane. The spectrum of RHA has been subtracted.

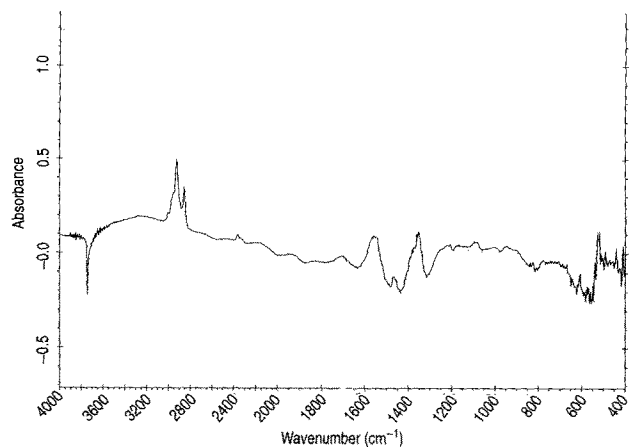


FIG. 7. The Fourier transform infrared spectra of rice hull ash (RHA) incubated for 15 min with 100 mL of 0.05M oleic acid and 0.05M isopropanol in hexane and subsequently washed with 100 mL of 0.05M isopropanol in hexane. The spectrum of RHA has been subtracted.

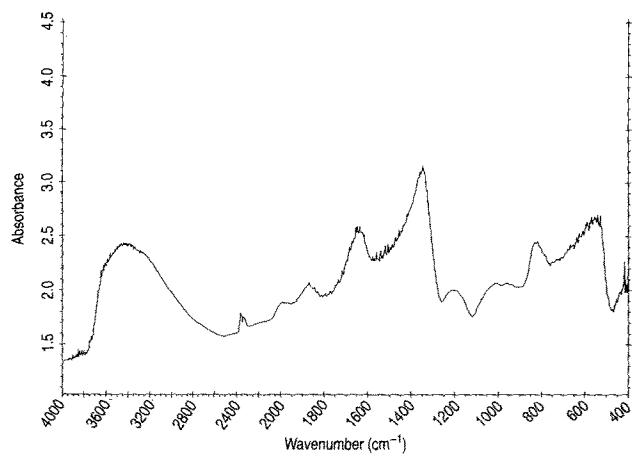


FIG. 8. The Fourier transform infrared spectra of laboratory-prepared rice hull ash with 40% moisture.

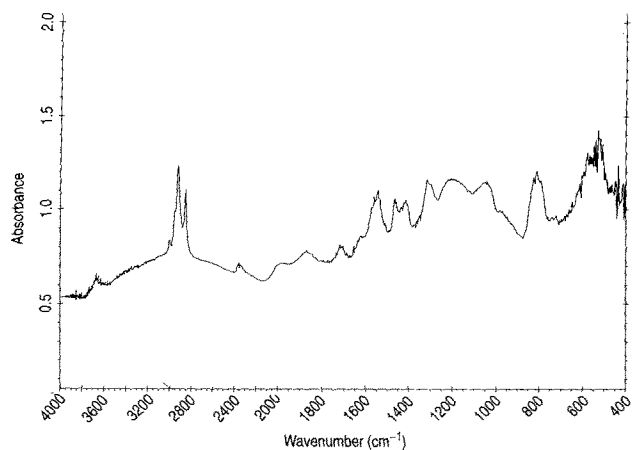


FIG. 9. The Fourier transform infrared spectra of 40% moisture rice hull ash (RHA) incubated for 15 min with 100 mL of 0.05M oleic acid in hexane. The spectrum of RHA has been subtracted.

carboxylate ion peak intensity was independent of IPA (Fig. 4).

Effect of moisture content on OA adsorption. Figure 8 shows the FTIR spectrum of RHA with 40% moisture. There was a large broad water peak (2800–3600 cm^{-1}) which was not found on dry RHA (Fig. 1). Bound water was, therefore, covering much of the surface. Figure 9 shows the surface species produced by exposure of the 40% moisture RHA to OA in hexane. This experiment was performed to observe if bound water causes a change in the carbonyl shift of adsorbed OA or affects carboxylate ion formation and binding. The low intensity of the band at 1715 cm^{-1} indicated that little OA hydrogen-bonded to the wet surface, and the small amount that

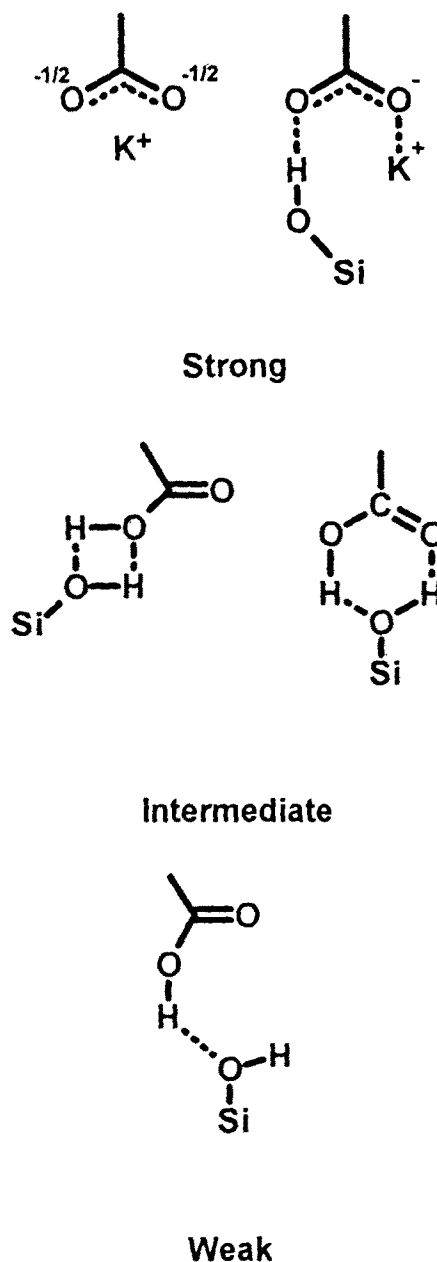


FIG. 10. Relative bonding strengths of proposed oleic acid/rice hull ash complexes.

did adsorb had the carbonyl peak shifted to the normal extent for RHA. The reduced OA adsorption was attributed to water on the wet RHA surface hydrogen-bonding with the free silanol OH groups to cover the binding sites used by OA on dry RHA. This was supported by the spectrum in Figure 8, which lacks a positive free OH band at 3747 cm^{-1} , and Figure 9, which lacks a negative free OH band at 3745 cm^{-1} . However, OA adsorption by carboxylate ion formation occurred as usual, as shown by the 1550 cm^{-1} band in Figure 9. Thus, the surface bound water did not prevent the OA from reacting with the potassium oxide on the surface.

To summarize, FTIR studies showed that RHA has structural similarities to SA, including silanol groups and a silica structure, but with less hydrogen-bonded surface water, as indicated by the reduced peak intensity. The OA carboxyl group was H-bonded to the surface, with the hydrocarbon chain perpendicular to the surface. There was evidence of formation and adsorption of carboxylate ions, which are strongly held by ionic adsorption (Fig. 10), despite exposure to IPA. IPA did reduce the amount of bound OA, but IPA was not itself adsorbed to much extent. It is proposed that OA is adsorbed by intermediate-strength and weak H-bonding as shown in Figure 10. Marshall and Rochester (13) suggested that the best representation of an organic acid adsorbed on surface silanol groups has the six-membered ring structure held by two H-bonds (Fig. 10). This complex may be less readily disrupted by IPA than more weakly bound OA, which is adsorbed by a single hydrogen bond, as has been proposed for alcohols (14) (Fig. 10). High-moisture RHA adsorbs OA slightly by H-bonding and strongly by adsorption of carboxylate ions. Alkaline RHA is capable of OA reaction and adsorption. However, the products, carboxylates, are strongly bound.

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