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ORIGINAL PAPER

Decolorization of Rice Bran Oil Using Modified Kaolin

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Abstract Measurements show that kaolin from Ranong, obtained from a major deposit in southern Thailand, can be modified to produce a material that is suitable for decolorizing rice bran oil. Its sorption properties were determined after various physical and chemical modifications of this kaolin. Physical modification was achieved by grinding via a planetary ball mill (300 rpm for 1 h), and this was followed by chemical treatment using sulfuric or oxalic acids. The optimum decolorization capacity (∼80%) was achieved by using 2 M sulfuric acid. With oxalic acid, the best results were obtained with 0.7 M, but these were slightly lower than those obtained with 2 M sulfuric acid. Compared to the original kaolin sample, the specific surface area of the modified clay increased from ∼13 to ∼244 $\mathrm{cm}^2\ \mathrm{g}^{-1}$, and the total pore volume from 0.06 to 0.43 $\mathrm{cm}^3\ \mathrm{g}^{-1}$. The pore size distribution curves show that most pores are in the mesoporous region with their diameters between 3.0–4.5 nm, and are suitable for adsorption of pigment molecules that are present in rice bran oil. Desorption and spectroscopic studies suggest that both electrostatic and chemical processes are involved in the interaction between pigments and active sites on the clay surface.

Keywords Modified kaolin · Decolorization · Rice bran oil · DR-FTIR · EPR spectroscopy

Introduction

Plant-derived oils contain many nutritionally beneficial compounds, such as chlorophyll, carotenoids, and xanthophylls, and in recent years there has been increasing interest in the health and nutritional aspects of rice bran oil, as well as in its potential industrial applications. Several constituents that are regarded as having health benefits are found in rice bran oil at concentrations that are appreciably greater than in most other vegetable oils. For example, it contains >4.2% unsaponifiable matter, which includes various antioxidants and micronutrients, whereas this component in most other oils is in the range <1–2% [1]. Nevertheless, the overall color quality of rice bran oil is considered to be unacceptable to the consumer, and bleaching treatments are commonly performed to decolorize it and improve quality. Bleaching of rice bran oil, however, is more difficult than for most vegetable oils, because of its high contents of chlorophyll [2].

Adsorbents commonly used for vegetable oil decolorization include activated clays, activated carbon, and various silica-based products, but the relatively low cost of

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activated clays makes them the most attractive class of adsorbent. Bentonite (calcium-montmorillonite) is the most popular clay used for stabilization, color removal and purification of plant-derived oils [3, 4], but the use of magnesium aluminosilicate minerals, such as sepiolite [5, 6] and attapulgite [7] has also been documented. Since the major components removed from the oils are of a relatively high molecular mass (e.g. chlorophyll, β-carotene, etc.), such adsorption is largely confined to external surfaces and edge sites and intercalation plays only a minor role in their adsorption by montmorillonite. Thus other aluminosilicate minerals might be able to be used for vegetable oil decolorization.

The principal objective of the present paper was to determine whether kaolin, a mineral with abundant deposits in Thailand, could be developed for use in vegetable oil bleaching, and thus to avoid the expense of importing bleaching clay. These investigations involved various samples produced by physical and chemical modification of a natural kaolin specimen from the Ranong deposit in southern Thailand. Their sorption properties were investigated in order to determine the optimum conditions for producing material for the most effective decolorization of rice bran oil.

Materials and Methods

Materials

Rice bran oil that had been degummed and neutralized was obtained from the Thai Edible Oil Co. Ltd., Thailand. The kaolin, from Ranong Province in southern Thailand, was supplied by Had Som Pan Co. Ltd. This natural kaolin, yellow in color, was purified by washing with distilled water and drying in an oven at 100 °C for 24 h. This sample was then gently crushed and sieved to 200 mesh; it is designated as natural kaolin (NK). A commercial bleaching clay (CBC) was purchased from Taiko Clay Marketing Sdn. Bhd., Malaysia. Sulfuric acid (H_2SO_4) and oxalic acid ($H_2C_2O_4$) used for chemical treatments were AR grade and purchased from Merck, Germany and Ajax Finechem, Australia, respectively.

Methods

Chemical Treatment of Natural Kaolin

Acid treatments were performed by adding the natural kaolin (NK) to various concentrations of sulfuric acid under mechanical stirring where the ratio of clay:acid was 1 g:50 ml. Samples were then refluxed with 2.0, 3.0, 3.7, or 5.0 M H_2SO_4 at 90 °C for 4 h, washed with distilled water, and dried at 100 °C for 24 h. These samples are designated as UGKS 2, 3, 3.7, and 5.

Physical Treatment of Natural Kaolin

The natural kaolin (NK) was ground using a Retsch planetary ball mill (model Retsch S 100) in which both the pot and milling media were stainless steel. Grinding was carried out for 1 h with a rotation speed of 300 rpm; the weight ratio of balls to kaolin was 30:1. The extensive grinding time was necessary to breakdown the structures of the kaolin minerals, which was a necessary preliminary step prior to acid activation (see e.g. [8–11]). This ground kaolin sample is designated as GK.

Combined Physical and Chemical Treatments of Kaolin

Ground kaolin powder (GK) was added to 1.7, 2.0, 2.5, 3.0 or 3.7 M H_2SO_4 under mechanical stirring where the ratio of clay:acid was 1 g:50 ml. Samples were refluxed at 90 °C for 4 h, then washed with distilled water and dried at 100 °C for 24 h, and are designated GKS 1.7, 2, 2.5, 3, and 3.7. Similar samples (designated GKO 0.5, 0.7, and 0.9) were prepared using oxalic acid instead of sulfuric acid with acid concentrations of 0.5, 0.7, or 0.9 M.

Determination of the Point of Zero Charge

The P_{zc} was determined by titration with different pH systems [12]. N_2 was bubbled through a mixture of 10% (w/v) modified kaolin and deionized water (pH 7) for 15 min, and it was then shaken at 250 rpm at 30 °C for 1 h. Titration was carried out with 0.1 M NaOH and 0.1 M HNO_3. After equilibration ($\sim$10 min), the pH was measured using a Mettler (UK) Delta 340 pH meter. The surface charge (Q) was calculated using the equation:

$$Q = (C_a - C_b - [H^+] + [OH^-])/W \quad (1)$$

where Q = the surface charge (mol g^{-1} of adsorbent dry weight)

C_a = the added acid (mol L^{-1})

C_b = the added base (mol L^{-1})

W = the dry weight of the adsorbent (g)

The point of zero charge ($Q = 0$) was obtained from plots of Q versus pH.

Surface Charge Modification by Varying the pH of the Clay Suspensions

The surface charge of modified kaolin samples prepared using subsequently determined optimum concentrations of sulfuric acid or oxalic acid (2 and 0.7 M, respectively) were further modified by suspension in solutions of the corresponding acids at pH 2.0, 2.5, 3.0, and 3.5. After separation by centrifugation, the kaolin samples were dried at 100 °C for 24 h.

The acidity of modified kaolin was determined by a titration with 0.1 M NaOH using phenolphthalein as indicator. The results are expressed as % acidity, and the physical properties of modified kaolin, GKS 2 are illustrated in Table 1.

Specific Surface Area Analysis Using the Brunauer-Emmet-Teller (BET) Method

The specific surface area (S_{BET}) was measured on a Quantachrome Autosorb-1 instrument, by the Brunauer-Emmet-Teller (BET) method, using N_2 gas adsorption at 77.35 K, and outgas at 523 K; the relative pressure (P/P_O) ranged up to 0.3. Three porosity parameters were obtained: the BET surface area (S_{BET}) was calculated from the linear part of the BET plot according to IUPAC recommendations [13] using the adsorption isotherm. Total pore volumes (V_p) were obtained from the maximum adsorption by the Barrett-Joyner-Halenda (BJH) method [11] at P/P_O of $\sim$0.989–0.900, average pore diameters ($\bar{r}$) were derived from the relationship $= 2V_p/S_{BET}$ [14], and the pore size distributions were measured by applying the BJH method to the desorption branch of the nitrogen isotherms at 77 K.

Adsorption Studies

The bleaching efficiency of the modified kaolins was determined on the basis of the amounts of pigments that could be removed from rice bran oil. Unbleached rice bran oil was placed in a flask held in an oil bath. When the temperature reached 90 °C, modified kaolin (2% w/w) was added to the flask, and the bleaching process carried out with stirring at 90 °C for 30 min. The clay and oil were separated by centrifugation (2,500 rpm and 10 min), then filtered (Whatman No.41) under vacuum, and the amount of pigment removed, (to assess the decolorization capacity of various modified kaolin samples) was determined by UV–visible spectroscopy using a Bausch & Lomb Spectronic 21 spectrophotometer. The oil samples were diluted in hexane (1:4 v/v), and the absorbance measured at the maximum absorption wavelength (410 nm) using hexane as reference after having measured the full spectrum of the oil sample between 350–750 nm.

Table 1 Summary of the major physical properties of modified kaolin GKS 2 (i.e. ground kaolin treated with 2 M H_2SO_4)

Parameters	GKS 2
Apparent bulk density (g cm^{-3})	0.34
Free moisture (2 h, 105 °C) (%)	5.0
Loss on ignition (pre-dried, 2 h, 1,000 °C) (%)	12.8
pH (10% suspension)	3.0
Acidity (%)	0.29
Specific surface area (BET) (m^2 g^{-1})	243.6

The decolorization capacity was calculated using the following formula [15]:

$$\text{Decoloization capacity} = \frac{A_0 - A_b}{A_0} \times 100\,\% \tag{2}$$

where A_0 and A_b are, respectively the absorbances at 410 nm of the rice bran oil before and after bleaching with modified kaolin.

The chlorophyll contents of the rice bran oil before and after bleaching were determined from the absorbance at 630, 670 and 710 nm in a 10 mm spectrometer cell. The contents of chlorophyll a pigments, expressed in ppm of pheophytin a, were calculated using the following formula [16]:

$$C = 345.3(A_{670} - 0.5)(A_{630} - 0.5)(A_{710})/L \tag{3}$$

where $C =$ content of chlorophyll pigments in ppm of pheophytin a

$A =$ absorbance at the respective wavelength (nm)

$L =$ thickness of the spectrophotometer cell (nm)

In addition, manual color determination of rice bran oil before and after bleaching was made using a Lovibond Tintometer, Pardelo Model F according to the AOCS Cc 13d-55 with an optical path length of 25 mm glass cell. The color of light transmitted through a specified depth of oil was matched with the color of light transmitted from the same source through a set of colored glass slides.

Desorption Study

Desorption of adsorbed pigments from the modified kaolin samples was used to investigate their relative effectiveness for bleaching the rice bran oil. After washing with hexane in order to dissolve any rice bran oil remaining in the clay sample, the clay was eluted with absolute ethanol or 0.1 M NaOH, and the absorbance at 410 nm of the supernatant was determined. The percentage of pigments desorbed was calculated from the following equation.

$$\text{Desorption} = \frac{A_d}{A_a} \times 100\,\% \tag{4}$$

where A_a and A_d are the absorbance at 410 nm of the solutions before and after desorption of pigments from the clay, respectively.

Diffuse Reflection Infrared Fourier Transform Spectroscopy

Samples were prepared by mixing homogeneously 1 mg of sample with 100 mg of KBr, and then pressing into pellets for study by diffuse reflection infrared fourier transform Spectroscopy (DRIFT) spectroscopy. Diffuse reflectance infrared Fourier transform spectra were measured with a Perkin Elmer (Spectrum One) Fourier Transform infrared spectrometer operating in the mid-IR spectrum range (4,000–450 cm^{-1}); 16 scans were taken for each spectrum at a resolution of 4 cm^{-1}.

EPR Spectroscopy

EPR spectra were recorded at ambient temperature using a JEOL (JES-RE2X) CW spectrometer operating at X-band frequencies. Most spectra were acquired in 4,096 points using a sweep width of 500 mT, 10 mW microwave power, 100 kHz modulation frequency, and 1.0 mT modulation amplitude. Measurements of free radical signals, however, were performed with a 10 mT sweep width, 5 mW microwave power and 0.5 mT modulation amplitude. g-values are expressed relative to DPPH ($g = 2.0036$), which was used as an external standard.

Results and Discussion

Adsorption Study

The decolorization capacities (%) of the various modified kaolin samples are shown in Table 2. These increased with increasing acid concentration, but the values for unground kaolin samples were much lower than for ground kaolin with the same acid concentration [e.g. ~43% for UGKS 2 (unground) and ~80% for GKS 2 (ground)]. For acid activated ground samples, the optimum sulfuric acid concentration was 2 M, and that for oxalic acid was 0.7 M; higher acid concentrations resulted in lower decolorization capacities (Table 2). A similar result has been reported for smectite-derived bleaching clays, where it was interpreted as corresponding to a collapse of the clay lattice structure [17, 18]. In the present work a decrease in the specific surface areas of the minerals was observed at the highest acid concentrations (Table 3). For comparison, Tables 2 and 3 also show results from measurements of rice bran oil bleaching that were made using a commercial bleaching clay; these were slightly superior to those from the best of the modified kaolin samples, but not greatly so (~82% compared to ~80%). In addition, the chlorophyll contents of rice bran oil after bleaching were 0.062 and 0.052 ppm with GKS 2 and the CBC, respectively. The corresponding values for the yellow/red color were 8.0/1.6 and 6.0/1.1.

Table 2 Decolorization capacity (%) of modified kaolin samples

Sample [2%(w/w)]	Decolorization capacity (%)
Unground kaolin treated with various concentrations of sulfuric acid	
UGKS 2	43.30 ± 0.02
UGKS 3	52.70 ± 0.04
UGKS 3.7	54.15 ± 0.03
UGKS 5	59.80 ± 0.02
Physical treatment (grinding) of kaolin combined with chemical treatment using various concentrations of sulfuric acid	
GKS 1.7	71.94 ± 0.02
GKS 2	79.63 ± 0.03
GKS 2.5	75.73 ± 0.02
GKS 3	71.20 ± 0.05
GKS 3.7	65.20 ± 0.01
Physical treatment (grinding) of kaolin combined with chemical treatment using various concentrations of oxalic acid	
GKO 0.5	72.79 ± 0.03
GKO 0.7	78.40 ± 0.04
GKO 0.9	75.40 ± 0.03
Commercial bleaching clay (CBC)	81.93 ± 0.02

The specific surface area (S_{BET}), total pore volume (V_p), and pore size distribution of the kaolin samples were measured in order to gain further understanding of their decolorization capacities (DC). The decolorization capacity increased with increasing specific surface area of the modified kaolin (Table 3). The highest decolorization capacity was observed with the ground sample that had been treated with 2 M H_2SO_4, but high values (>75%) were also observed with ground samples treated with 2.5 M H_2SO_4 and 0.7 M $H_2C_2O_4$. The fact that sample GKS 2 has the largest value for the specific surface area (~244 $m^2\ g^{-1}$), suggests that this could be an important factor in the bleaching process.

The pore size distribution (PSD) curves of natural kaolin, ground kaolin, modified kaolin samples and commercial bleaching clay are shown in Fig. 1A–C. It is seen that grinding kaolin increased the proportion of pores in the ~3.0–4.5 nm range and that there was a further increase in the proportion of pores in this region after acid treatment (Fig. 1A, B). The pore size distribution plots indicate that the dv/dr ratio (ratio of change in volume relative to the radius) increased as a result of grinding followed by leaching with 2 M H_2SO_4 (GKS 2) compared to the natural sample and acid treatment products (UGKS 2 and 3.7) (Fig. 1A, B). The GKS 2 sample exhibited a maximum in differential pore volumes at ~3.6 nm and was similar to the CBC; GKS 2 and GKS 2.5 also had sharp peaks at a radius of 3.6 nm (Fig. 1B).

Although it is often assumed that bleaching clay decolorization capacities are determined primarily by their surface areas (e.g. [17, 19]) Table 3 shows that different decolorization capacities can be observed with samples having similar specific surface areas. For example,

Table 3 Specific surface area (S_{BET}), total pore volume (V_{p}), mesopore–micropore volumes (V_{me}, V_{mi}), average pore diameter ($\bar{r}$), and decolorization capacities (DC) of some kaolin samples and a commercial bleaching clay (CBC)

Sample	S_{BET} (m^2/g)	V_{p} (cm^3/g)	V_{me} (cm^3/g)	V_{mi} (cm^3/g)	$\bar{r}$ (nm)	DC (%)
NK	13.1	0.06	0.06	0.00	19.7	–
GK	33.1	0.14	0.14	0.00	16.4	–
UGKS 2	46.0	0.10	0.10	0.00	8.3	43.30
UGKS 3.7	57.7	0.12	0.12	0.00	8.5	54.14
GKS 1.7	230.2	0.51	0.48	0.03	8.8	71.94
GKS 2	243.6	0.43	0.40	0.03	7.0	79.63
GKS 2.5	216.8	0.47	0.44	0.02	8.6	75.73
GKS 3	214.1	0.51	0.49	0.02	9.4	71.20
GKS 3.7	201.6	0.49	0.47	0.02	9.7	65.20
GKO 0.5	195.6	0.32	0.28	0.03	6.6	72.79
GKO 0.7	225.8	0.37	0.34	0.03	5.6	78.40
GKO 0.9	228.5	0.32	0.29	0.03	6.5	75.40
CBC	153.2	0.29	0.29	0.00	7.5	81.93

GKS 2.5 ($S_{\mathrm{BET}} = {\sim}217\ \mathrm{m^2\ g^{-1}}$) and GKS 3 ($S_{\mathrm{BET}} = {\sim}214\ \mathrm{m^2\ g^{-1}}$) had decolorization capacities of 75.7 and 71.2%, respectively, thus indicating that the specific surface area is not the only factor controlling the bleaching process. A similar conclusion was reached by Christidis [20] for acid activated bentonites. The pore size distribution curve (Fig. 1B) shows that GKS 2.5 contained a higher proportion of pores in the ~3.0–4.5 nm region than GKS 3, which is the size range that has been proposed as being most effective for oil bleaching (e.g. [5, 6, 21–24]). Thus, the higher decolorization capacity of CBC compared to GKS 2 could be the result of it having more pores in the ~3.0–4.5 nm range, even though its specific surface area was lower than that of GKS 2. This pore size is appreciably larger than the cross sectional dimensions of the monomeric chlorophyll molecule (ca. 1.2 × 1.5 nm), and is consistent with the report by Brimberg [25] that chlorophyll molecules are in a colloidal state when were adsorbed.

The pore size distribution curves for ground kaolin samples modified by oxalic acid (GKO 0.4, 0.7 and 0.9) are shown in Fig. 1C, and are similar to those from the GKS samples (Fig. 1B). However, the chelating properties of the oxalate ion enhance the leaching of Al from the physically modified kaolin. For example, Ward and Brady [26] have reported that in acidic and near neutral pH solution, negatively charged oxalate species adsorb at exposed Al sites on kaolinite surfaces. Furthermore, Wieland and Stumm [27] concluded that kaolinite dissolution in oxalate solution first involves adsorption of negatively charged oxalate onto edge Al sites forming surface complexes, which are then removed into solution as Al oxalate complexes. The GKO samples contained a lower proportion of pores in the 3.0–4.5 nm region than the GKS samples, resulted in slightly lower decolorization capacity than GKS samples.

Effects of Physical and Chemical Modification of Kaolin on Its Structural and Surface Properties

The specific surface areas (S_{BET}) and the total pore volumes (V_{p}) for the Ranong kaolin before and after modification are shown in Table 3. The grinding procedure resulted in an increase in the value of S_{BET} from ~13 to ~33 $\mathrm{m^2\ g^{-1}}$ and of V_{p} from 0.06 $\mathrm{m^2\ g^{-1}}$ to 0.14 $\mathrm{cm^3\ g^{-1}}$. Subsequent acid leaching of the ground sample, however, produced a further increase in S_{BET} from ~33 to ~200–243 $\mathrm{m^2\ g^{-1}}$ and a further increase in V_{p} from 0.14 to 0.32–0.51 $\mathrm{cm^3\ g^{-1}}$. Thus the combination of physical and chemical treatments produced ~17-fold and ~7-fold increases in S_{BET} and V_{p}, respectively. Much smaller changes were observed with chemical treatments of unground kaolin samples. For example, compared to the original kaolin UGKS 2 and UGKS 3.7 had respectively 3.5-fold and 4.3-fold increases in S_{BET} (from ~13 to ~46 and ~57 $\mathrm{m^2\ g^{-1)}}$ and 1.5-fold and 1.9-fold increases in V_{p} (from 0.06 to 0.10 and 0.12 $\mathrm{cm^3\ g^{-1}}$). These results are comparable with those observed by other workers for modified kaolins. For example Temuujin et al., [28] found that the S_{BET} of their kaolin increased from ~15 to ~300 $\mathrm{m^2\ g^{-1}}$ as a result of mechanical activation followed by acid leaching; V_{p} increases of 0.28–0.31 $\mathrm{cm^3\ g^{-1}}$ were observed.

The results in Table 3 indicate that major changes are produced in the physical properties of the kaolin by grinding followed by acid leaching. The high surface area, total pore volume and especially the pore size distribution in the range 3.0–4.5 nm as mentioned above are considered to be the most important properties for pigment adsorption. With both sulfuric acid and oxalic acid treatments of physically modified kaolins, the products were mesoporous, but there were differences in their pore size distribution.

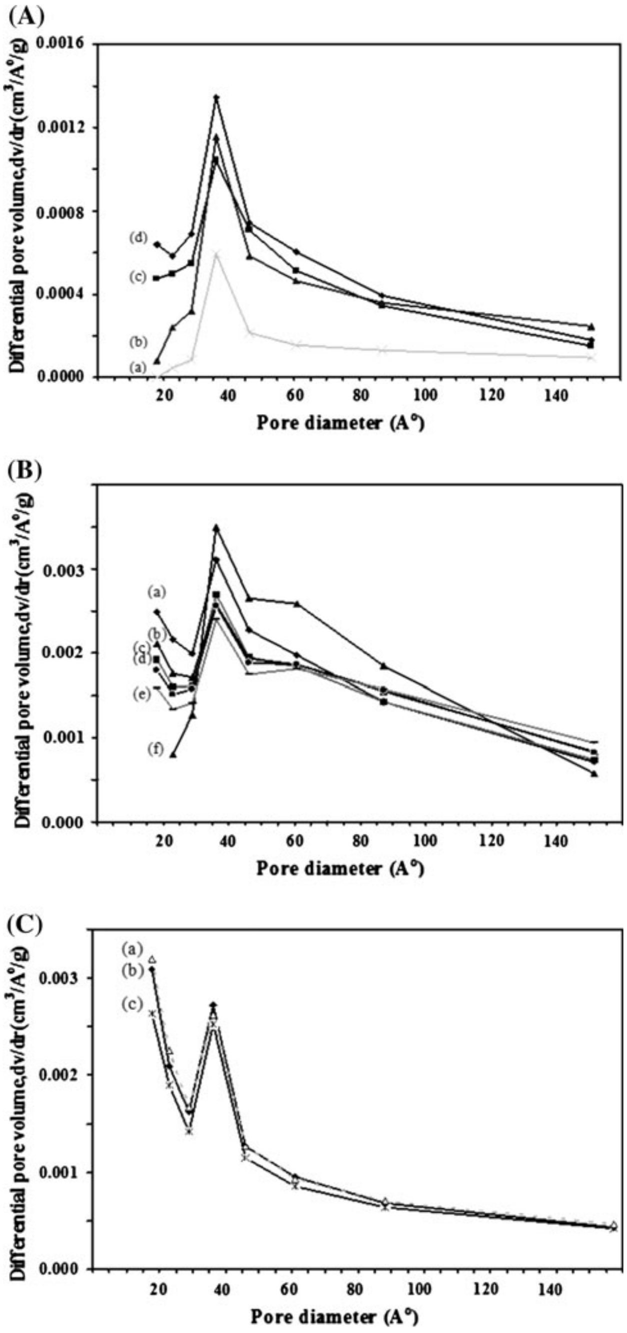

Fig. 1 **A** Pore size distribution (PSD) of *a* natural kaolin (NK), *b* ground kaolin (GK), and NK after leaching with 2 M H_2SO_4 (UGKS 2) (*c*) and 3.7 M H_2SO_4 (UGKS 3.7) (*d*). **B** PSD of GK after leaching with various concentrations of H_2SO_4 *a* 2 M (GKS 2), *b* 2.5 M (GKS 2.5), *c* 1.7 M (GKS 1.7), *d* 3.0 M (GKS 3.0), *e* 3.7 M (GKS 3.7), and *f* a commercial bleaching clay (CBC). **C** PSG of GK after leaching with various concentrations of $H_2C_2O_4$ *a* 0.5 M (GKO 0.5), *b* 0.7 M (GKO 0.7), and *c* 0.9 M (GKO 0.9)

Mechanical treatment of the natural Ranong kaolin, as used in the present work, results in structural damage that is seen by a reduction in the intensities of the FTIR peaks associated with kaolinite by ~65% (data not shown). Acid leaching did not result in any further reduction of the characteristic kaolinite vibrations, indicating that the effects of acid are restricted to the new phase generated by mechanical damage. Since the Al content of acid leached ground kaolin is considerably lower than that of acid–leached unground kaolin (data not shown), acid leaching must selectively remove Al from the phases created by structural degradation of kaolin, and results in the formation of a Si-rich product.

Influence of Surface Charge on the Decolorization Capacity of Modified Kaolin Samples

The point of zero charge (P_{zc}) is the pH at which the net charge of the clay surface is zero. Above the P_{zc}, cations or positively charged regions of polar molecules would be expected to dominate adsorption by the clay, whereas adsorption of anions or negatively charged regions of polar molecules would be expected to be more important at lower pH values. Plots of the variation of net surface charge with pH (Fig. 2a, b) show P_{zc} values of ~3.5 and ~3.7, respectively for the products from Ranong kaolin after grinding and treatment with sulfuric acid or oxalic acid.

The influence of the pH of the suspension from which the kaolin sample was prepared on the percentage decolorization of rice bran oil is illustrated in Table 4. The most effective samples were those prepared with pH values below that of the P_{zc} (i.e. ~2.0–3.0). Similar trends were observed for sulfuric acid and oxalic acid treatments of ground kaolin. Thus these results show that the pigments in rice bran oil tend to be anionic in nature and that the pH of the clay surface plays an important role in determining the bleaching ability of modified kaolin.

These results are consistent with reports by other workers on the effects of pH on clay adsorption properties. For example, Velde [29] found that the highest adsorption of organic molecules by clays occurred in the pH range 2–4, and Adel [30] reported that the optimum pH for the removal of color from vegetable oil by bleaching earth was in the range 2.5–3.0.

Characterization of the Interaction Between Pigments in Rice Bran Oil and Modified Kaolins

The modified kaolin samples changed color from pale yellow to green as a result of adsorption of pigments during bleaching rice bran oil; it was suspected that an appreciable fraction of these pigments could be chlorophyll-a or its derivative, pheophytin, since these are major pigments in rice bran oil. After the bleaching process, the adsorbent was washed several times using hexane with stirring and soaked overnight in order to dissolve any rice

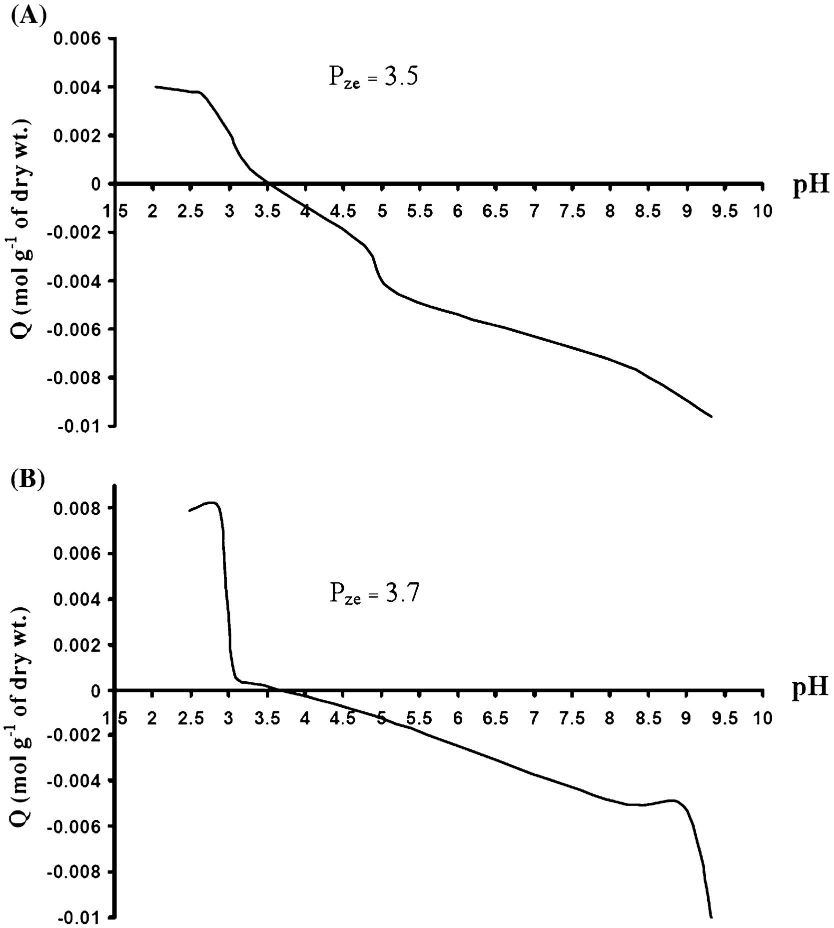

Fig. 2 Determination of the point of zero charge (P_{zc}) for modified kaolin samples **a** GKS 2 and **b** GKO 0.7

Table 4 Decolorization capacity (%) for kaolin samples GKS 2 and GKO 0.7 after surface modification using various values for the pH of for aqueous clay suspensions

pH	Decolorization capacity (%)	
	GKS 2	GKO 0.7
2.0	80.88 ± 0.03	79.79 ± 0.02
2.5	80.64 ± 0.01	79.59 ± 0.01
3.0	80.51 ± 0.03	78.69 ± 0.02
3.5	78.95 ± 0.03	78.30 ± 0.02

bran oil remaining in the clay sample; but the clay remained green. This result indicated that there is a strong interaction between the pigment and the modified kaolin. In order to gain additional understanding of the chemical/physical nature of the adsorption process, further investigations were performed to identify changes induced in the most effective of the modified kaolin samples as a result of their use in the bleaching process. These involved desorption studies supplemented by physical investigations by DRIFT and electron paramagnetic resonance (EPR) spectroscopies.

Desorption Studies

Desorption studies are useful in helping to elucidate the nature of adsorption processes. In the present study, the desorption values for pigments adsorbed on the modified kaolin GKS 2 were ~53% and ~90% for absolute ethanol and 0.1 M NaOH. Thus the bonding between pigments and the modified kaolin GKS 2 was strongly attacked by 0.1 M NaOH, and to a much lesser extent by the weakly polar solvent (ethanol).

DRIFT Spectroscopy

DRIFT spectra are presented in Fig. 3a–c for crude rice bran oil and modified kaolins GKS 2 and GKO 0.7 before and after bleaching rice bran oil and removal of any associated oil. Pigment adsorption resulted in the appearance of new bands at 2,855, 2,926, and 3,009 cm^{-1}; these correspond to the symmetric, asymmetric –CH_2 stretching vibrations of hydrocarbon chains, and the C–H stretching vibration of the *cis*-double bond, respectively. The sharp band at ~2,926 cm^{-1} may correspond to phytol in adsorbed chlorophyll (pheophytin), since this gives a

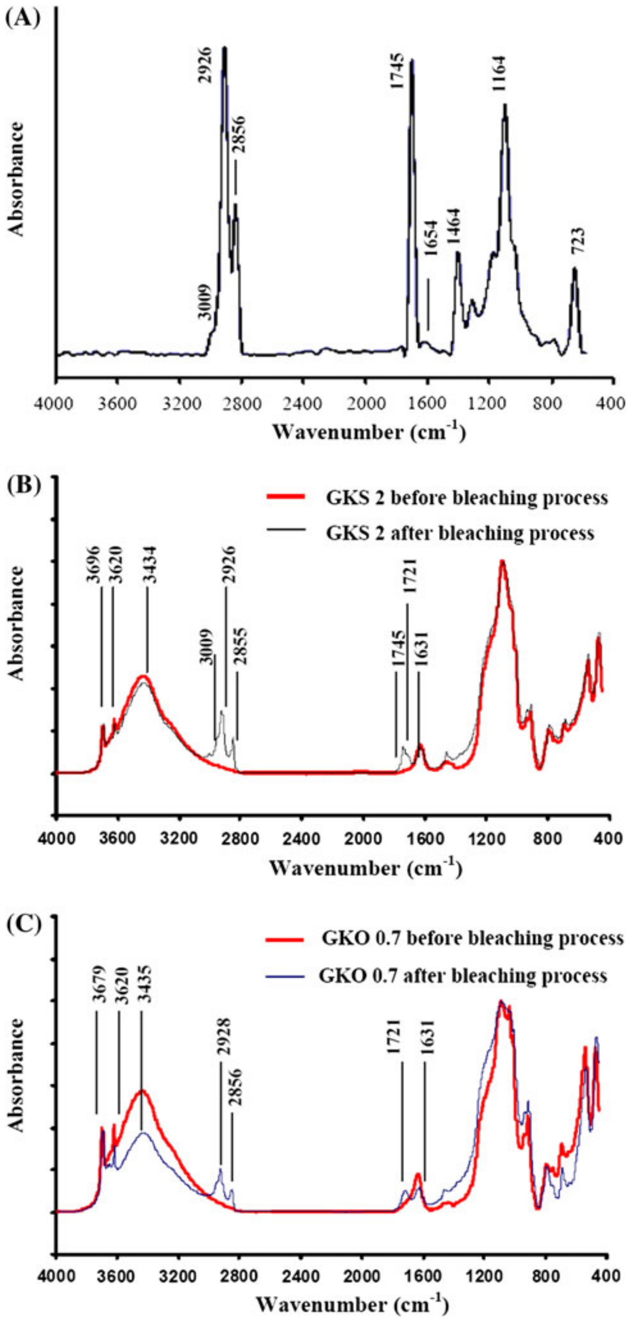

Fig. 3 DRIFT spectra of **a** crude rice bran oil **b** modified kaolin GKS 2 before and after adsorption of colored material from rice bran oil, and **c** modified kaolin GKO 0.7 before and after adsorption of colored material from rice bran oil

strong C–H stretching band [31, 32]. Another band at ~1,745 cm^{-1} is consistent with ester carbonyl groups of chlorophyll [31, 32]. However, in this study spectral changes were also observed in the C=O region (~1,745 cm^{-1}), and the appearance of a shoulder at ~1,721 cm^{-1} that may be attributed to the interaction of acidic sites on the kaolin surface and ester carbonyl groups of chlorophyll.

Thus this result suggests chemical interactions occur between the adsorbent and pigments in rice bran oil, probably involving interactions of the ester carbonyl group of chlorophyll with acidic sites on the clay surface. Sabah [5] has reported that chlorophyll adsorption on acid activated sepiolite involves active sites on the mineral surface, whereas Mehraban and Farzaneh [33] reported that chlorophyll adsorption by the zeolite MCM-41 involves electrostatic interactions between chlorophyll and surface silanol groups. Our studies indicate that the interaction between pigments and acidic sites on the modified clay involve a combination of electrostatic interactions and chemical bonds.

EPR Spectroscopy

EPR spectra of the Ranong kaolin before and after its use for bleaching rice bran oil (Fig. 4) showed no changes in the signal from Fe^{3+} in octahedral sites [34, 35], but there was considerable distortion of the Mn signal, which is thought to correspond to Mn^{4+} in tetrahedral sites (data not shown). Thus it appears that the material adsorbed from the oil causes distortions at the tetrahedral surface, but has little effect on the octahedral surface. An alternative explanation of this observation is that there is some adsorption of Mn-containing material from the oil, and this interferes with the signal from Mn in the kaolinite structure. One possible source of the Mn could be chlorophyll, since some Mn^{2+} is associated with chlorophyll in plant leaves [36]. However, no Mn signal was observed in the EPR spectrum of the unbleached rice bran oil (spectrum not shown), so a change in the symmetry of the Mn-containing sites in the kaolinite structure is considered to be the more likely explanation for the changes in the EPR spectra as a result of pigment adsorption.

In addition to changes to the Mn signal, there was an increase in the broad background signal, and an increase in the free radical signal centered on $g = 2.00$ (~350 mT) after use of the kaolin for bleaching the oil. The background signal corresponds to magnetically interacting ions, and is not definitive for any particular chemical species. However, in natural samples, it is generally associated with iron oxides [37], and could, therefore, be associated with the adsorption from the rice bran oil of ferritin (the main iron storage protein in plants), which can be associated with chloroplasts as well as mitochondria. Characterization of the spectral properties of the free radical signal produced as a result of the sorption process is also difficult, because of its overlap with a free radical signal associated with defects in the mineral structure, but it appears to be a single peak resonance with line width around 0.5–0.6 mT. This is similar to the weak free radical seen in the unbleached oil (spectrum not shown) and to the colored material

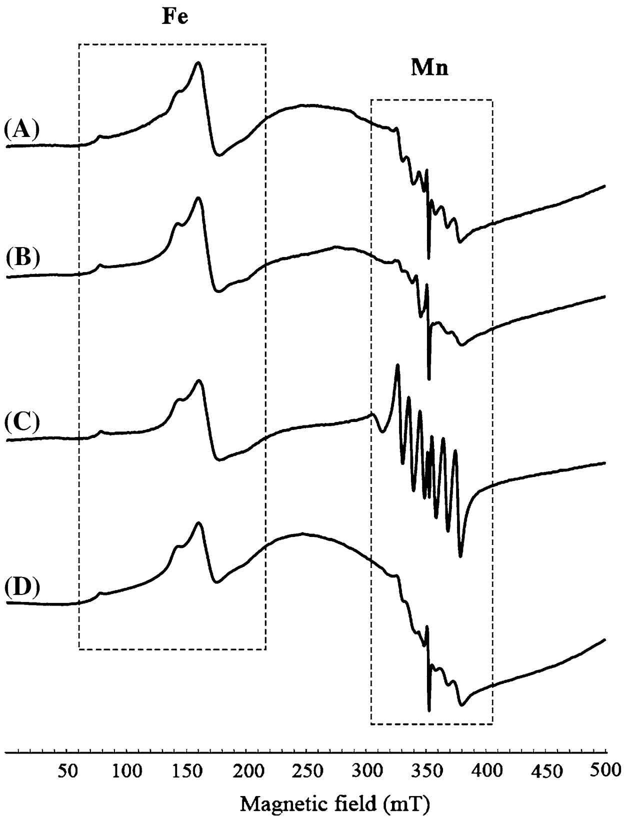

Fig. 4 EPR spectra of kaolin samples GKS 2 **a** before, and **b** after adsorption rice bran oil, GKO 0.7 **c** before, and **d** after adsorption rice bran oil

(melanoidins) seen in many plant pigments, such as seed testa [38]. Hence this free radical probably corresponds to adsorption of similar material.

Conclusions

This work shows that an acceptable degree of decolorization of rice bran oil (~80%) can be achieved using kaolin that had been modified by combined physical and chemical treatments to increase the specific surface area, total pore volume, pore size distribution in the ~3.0–4.5 nm range and number of acidic sites. Although the performance of the modified kaolin was slightly inferior to that of a commercial bleaching clay, its relatively low cost suggests that it could be developed as a practical alternative for use in situations in which optimum bleaching capacity is not of paramount importance. However, one step acid activation or chemical treatment as used to improve adsorption efficiency of other clay minerals, such as montmorillonite, sepiolite, or attapulgite, was ineffective. With kaolin, it was necessary first to destroy the ordered structure by mechanical activation before chemical treatment in order to produce a material with suitable adsorption properties. This was achieved by first of all grinding to reduce the kaolin particle size and to produce a more disordered structure. It was then necessary in a second step to treat the ground kaolin sample with hot acid solutions to generate products that are suitable for adsorption of large molecular pigments, such as chlorophyll-a. For Ranong kaolin, the optimum chemical modifications for its use as an adsorbent for the removal of color from rice bran oil were obtained by treatment with 2 M H_2SO_4 after grinding in a planetary ball mill. Although the adsorption efficiency was influenced by specific surface area, pore size distribution and pH of the suspension from which the kaolin sample was prepared, the pore size distribution in the ~3.0–4.5 nm range is thought to be the most important factor.

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