J Am Oil Chem Soc (2015) 92:295–304
DOI 10.1007/s11746-014-2583-2

ORIGINAL PAPER

Effect of Alumina Content and Surface Area of Acid-Activated Kaolin on Bleaching of Rice Bran Oil

Lei Lei Aung · Emmanuel Tertre · Parinda Suksabye · Niramon Worasith · Paitip Thiravetyan

Received: 20 February 2014 / Accepted: 12 December 2014 / Published online: 30 December 2014

Abstract This study investigated the effect of kaolin acid activation on alumina losses, surface area changes and oil bleaching performance. Ground kaolin was treated with hydrochloric or citric acid, and bleaching tests were performed on rice bran oil. The adsorption studies showed that the optimal bleaching of ~83 or ~81 % were achieved by activation with 0.5 M hydrochloric or citric acid, respectively, whereas bleaching with a commercial clay was ~82 %. The highest bleaching value was not associated with the maximum clay surface area or porosity. X-ray fluorescence showed that alumina contents of 31–34 % were suggestive for optimum bleaching depending on the different acid used. Treating ground kaolin with the same hydrochloric acid strength by varying the acid concentration and clay/acid ratio also confirmed that the best Al^{3+} content was ~32 %, and a value lower than one indicated the extensively destruction of kaolinite proportions leading to a decrease in its bleaching capacity, even though it had the maximum surface area. The decrease in capacity was due to the reduction of alumina content, and the parallel formation of high amorphous silica was favorable for the adsorption of anionic pigments, such as chlorophyll-a.

Keywords Kaolin · Kaolinite proportions · XRF analysis · Alumina to silica ratio · Bleaching · Rice bran oil

Introduction

Rice bran oil, extensively used as cooking oil in Asian Countries, such as Japan, Korea, and Thailand, is extracted from the germ and the inner husk of rice. Rice bran is a valuable by-product of the milling of brown rice to white rice and contains protein, 13.0–16.0 % oil, 15.0–22.0 % fiber, 6.2–14.4 % ash, 8.0–17.7 % vitamins, and trace minerals [1]. Currently, rice bran is used mostly as animal feed (60 %), while the rest is used to produce value-added edible cooking oil [2]. Rice bran oil contains higher amounts of bioactive components, such as phytosterols, tocopherols and tocotrinols, which are nutritious. Rice bran oil is of interest as “heart oil” because it is very delicious and has a high hypocholesterolemic effect. Although it is a nutritive oil, rice bran oil is dark greenish brown due to the presence of chlorophyll-a, which thermally decomposes into pheophytin. The pigment pheophytin gives the dull dark color to the oil and promotes off-flavors that reduce shelf-life [3]. Although the presence of high levels of chlorophyll in crude rice bran oil creates difficulties for the refiner, chlorophyll can be removed by oil bleaching [4].

Among activated clays, acid-activated montmorillonite clay has been widely used as an adsorbent in edible oil bleaching due to its higher sorption properties for

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L. L. Aung · P. Thiravetyan (✉)
Division of Biotechnology, School of Bioresources and Technology, King Mongkut’s University of Technology Thonburi, Bangkhuntien, Bangkok 10150, Thailand
e-mail: paitip.thi@kmutt.ac.th

L. L. Aung · E. Tertre
CNRS, UMR 7,285 IC2MP, Equipe HydrASA, Université de Poitiers, rue Albert Turpain, Bat. B8, 86022 Poitiers Cedex, France

P. Suksabye
Department of Environmental Sciences, Science and Technology Faculty, Suan Dusit Rajabhat University, Bangkok 10300, Thailand

N. Worasith
Department of Chemistry, Faculty of Science and Technology, Rajamangala University of Technology Krungthep, 2 Nang Lin Chi Road, Soi Suan Plu, Sathorn, Bangkok, Thailand

chlorophyll and other trace pigments. Kaolin, a low-cost adsorbent that is used in wastewater treatment [5], is abundant in Thailand. It consists mainly of kaolinite, non-clay minerals, quartz, and less frequently feldspar, illite, halloysite, montmorillonite, anastase, and gibbsite [6]. Kaolinite is a 1:1 aluminosilicate clay, $(Si_4)^{IV}(Al_4)^{VI}O_{10}(OH)_8$, which has the theoretical composition expressed in oxides of SiO_2 (46.54 %), Al_2O_3 (39.50 %), and H_2O (13.96 %). The formula indicates that there is no substitution of Si^{4+} with Al^{3+} in the tetrahedral sheet and no substitution of Al^{3+} with other ions (e.g., Mg^{2+}, Zn^{2+}, Fe^{2+}, Ca^{2+}, Na^+, or K^+) in the octahedral sheet. Thus, the net layer charge of kaolinite is zero, but, in nature, kaolinite has a small net negative charge arising from broken edges on the clay crystals. This small negative charge makes the surface active [7–9]. Many researchers have reported that the small negative permanent charge is due to an isomorphic substitution of Si^{4+} by Al^{3+} in a silica tetrahedral sheet. The edge surface contributes variable charges, which may be positive or negative depending on the pH, on the alumina face and on the edges arising from the protonation and deprotonation of exposed hydroxyl groups [10, 11]. Generally, acid treatment causes the kaolinite structure to change into amorphous metakaolin and leaches the alumina ions from the clay, leading to changes in the specific surface area, porosity, and the formation of highly active silanol and aluminol groups [6]. Acid treatment also increases the proportion of mesopores in the range of ~3–4.5 nm, which has been proposed to be suitable for the adsorption of pigment molecules into the clay [12]. Many researchers have prepared porous silica by mechanically or thermally treating amorphized kaolinite with sulfuric acid and have reported on the effects on kaolin's structural, mineral, and sorption properties [6, 12, 13]. Kaolins can be used effectively as adsorbents in the removal of dyes, such as toxic brilliant green dye [5], and of toxic heavy metals [8] from aqueous solutions, although these materials are rarely used to decolorize vegetable oil. Moreover, there is no study about the correlation between the structural, mineral and textural properties of hydrochloric or citric acid-activated Ranong kaolin and its bleaching performance. In previous studies, it has been reported that kaolin collected from Ranong province in southern Thailand has a pale yellow color and is mainly composed of kaolinite. The kaolin's structure needed to be first destroyed by mechanical activation before sulfuric acid/oxalic acid treatment could be used to enhance its adsorption capacities [12]. Kaolinite dissolution depends on the acid and its concentration [6]; kaolinite is more soluble in sulfuric acid than hydrochloric acid. Hydrochloric acid is a strong acid, and the HCl-activated clays are more effective in bleaching oil than sulfuric acid -treated clay [14]. In contrast, citric acid is a weak acid, and hence it may preserve the clay's crystal structure. It is less effective at forming surface acid sites compared with hydrochloric acid at the same concentration [15].

Thus, it was our purpose to establish a bleaching test, and this study specifically focused on the effect of chemical activation with different concentrations of hydrochloric and citric acids on the capacity of ground kaolins to remove pigments, such as chlorophyll-a molecules, from rice bran oil. Moreover, hydrochoric acid is cheaper and has been reported to be more effective than organic acids. Additional experiments on the effect of the same acid strength were done by activating the ground kaolin with different hydrochloric acid concentrations and different clay-to-acid ratios. For example, ground kaolin was treated with 2 M hydrochloric acid with a clay-to-acid ratio of 1:12 (w/v) and with 4 M hydrochloric acid with a clay-to-acid ratio of 1:6 (w/v), which gives the same acid strength as 0.5 M hydrochloric acid with a clay-to-acid ratio of 1:50 (w/v). The aim of this work was to examine the effect of surface area and alumina contents of activated Ranong kaolin on the bleaching of rice bran oil.

Materials and Methods

Materials

Pale yellow kaolin from Ranong in southern Thailand was obtained from Had Som Pan. It was washed with distilled water to remove soluble impurities, dried in an oven at 80 °C for 24 h, and then screened though a 200-mesh sieve. The sample was then ground with a Retsch planetary ball mill at 300 rpm for 1 h with a clay-to-ball weight ratio of 1:30. This sample is regarded as ground kaolin (GK). The commercial bleaching clay (montmorillonite) from Taiko Clay Marketing, Malaysia, was used as the reference clay for the bleaching tests. Degummed and refined rice bran oil was obtained from the Thai Edible Oil, Thailand. Hydrochloric and citric acid acids were AR grade and were purchased from Merck, Germany, and Ajax Finechem, Australia, respectively.

Methods

Acid Activation of Kaolin

Ground kaolin was activated with different concentrations of citric acid (0.1, 0.3, 0.5, 1.3 or 2.0 M) with a clay-to-acid ratio of 1:50 (w/v). Acid activation was carried out with mechanical stirring at 90 °C for 4 h. Samples were washed with distilled water until they reached pH 3, a value at which the sorption properties of acidified kaolin have been considered to be good [13]. Other researchers have also reported an optimum pH range of 2–4 for the clay's sorption of organic molecules [16] and 2.5–3.0 for the bleaching of vegetable oil [17]. The washed kaolin samples were then dried in an oven at 80 °C for 24 h and were gently ground with a mortar and pestle. These samples are referred to as GRC 0.1, 0.3, 0.5, 1.3, and 2. Similar samples were prepared with hydrochloric acid in concentrations of 0.5, 0.7, or 2.0 M. These samples are regarded as GRH 0.5, 0.7, and 2, depending on the acid concentration used. Preliminary studies showed that various factors, including the acid type, concentration, and the clay-to-acid ratio, all influenced the activation of kaolin and their bleaching of rice bran oil. In this regard, for this study, a temperature of 90 °C, clay-to-acid ratio of 1:50 (w/v), and a contact time of 4 h can already be considered as being optimal for bleaching. Further experiments on the effect of acid strength on kaolin's bleaching capacities, activated kaolins (designated 0.5GRH 1:50, 2GRH 1:12, and 4GRH 1:6) were also prepared with different combinations of acid and clay-to-acid ratios, i.e., 0.5 M concentration at 1:50 (w/v) ratio; 2.0 M concentration at 1:12 (w/v) ratio; and 4.0 M concentration at 1:6 (w/v) ratio. These different acid concentrations with different clay-to-acid ratios gave the same total acid strengths for each of the total acid solutions.

Characterization of Kaolin

X-ray diffraction data was collected for GK and the acid-activated samples with a Bruker® AXS model D8 Advance X-ray diffractometer equipped with Ni-filtered CuKα radiation. A Bruker® AXS model D8 Discover X-ray diffractometer equipped with a β-filtered CuKα radiation was used to investigate the initial and modified samples. Kaolin powder was randomly orientated, and diffraction patterns were collected in the 2θ range between 5 and 65° with a 0.02° step, an acquisition time of 0.4 s per step, and power at 40 kV and 40 mA. Mineral components in the X-ray diffractograms were identified by comparison with standards from the JCPDS Powder Diffraction File. FTIR spectra of activated kaolins were obtained with a Perkin Elmer (Spectrum One) spectrometer. One milligram of each sample was mixed thoroughly with 100 mg of ground potassium bromide, and the mixture was pressed into pellets. Spectra were recorded by accumulating 16 scans at 4 cm^{-1} resolution in the mid-IR range (4,000–450 cm^{-1}). For chemical analysis, kaolin was made into pellets and the chemical compositions were measured with a Bruker AXS model S4 spectrometer. Specific surface area and pore volume were determined with a Quantachrome Autosorb-1 instrument. The analysis was automated and performed with N_2 at a batch temperature of 77.3 K and a relative pressure (P/P_0) ranging up to 0.3. Before each analysis, the sample was outgassed at 300 °C. Isotherms were used to determine the specific surface area by applying the Brunauer–Emmet–Teller equation [18]. Total pore volume (V_T) was obtained from the maximum isotherm until P/P_0 was equal to ~0.99, according to the Barrett–Joyner–Halenda method [19].

Bleaching Test

The degummed and refined rice bran oil was preheated to 90 °C in an oil bath. When the oil reached the temperature, dried kaolin was added. The mixture was continuously agitated at that temperature for 30 min. The bleaching experiment was carried out at temperatures of 80–120 °C and dosage of 2–5 wt% of bleaching earth to crude oil as recommended [20]. The clay suspension was centrifuged at 3,000 rpm for 15 min and then filtered through Whatman No.5 paper to separate the clear oil and clay. Bleaching experiments were triplicated. The color change in the bleached oil was determined by means of a Spectronic 21 spectrophotometer of Bausch & Lomb with hexane used as a reference. The oil sample was diluted with hexane (1:4 v/v) and the bleaching capacity of kaolin was determined by measuring absorbance at 410 nm, which was the maximum absorption observed after running a 350- to 750-nm scan of the oil. The bleaching capacity was calculated according to the formula [21]:

$$\text{Bleaching capacity (\%)} = [(A_0 - A)/A_0] \times 100$$

where A_0 and A are the absorbance of the unbleached and bleached oil, respectively.

Triplicate measurements were carried out and the results were compared with those of commercial bleaching clay. Duncan multiple range test with 95 % confident level was conducted to classify the data for statistical analysis.

Results and Discussion

Effect of Different Acids on the Structural, Mineral, Textural Properties of Kaolins and Their Bleaching Performances

X-ray Diffraction Analysis

The XRD patterns of GK and some activated kaolins are given in Fig. 1. Kaolinite was the dominant mineral, and other nonclay minerals, quartz, illite and K-feldspar, were also found in the GK. Some kaolinite peaks overlapped with peaks for quartz and illite. The XRD patterns showed that the crystallinities of kaolinite decreased when treated with 2 M hydrochloric acid (Fig. 1a). Little variation in the patterns was observed when 0.1–0.5 M citric acid concentrations were used for activation (data not shown). The peak intensities of kaolinite slightly decreased when the concentration used exceeded 0.5 M citric acid (Fig. 1b). Acid

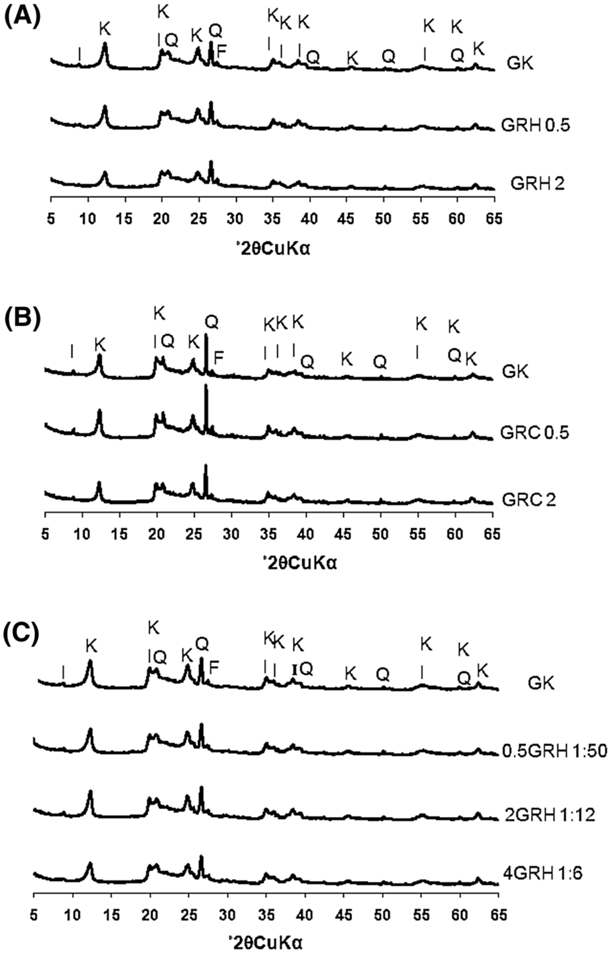


Fig. 1 Comparison of the XRD patterns obtained from randomly orientated preparations of the initial and activated samples treated with different acid concentrations: **a** ground kaolin (*GK*) and hydrochloric acid-treated kaolin (*GRH 0.5* to *GRH 2*); **b** ground kaolin (*GK*) and citric acid-treated kaolin (*GRH 0.5* to *GRH 2*); **c** ground kaolin (*GK*) and samples (*GRH*) reflux with different combinations of hydrochloric acid concentration and clay-to-acid ratios (*0.5GRH 1:50*, *2GRH 1:12* and *4GRH 1:6*)

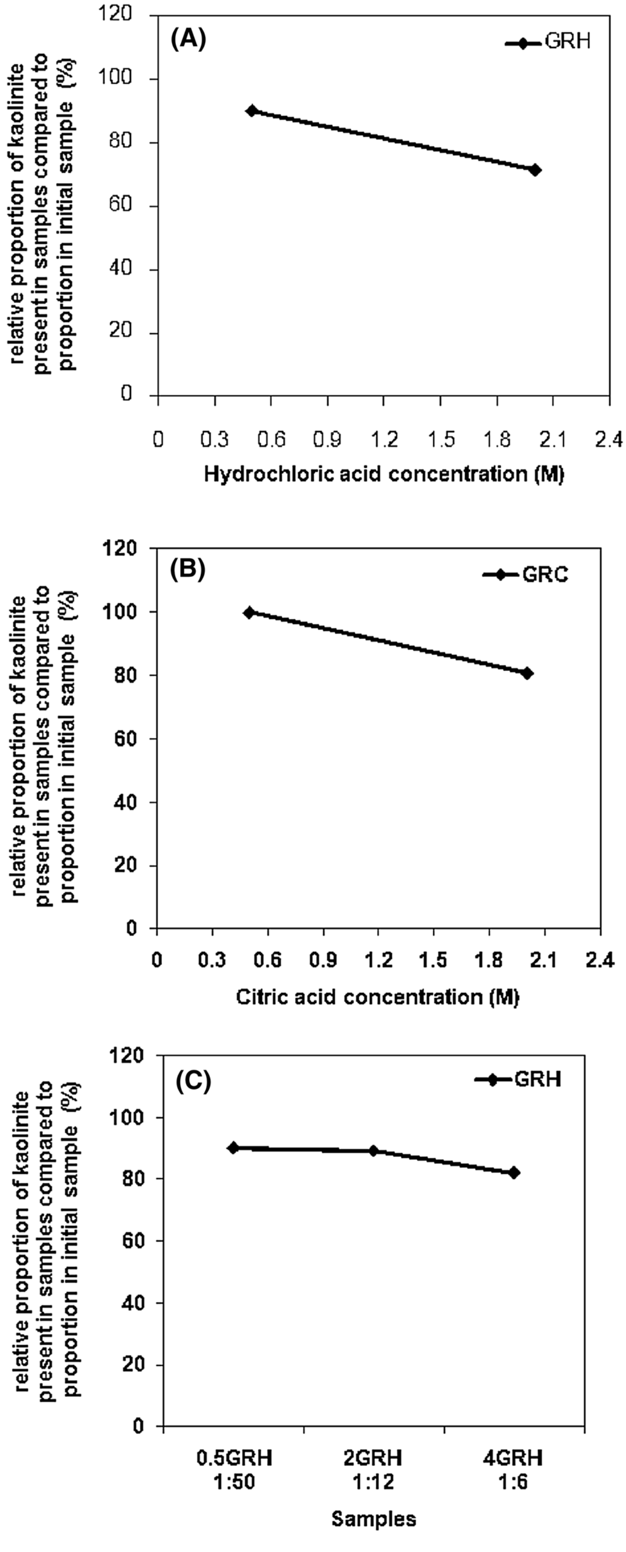
treatment caused mineral dissolution and disordered the clay structures resulting in the decrease in kaolinite crystallinity. The non-clay minerals, quartz, illite, and K-feldspar, were resistant to the acid treatments. These results are similar to those of Noyan [22], who found that sulphuric acid treatment has an effect on smectite groups but not on non-clay minerals. The relative proportion of kaolinite present in these samples was calculated based on the intensities for the d_{001} reflection of kaolinite (Fig. 1) and assuming 100 % kaolinite for the GK sample. For hydrochloric acid-leached kaolin, the kaolinite proportions decreased to ~90 % for GRH 0.5 and further decreased to ~85 % for GRH 2 (Fig. 2a). The intensities of kaolinite also decreased when the kaolin was treated with citric acid (Fig. 2b). The relative proportion of kaolinites was ~100 % for GRC 0.5, and it decreased to ~81 % for GRC 2, indicating that weak organic acid also destroys kaolin's structure.

Fourier Transform Infrared Spectroscopy

FTIR spectra of GK and some of the acid-activated kaolins are shown in Fig. 3, and the corresponding band assignments are shown in Table 1. For GK, hydroxyl absorption bands were observed at 3,620 and 3,696 cm^{-1} corresponding to the hydrogen bonded hydroxyl groups situated between the tetrahedral and octahedral sheets and free hydroxyl groups at the dioctahedral layer surface of kaolinite, respectively (Fig. 3a-I, b-I). There was little change in the hydroxyl peaks when the kaolin was treated with 2 M hydrochloric acid or 2 M citric acid. The hydroxyl vibration bands decreased in GRH 2 and GRC 2 samples, indicating that the hydrated protons penetrated into the octahedral network and attacked the structural hydroxyl groups. In this way, dehydroxylation occurred and alumina leached successively from the octahedral sheet of the activated kaolins [23].

The bands at 1,031 and 1,008 cm^{-1}, which correspond to Si–O stretching vibrations of kaolinite in activated kaolin, diminished when the GK was treated with 2 M hydrochloric acid (Fig. 3a-II) due to structural changes in the tetrahedral cations. The shoulder at 1,090 cm^{-1} increased with increasing acid concentration, and the most intense peak was obtained for GRH 2. This result suggests the presence of a significant proportion of a Si-rich amorphous phase in this sample. The intense 912 cm^{-1} peak, due to Al–Al–OH bending vibrations, was also reduced for the GRH 2 sample. This indicates that the alumina was leached when the kaolin was treated with 2 M hydrochloric acid. The band at 805 cm^{-1} for the HCl-treated kaolin increased intensity with increasing acid concentration. This peak is due to the formation of free amorphous silica. Quartz showed a peak at 790 cm^{-1} [24, 25] that was present in the initial and acid-treated samples. The band at 753 cm^{-1} was assigned to Si–O–Al stretching vibration of the clay sheet; the band at 693 cm^{-1} corresponded to Si–O stretching of kaolinite, the band at ~537 cm^{-1} corresponded to Si–O–Al (octahedral) stretching, and those at 469 and 430 cm^{-1} corresponded to Si–O bending vibrations [26], which also decreased in the GRH 2 sample.

There were few structural changes due to citric acid treatments as compared with the changes due to hydrochloric acid treatments. The shoulder at 1,090 cm^{-1} increased and the bands at 912 cm^{-1} decreased in the citric acid-treated kaolins with increasing acid strength. This showed that citric acid treatment also attacked the kaolin's structure, leached the alumina, and enhanced the silica phase formation. FTIR results are in agreement with the XRD results, indicating that the kaolinite structure was partially preserved in the acid-activated samples (Fig. 1). These results also agree and show that the alumina was leached and the silica phase was formed simultaneously during acid treatment (Table 2).



◀ **Fig. 2** Relative proportions of kaolinite present in the activated kaolins as a function of the different acid concentrations for hydrochloric acid-activated kaolins (*GRH 0.5* to *GRH 2*) (**a**); citric acid-activated kaolins (*GRH 0.5* to *GRH 2*) (**b**); and the different hydrochloric acid concentration using different clay-to-acid ratios (*0.5GRH 1:50*, *2GRH 1:12* and *4GRH 1:6*) (**c**). The relative proportions of kaolinite were calculated based on 100 % kaolinite in the initial ground sample prior to acid activation. The proportions were calculated based on the intensity values recorded using XRD for the d_{001} reflection of kaolinite

Adsorption Studies, Textural Properties and Chemical Compositions

The bleaching capacities of GK and acid-activated kaolins (GRH and GRC samples) are shown in Table 2. When GK was treated with 0.5 M hydrochloric acid, the capacity was dramatically increased from ~50 to ~83 %. Among GRH samples, GRH 0.5 gave the optimum bleaching value of ~83 %, which was comparable to that of commercial clay (~82 %). Beyond this optimum condition, the capacities decreased with increasing acid concentration and reached ~78 % at the 2 M hydrochloric acid concentration. Citric acid ground kaolins gave the same results as hydrochloric acid-treated samples. Kaolin's sorption property was increased to ~71 % at 0.1 M citric acid concentration (for GRC 0.1). The bleaching capacities continuously increased with increasing acid concentrations. At the optimum condition, GRC 0.5 sample had a bleaching capacity of ~81 % which was very close to that of commercial clay. After that, the capacities slightly decreased to ~75 % when the citric acid concentration was further increased to 2 M. The results indicated that hydrochloric acid treatment was more effective in removing color from the oil than the citric acid treatment. Christidis [27] studied the effects of hydrochloric acid leaching of smectites and reported that hydrochloric acid is a strong acid and is degraded into H^+ and Cl^- ions in the presence of water. The clay is protonated and the metal chlorides produced are soluble in water and can be removed in the clay washing step.

The bleaching capacities were not associated with the changes of the surface area, pore volume and pore size with acid treatment (Table 2). The specific surface area, for activated samples, showed a regular trend of increasing when treated at low concentration and decreasing with increasing acid concentration. The optimum value of the bleaching capacities obtained for both GRH 0.5 and GRH 0.7 were ~83 %, although GRH 0.5 had the lowest specific surface area among the HCl-activated ground samples. Compared with GK, GRH 0.5 showed an approximately 3.3-fold increase in specific surface area from ~61 to ~204 m^2/g and a 1.3-fold increase in pore volume from 0.3 to 0.4 cm^3/g, whereas GRH 0.7 had an approximately 4.4-fold increase in the specific surface area to ~269 m^2/g and a 1.7-fold increase in the total pore volume to 0.5 cm^3/g. A previous

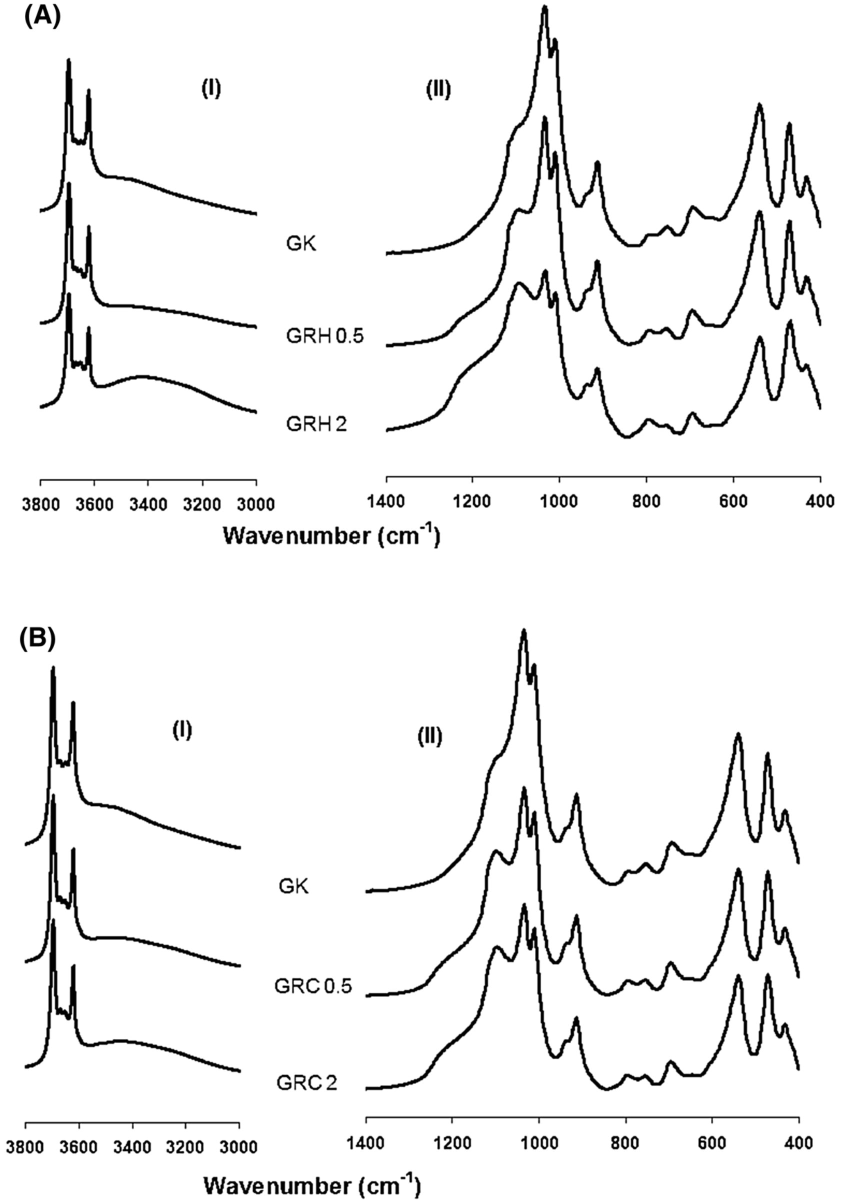


Fig. 3 Comparison of the FTIR spectra of the initial and activated samples. **a** Ground kaolin (*GK*) and samples refluxed with 0.5 M to 2 M citric acid (*GRH 0.5* to *GRH 2*); **b** ground kaolin (*GK*) and samples refluxed with 0.5 M to 2 M hydrochloric acid (*GRH 0.5* to *GRH 2*)

study [12] demonstrated that a combined grinding and sulfuric acid treatment dramatically increased the specific surface area, pore volume, and number of mesopores in the 3.0–4.5 nm range of kaolins, and had better bleaching capacity than untreated kaolins. But, in this study, increasing mesopore contents with increased hydrochloric or citric acid concentration did not relate to decolorization capacity (Table 2). This means that not only is mesopore content involved in decolorization but alumina contents might be another important factor. The acid activation enhances the sorption properties of clays by manipulating its structural, mineral and physico-chemical properties with a limited decomposition of its crystal structure [29–31]. Acid treatments partially or totally destroy the kaolin's crystal structure, disintegrate the clay particles, and decompose the minerals, thereby forming an amorphous silica phase [6, 13, 25]. Results from SEM/EDX analysis of the Ranong kaolin in previous studies indicated that hot sulfuric or oxalic acid treatments of the ground sample resulted in the formation of products with globular morphology [25]. Upon acid activation, specific surface area, porosity and number of acid centers are also changed in the activated clay due to the leaching of alumina and other mineral impurities [28, 32–40]. The increase in surface area and surface acidity of the activated clays largely affect their bleaching properties. Smectite-derived clays have high sorption properties due to their high surface area, and these properties are enhanced with acid activation [41–44]. After getting the maximum conditions for the GRH 0.7 sample, the specific surface area decreased to ~260 m^2/g and pore volume increased to

~0.6 cm^3/g in GRH 2. This result is in agreement with the report of smectite-derived clays that described high acid concentration destroying the clay lamellar structure, leading to decreased specific surface area [45, 46].

Although GRH 2 had the higher specific surface area and pore volume than GRH 0.5, it had the lower bleaching value of ~78 % as a result of the continuous dissolution of the kaolinite and deposition of amorphous silica (Figs. 1a, 2a, 3a). Similar results had been reported for citric acid treated clays, where the maximum values of the specific surface area obtained for GRC 1.3 was ~296 m^2/g, although its bleaching value was less than that of GRC 0.5, which had the specific surface area of ~246 m^2/g. GRC 0.5 had the greatest bleaching value of ~81 %, whereas that of GRC 1.3 was ~77 %, indicating that the surface area is not a sole parameter for getting the maximum bleaching performance. The highest bleaching value is not related to maximum surface area and pore volume because the pigments attach the adsorbent acidic sites through the combination of electrostatic interactions and chemical bonds [25, 28, 34, 47–49]. The bleaching capacity was decreased to ~75 % following the reduction in specific surface area to ~260 m^2/g in GRC 2.

Table 1 Important FTIR bands of initial and activated kaolin clays with their possible assignments

Bands (cm^{-1})	Assignments
3,696	γOH (structural hydroxyl group) valence linked to Al–OH
3,620	
3,445	γOH (physisorbed water)
1,008, 1,031, 1,114	γSi–O
912	δOH deformation AlOH
790	Quartz
753	γSi–O
693	γSi–O valence characteristic of kaolinite
537	γSi–O–Al
469	δSi–O
430	Related Si–O–Si

The chemical compositions of the activated samples (GRH and GRC) are also reported in Table 2. The SiO_2 content increased with increasing acid concentration. When the GK sample was treated with 0.5 M hydrochloric acid, the SiO_2 content increased from ~54 to ~64 %. Further increasing the acid concentration to 2 M hydrochloric acid increased the silica content to ~73 %. In parallel, the Al_2O_3 content decreased from ~42 to ~32 % for GRH 0.5 and ~24 % for GRH 2. Citric acid treatment also showed the same concentration trend as hydrochloric acid. The SiO_2 content slightly increased to ~62 % in GRC 0.5 and dramatically increased to ~70 % in GRC 2, indicating formation of an amorphous silica phase as detected by FTIR (Fig. 3). The Al_2O_3 content decreased to ~34 % in GRC 0.5 and ~27 % in GRC 2. After acid treatment on GK, the Al-to-Si ratio decreased from ~0.9 to ~0.4 in both GRH 2 and GRC 2.

Previous studies found that the bleaching capacity of initial unground kaolin lower than that of initial ground kaolin samples after the same sulfuric acid concentrations [12].

Table 2 Some elemental analyses, specific surface area (*SSA*), pore volume (V_p), mesopore volume (V_{me}) and bleaching capacities (*BC*) of the initial ground kaolin and the activated samples

Sample	SiO_2 (%)	Al_2O_3 (%)	Al:Si	SSA (m^2/g)	V_p (cm^3/g)	V_{me} (cm^3/g)	BC (%)
GK	54.1	42	0.9	60.7	0.30	0.30	49.8 ± 8.5^{a}
CBC	–	–	–	–	–	–	82.1 ± 3.2^{c}
Samples ground and heated at 80 °C prior to reflux with different concentrations of hydrochloric acid equal to 0.5, 0.7, and 2 M using clay/acid ratio of 1:50							
GRH 0.5	64.4	32.1	0.6	204.1	0.40	0.38	83.3 ± 2.4^{c}
GRH 0.7	65.1	31.2	0.5	268.6	0.51	0.49	82.6 ± 0.8^{c}
GRH 2	72.7	24.4	0.4	259.2	0.56	0.54	$77.7 \pm 0.3^{b,c}$
Samples ground and heated at 80 °C prior to reflux with different concentrations of citric acid equal to 0.1, 0.3, 0.5, 1.3 and 2 M using clay/acid ratio of 1:50							
GRC 0.1	58.3	37.3	0.7	159.6	0.32	0.29	70.6 ± 5.0^{b}
GRC 0.3	62.3	34.2	0.6	201.7	0.40	0.19	$80.4 \pm 2.0^{b,c}$
GRC 0.5	62.4	34.2	0.6	245.9	0.54	0.51	81.1 ± 0.9^{c}
GRC 1.3	67.4	29.5	0.5	295.5	0.58	0.55	$77.1 \pm 4.4^{b,c}$
GRC 2	69.9	26.8	0.4	260.3	0.62	0.60	$75.0 \pm 3.9^{b,c}$
Samples ground and heated at 80 °C prior to reflux with same hydrochloric acid strength using different acid concentrations and different clay/acid ratio							
0.5GRH 1:50	64.4	32.1	0.6	204.1	0.40	0.38	83.3 ± 2.4^{c}
2GRH 1:12	72.2	24.8	0.4	213.9	0.45	0.44	$79.6 \pm 13.7^{b,c}$
4GRH 1:6	76.3	20.9	0.3	266.9	0.69	0.68	$74.4 \pm 5.7^{b,c}$

Duncan multiple range test with 95 % confident level was used to classify the group of data in the following column

GK initial ground kaolin, *CBC* commercial bleaching clay, *0.5GRH 1:50* samples ground and reflux with 0.5 M hydrochloric acid with clay-to-acid ratio of 1:50 (v/w), *2GRH 1:12* samples ground and reflux with 2 M hydrochloric acid with clay-to-acid ratio of 1:12 (w/v), *4GRH 1:6* samples ground and reflux with 4 M hydrochloric acid with clay-to-acid ratio of 1:6 (w/v)

In agreement with the other authors [25, 50], acid leaching of ground kaolin enhances the alumina dissolution from the activated samples. Sugiyarma et al. [51] studied the effect of grinding on kaolinite's structure based on the XRD patterns of ground kaolinite using a radial distribution function. They reported that grinding decreased the oxygen coordination number and the corresponding interatomic distance around alumina, whereas it did not affect the SiO_4 tetrahedra of kaolinite. This study also found that leaching the alumina content from the kaolin affected the kaolin structure and, consequently, decreased the relative proportions of kaolinite in the activated samples (Table 2; Figs. 1, 2). In the present work, bleaching performances were found to be largely dependent on the alumina contents that were associated with the partial preservation of the kaolin's structure. Kaolin's sorption properties were high at low acid concentrations for both GRC and GRH samples. At optimal conditions, the maximum bleaching values were 83.3, 82.6 and 81.1 % (Table 2), while the alumina contents were ~32, ~31, and ~34 % in GRH 0.5, GRH 0.7, and GRC 0.5, respectively. In activation of the ground kaolin with high acid concentrations (≥1.3 M), the bleaching performances decreased following the leaching of alumina content in the activated samples. This is due to the leaching of alumina, and consequently a reduction in kaolinite proportion and phase transformation to amorphous silica (Table 2; Figs. 2, 3).

Effect of the Same Hydrochloric Acid Strength Using Different Clay/Acid Ratios and Different Acid Concentrations on the Structural, Mineral, Textural Properties of Kaolin and Their Bleaching Performances

For further studies of the effects of hydrochloric acid volume used on the kaolin's structural and sorption properties, ground kaolin GK was treated with different concentrations and different clay-to-acid ratios (2 M hydrochloric acid with clay-to-acid ratio of 1:12; 4 M hydrochloric acid with clay-to acid-ratio of 1:6) to give the same acid strength as 0.5 M hydrochloric acid with a clay-to-acid ratio of 1:50. Although these samples were treated with the same total acid strength, the intensities of kaolinite decreased with increasing acid concentration from 0.5 to 4 M hydrochloric acid (Fig. 1c). The relative proportion of kaolinite decreased from ~90 to ~86 % when the acid concentration used was increased from 0.5 to 4 M hydrochloric acid (Fig. 2c).

These activated samples also had different bleaching capacities (see Table 2). For example, 0.5GRH 1:50 gave the value of ~83 %, 2GRH 1:12 gave about ~80 %, and 4GRH 1:6 gave ~74 %. This means that treating the ground kaolin with a lower acid concentration but with a high clay-to-acid ratio (e.g., 0.5 M HCl with clay to acid ratio of 1:50) gave better results than did the higher acid concentration with the low clay-to-acid ratio (e.g., 4 M HCl with clay-to-acid ratio of 1:6). Moreover, low acid concentration and high clay-to-acid ratio was sufficient to get the optimum bleaching value of the kaolin, although its surface area and pore volumes were the lowest among the three acid treatments. Similarly, the sample 4GRH 1:6 had the lowest bleaching capacities although its surface area and pore volumes were the highest among these samples. The surface area and pore volume of 0.5GRH 1:50 were ~204 m^2/g and ~0.4 cm^3/g, whereas those of 4GRH 1:6 were ~267 m^2/g and ~0.7 cm^3/g, respectively. This also confirmed that the bleaching capacities were not related to the surface area and pore volumes of the activated kaolins. The smectite-derived clays also needed to be treated with diluted acid to get the maximum bleaching values, which were not directly related with the highest surface area [27, 28, 34].

Although 0.5GRH 1:50 had the lowest surface area, it had ~32 % Al_2O_3 content, which gave the maximum bleaching value of ~83 %. When the acid concentration was increased to 4 M with an clay-to-acid ratio of 1:6, the alumina content continuously decreased to ~21 % along with steadily decreasing bleaching performances for 4GRH 1:6. This may be due to the extensive leaching of alumina from the activated kaolin. These results also agreed with the finding that the alumina content in the activated kaolins influenced their bleaching properties. Similar results have been reported for smectites by many authors [35], who described the acid treatments opening the edges of the clay platelets and causing a charge deficiency in the activated samples, which consequently enhanced their bleaching performance corresponding to the partial dissolution of alumina from the samples. They, however, also reported that sorption properties decreased at high acid concentration along with extensive leaching of alumina from the clay, corresponding to a collapse in clay structure.

Conclusions

The bleaching capacities of ground kaolin were enhanced with acid activation. The highest sorption values were not associated with maximum surface area, pore volume and pore size of the treated clays. Acid treatment increased clay surface area and later decreased clay surface area corresponding with the dissolution of alumina at severe treatment. This study found that the dilute organic or inorganic acids (e.g., at 0.5 M concentration) can enhance color removal of ground kaolin due to the formation of the active acid centers. The weak acid concentrations also partially preserve the kaolinite structure, which is related to the alumina contents in the samples. Thus, the preservation of the kaolinite structure is a key parameter for optimizing the bleaching performance of Ranong kaolin. The aluminum sites on the kaolinite structure play a vital role in the sorption of chlorophyll-a molecules from the rice bran oil.

Acknowledgments We acknowledge financial support from the Thailand Research Fund, Thailand International Cooperation Agency, and French Embassy in Thailand according to the Royal Golden Jubilee Program (RGJ program), as well as support from the Agricultural Research Development Agency (Public Organization).

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