Clay Minerals, (2014) **49**, 513–526

The capacity of activated kaolins to remove colour pigments from rice bran oil: the effects of acid concentration and pre-heating prior to activation

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(*Received 17 January 2014; revised 23 July 2014; Editor: George Christidis*)

ABSTRACT: This study focuses on the effects of both thermal treatment (between 80 and 700ºC) and chemical activation (concentration of sulfuric acid between 0.3 and 2 M) of natural Ranong kaolins (ground or not) from Thailand to remove the undesirable colour of rice bran oil. The mineralogical, physical and physicochemical properties of the initial and activated kaolins are discussed in relation with the bleaching effectiveness of the activated sample investigated. Generally, the greater the temperature used before the activation step and the concentration of sulfuric acid used during activation, the greater the structural degradation of the kaolinite; Al is removed from the octahedral sheet of kaolinite and amorphous SiO_2 dominates the samples. The measured maximum bleaching capacity is not necessarily obtained when using the activated kaolin having the highest specific surface area and pore volume; rather, the bleaching capacity is dependent on both alumina contents and proportion of kaolinite in the samples. Indeed, the partial preservation of the kaolinite structure is crucial to obtain a good bleaching capacity of kaolin in relation to the preservation of the aluminol sites which are likely to be involved in the adsorption of unsaturated molecules present in the rice bran oil. Moreover, as previously demonstrated, a partial leaching of Al from octahedral sheets of kaolin is also an important factor in order to obtain good bleaching capacities. Finally, the optimal preheating temperature and concentration of sulfuric acid which permit the best bleaching capacity of kaolin are reported.

KEYWORDS: natural clay material, kaolinite, colour organic pigments, bleaching, rice bran oil.

Rice bran oil, which is produced from rice bran and the germ of *Oryza sativa* seeds, is primarily consumed in Asian countries and is of interest for its potential health benefits because it contains approximately 80% unsaturated fatty acids, mainly as linoleic acid (Bhattacharyya *et al.*, 1985). Crude rice bran oil and degummed and refined rice bran oil, however, have an undesirable colour due to different pigments such as chlorophyll-a ($C_{55}H_{72}MgN_4O_5$), for which the structural formula

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DOI: 10.1180/claymin.2014.049.4.02

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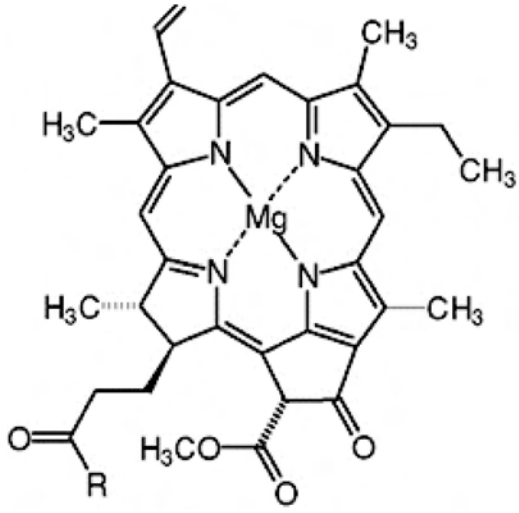

FIG. 1. Chemical structure of chlorophyll-a, one of the main unsaturated molecules in crude rice bran oil.

is illustrated in Fig. 1. During heating, this type of molecule is decomposed into pheophytin pigment compounds, which results in a dull and dark-coloured oil, causes an unpleasant flavour, and promotes oil oxidation, consequently reducing the shelf-life of the oil (Diosady, 2005).

Adsorption is the most widely used method to remove pigments from edible oils. The main sorbents that have been studied for the removal of carotene, chlorophyll and other unwanted components from edible oils are different activated clays (Stout *et al.*, 1949; Kheok & Lim, 1982; Falaras *et al.*, 1999; Hussein *et al.*, 2001; Temuujin *et al.*, 2006; Nguetnkam *et al.*, 2008, among others), activated carbon (Madu & Lajide, 2013), and silica-based products (Krishna, 1992; Rossi *et al.*, 2003) due to their low cost and/or high cation exchange capacity and/or high specific surface area (SSA). Acid treatment induces the leaching of Al^{3+} from the clay structure, causing a charge deficiency in the clay lattice and, hence, enhancing the sorption properties of the clays (Kheok & Lim, 1982). However, some authors (James *et al.*, 2008; Didi *et al.*, 2009) have also observed that when high sulfuric acid concentrations (>5 M) are used during the reflux step, the sorption properties of some swelling clays are reduced due to the collapse of the clay structure, caused by excessive leaching of alumina from the octahedral sheet. Moreover, an increase of temperature during the adsorption step generally enhances the adsorption capacity of the activated clays towards organic pigments (Nguetnkam *et al.*; 2008; Wu & Chin, 2009). Furthermore, although natural kaolins, complex assemblages rich in kaolinite, can efficiently adsorb basic dyes (Nandi *et al.*, 2009) and toxic brilliant green dye (Shirsath *et al.*, 2013) from aqueous solution, these materials generally exhibit low extent of pigment sorption. In this context, several methods have been reported to improve their sorption properties, such as chemical activation (Panda *et al.*, 2010), thermochemical treatment (de Sales *et al.*, 2013), and combined mechanical and chemical activation (Dudkin *et al.*, 2005; Tang *et al.*, 2010; Worasith *et al.*, 2011a,b). Generally, these treatments partially or completely destroy the structure of the kaolinite crystals and leach the constituent elements from the mineral, which in turn induces dramatic changes in the SSA, porosity, and nature and number of sorption sites located on the surface of the whole material. For example, Worasith *et al.* (2011a) demonstrated that a process combining mechanical and chemical treatment dramatically increased the SSA, pore volume, and number of mesopores in the 3–4.5 nm range of kaolins, which in turn leads to a material with a better bleaching capacity than untreated kaolins. However, to our knowledge, the effect of heating the kaolin or other clay materials prior to their mechanical and/or chemical treatment on their capacity of adsorb organic and colour pigments present in edible oils, like rice bran oil, has not been assessed.

The objectives of this study are (1) to prepare and characterize activated kaolins from natural material submitted to various thermal, mechanical, and chemical treatments and (2) to test the ability of these materials to remove organic and colour pigments present in rice bran oil. This study specifically focuses on the effect of both thermal treatment (between 80 and 700ºC) and chemical activation using different concentrations of sulfuric acid (between 0.3 and 2 M) on the pigments removal efficiency of ground or unground kaolins. The structural, chemical, and textural properties of each activated kaolin sample are first compared to those of the initial material. Then, the bleaching capacities of the activated samples are discussed as a function of their physico-chemical characteristics. Finally, our data obtained with a pre-heating step before acidic reflux are compared with data from literature obtained without a pre-heating step, and

industrial implications of the results obtained in this study are given.

MATERIALS AND METHODS

Materials

Kaolin obtained from Ranong, Thailand, was washed with distilled water to remove soluble impurities and dried in an oven at 80ºC for 24 hours. The sample was then gently crushed with a pestle and mortar and sieved to 200 mesh to obtain a clay powder, referred to as UGK (unground kaolin). Furthermore, a total of 10 g of UGK were ground for 1 hour using a Retsch planetary ball mill rotating at 300 rpm. This new material is referred to as GK (ground kaolin).

Degummed and refined rice bran oil was obtained from Thai Edible Oil Co. Ltd., Thailand. This oil has a greenish-brown colour (65 Yellow, 3.5 Red) due to the presence of chlorophyll-a (15.35 ppm). The acid value and peroxide value of rice bran oil are 0.28 (% oleic acid) and 16 meq/kg, respectively.

Methods

Sample preparation. UGK was heated for 1 hour in a muffle furnace at temperatures ranging from 100ºC to 700ºC. Then, 10 g of each heated sample was refluxed with 500 mL of 2 M sulfuric acid (Analar grade) at 90ºC for 4 hours under agitation. This procedure was chosen following the results of a previous study (Worasith *et al.*, 2011a) which reported that refluxing kaolin using 2 M sulfuric acid at 90ºC for 4 hours yielded maximum bleaching capacity without preheating kaolin. Then, samples were washed with distilled water until the pH of the clay suspension reached 3, corresponding to the pH for which bleaching vegetable oil is optimum (Girgis, 2005). Subsequently, the samples were dried at 80ºC for 24 hours and were gently crushed. These samples are referred to as 100UG 2 to 700UG 2 depending on the heating temperature used during preparation (FUG 2 samples as generic names; see Table 1 for the labelling of the samples).

GK was subjected to the same treatments to test the effect of small particles on the bleaching results. These samples were designated as 100GR 2 to 700GR 2 (FGR 2 samples as generic names; Table 1). Additional samples were also prepared from GK and by using a sulfuric acid concentration other than 2 M during the activation step (0.3, 0.5 and 1 M; 100GRS samples). These samples, which were obtained after heating at 100ºC prior to reflux, are referred to as 100GR 0.3, 100GR 0.5 and

TABLE 1. Relation between the sample names and some physicochemical parameters used for their preparation.

	Sample	*T* (ºC) treatment before chemical activation	H_2SO_4 concentration used for reflux (M)
Unground	UGK	–	–
	100UG 2	100	2
	300UG 2	300	2
	500UG 2	500	2
	700UG 2	700	2
Ground	GK	–	–
	100GR 2	100	2
	300GR 2	300	2
	500GR 2	500	2
	700GR 2	700	2
	100GR 0.3	100	0.3
	100GR 0.5	100	0.5
	100GR 1	100	1
	100GR 2	100	2
	80GR 0.3	80	0.3
	80GR 1	80	1
	80GR 2	80	2

100GR 1, depending on the concentration of sulfuric acid used during preparation (Table 1). Finally, some samples were also prepared using a preheating step at 80ºC and a reflux performed with sulfuric acid concentrations equal to 0.3, 1 and 2 M. These last samples were designated as 80GR 0.3, 80GR 1 and 80GR 2 (Table 1) with 80GRS as generic names.

Analytical procedures. X-ray diffraction (XRD) patterns were obtained using a Bruker® AXS D8 Discover X-ray diffractometer equipped with a beta-filtered Cu-$K\alpha$ radiation source. The patterns were recorded in the 2θ range 5 to 65º 2θ with a 0.02º 2θ step and an acquisition time of 0.4 s per step. FTIR spectra were recorded in KBr pellets samples at a resolution of 4 cm^{-1} in the mid-IR range of 4000−400 cm^{-1} with a Nicolet 510 FTIR spectrometer.

The elemental chemical compositions of the initial and activated samples were obtained using pellets and a Bruker AXS model S4 spectrometer equipped with a WD-XRF detector. An Autosorb Automated Gas Sorption instrument was used to determine the SSA and pore volume of the samples. The measurements were performed at a batch temperature of 77.3 K and a relative pressure (P/P_0) ranging from 0 to 1; prior to analysis, the samples were degassed with nitrogen gas at 300ºC. The SSA was determined by the Brunauer-Emmet-Teller (BET) method (Brunauer *et al.*, 1938). The total pore volume was obtained by treating the entire isotherm until P/P_0 was equal to ~0.99 according to the Barrett-Joyner-Halenda (BJH) method (Barrett *et al.*, 1951).

For the bleaching experiment, the activated samples were added to rice bran oil that had been preheated at 90ºC at a solid-oil ratio of 2 wt.%. The mixtures were agitated at approximately 150 rpm for 30 minutes and the oil was then centrifuged and filtered through Whatman® No.5 filter paper. After a full screening in the 350−750 nm range, we demonstrated that 410 nm corresponded to the wavelength for which absorbance of rice brain oil was maximum. Then, bleaching capacities of kaolins were determined by measuring the absorbance at 410 nm using UV-visible spectroscopy. Before measurements the oil was diluted in hexane. The bleaching capacities were calculated according to the following formula:

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

where A_o and A are the absorbances at 410 nm of the unbleached and bleached oil, respectively.

RESULTS AND DISCUSSION

Mineralogy, chemical composition, and textural properties of the initial and activated samples

Initial samples (UGK and GK). The XRD traces obtained for the UGK sample are shown in Fig. 2a. Kaolinite is the dominant mineral in this sample along with illite, quartz and minor K-feldspar. Fig. 3a-I shows the Fourier transform infrared spectroscopy (FTIR) spectrum of the UGK sample in the hydroxyl-stretching region of kaolinite (Van der Marel & Krohmer, 1969). The spectrum of UGK exhibits two well resolved bands at 3620 and 3696 cm^{-1}, and two less resolved additional bands at 3669 and 3653 cm^{-1}, corresponding to OH stretching vibrations in kaolinite (Ledoux & White, 1964; Barrios *et al.*, 1977; Rouxhet *et al.*, 1977). In the 1400−400 cm^{-1} range (Fig. 3a-II), the Si−O stretching vibrations of the clay network are clearly observed at 1114, 1031 and 1008 cm^{-1}. The FTIR spectrum also contains a band at 790 cm^{-1} that is attributed to quartz (Worasith *et al.*, 2011b), a phase clearly detected also by XRD. The bands at 753 and 693 cm^{-1} correspond to Si−O stretching (Ekkose, 2005), the one at ~537 cm^{-1} corresponds to Si−O−Al (octahedral) stretching, and those at 469 and 430 cm^{-1} correspond to Si−O bending vibrations (Farmer, 1974). This variable position of these bands could be due to the presence of different accessory minerals in the sample (quartz, kaolinite, illite and K-feldspars). UGK is characterized by a Al/Si ratio of ~0.9 and has a low SSA of ~42 m^2/g (see Tables 2 and 3 respectively).

Grinding does not change the bulk chemical composition and mineralogy of kaolin (see results obtained for GK sample in Table 2 and Fig. 2b). However, grinding produces small clay particles which leads to a smaller coherent scattering domain that causes a decrease of the relative intensities of some reflections in the XRD pattern of the GK sample compared to that of UGK (see Fig. 2). Grinding increases the SSA up to ~61 m^2/g (see Table 3).

Effect of pre-heating UGK and GK samples prior to acid treatment in 2 M H_2SO_4. The XRD patterns of unground samples activated in 2 M H_2SO_4 and preheated before activation at temperatures of 100−700ºC are shown in Fig. 2a. Preheating UGK at 100ºC prior to reflux with 2 M sulfuric acid did not affect the mineralogy of the sample, but the kaolinite diffraction maxima were slightly reduced

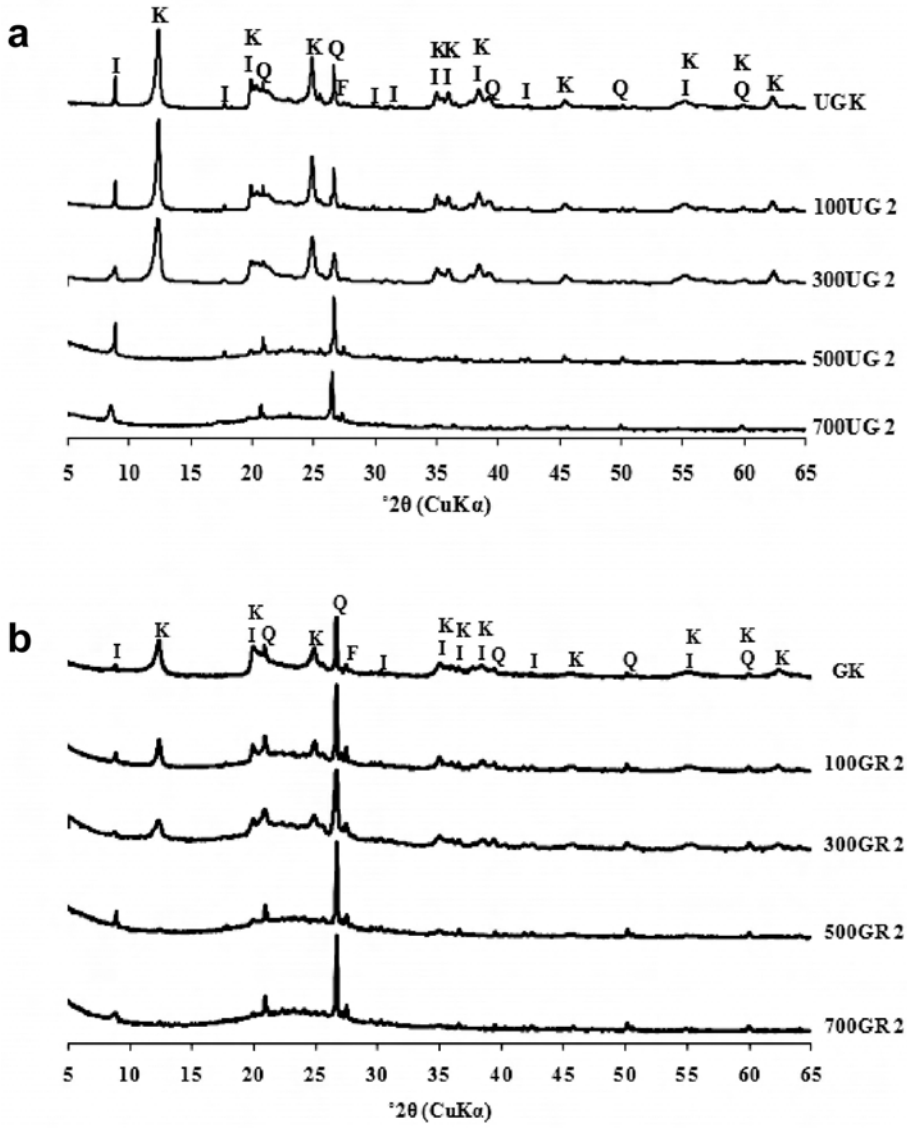

FIG. 2. Comparison of the XRD patterns obtained from randomly orientated preparations of the initial and activated samples heated at different temperatures from 100ºC to 700ºC prior to refluxing with 2 M sulfuric acid. (a) unground kaolin (UGK) and activated unground kaolins (100UG 2 to 700UG 2); (b) ground kaolin (GK) and activated ground kaolins (100GR 2 to 700GR 2). K = kaolinite, I = illite, Q = quartz, F = K-feldspars.

when the sample was heated at 300ºC (see Fig. 2a). When the preheating temperature was equal to or exceeded 500ºC, the kaolinite reflections disappeared, while those of illite, K-feldspar and quartz remained. The relative proportion of kaolinite in these samples was calculated based on the intensity values recorded for the d_{001} reflection of kaolinite in the XRD data (Fig. 2a) and assuming 100% kaolinite content for the UGK sample (initial sample submitted to any thermal treatment). The proportion of kaolinite in the sample preheated at 100ºC is the same as that of the original sample (UGK); it decreased slightly for the sample preheated at 300ºC (300UG 2 sample) and strongly decreased to ~3% for samples preheated at higher temperatures (500UG 2 and 700UG 2) (see Fig. 4a).

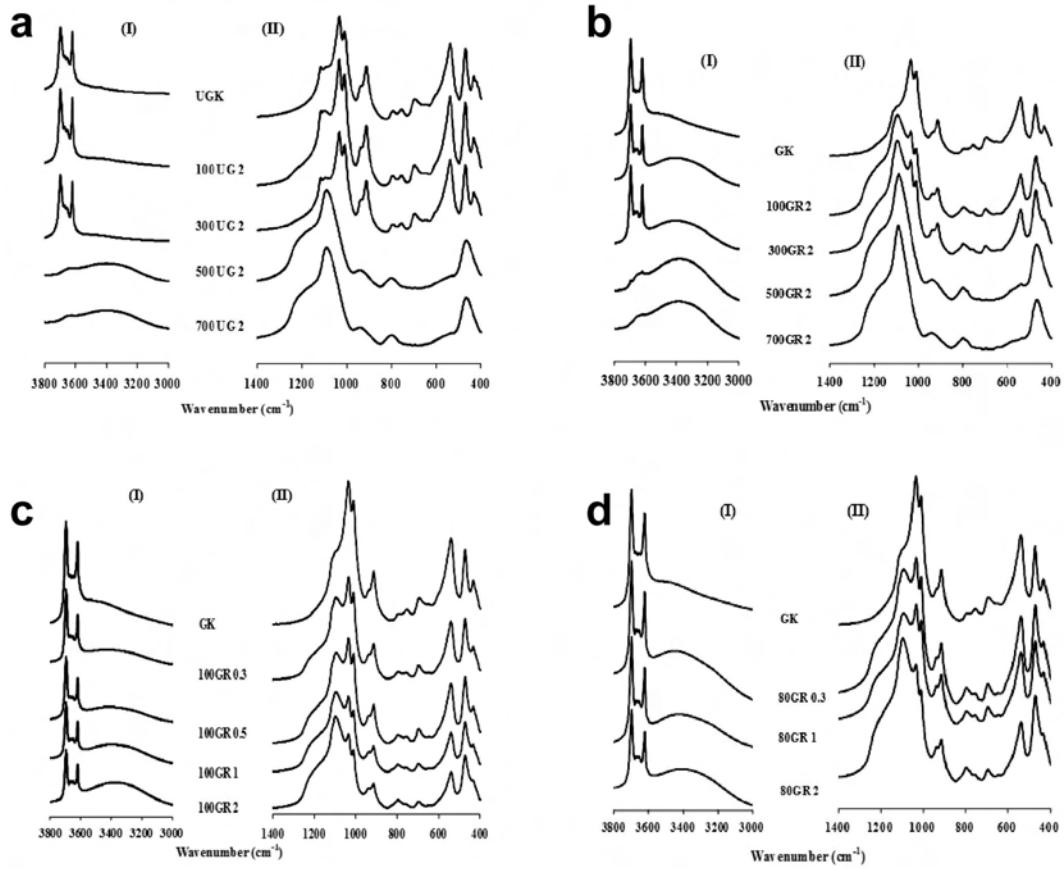

FIG. 3. Comparison of the FTIR spectra of the initial and activated samples. (a) Unground kaolin (UGK) and samples heated at different temperatures and refluxed with 2 M sulfuric acid (FUG 2); (b) ground kaolin (GK) and samples heated at different temperatures, ground, and refluxed with 2 M sulfuric acid (FGR 2); (c) ground kaolin (GK) and samples heated at 100ºC, ground, and refluxed with different concentration of sulfuric acid (100GRS); (d) ground kaolin (GK) and samples heated at 80ºC, ground, and refluxed with different concentration of sulfuric acid (80GRS).

The FTIR spectra of the 100UG 2, and 300UG 2 were comparable to the initial UGK samples (Fig. 3a), while in those samples preheated at 500 and 700ºC the bands at 3696, 3620, 1031, 1008 and 753 cm^{-1} disappeared (Fig. 3a). Both the XRD and FTIR results suggest that the kaolinite structure is preserved at $T \leqslant 300$ºC but is destroyed at a temperature $\geqslant 500$ºC, which corresponds to the dehydroxylation temperature of the mineral (Panda *et al.*, 2010, among others). In addition, the increase in the band intensity at 1092 cm^{-1} recorded for samples preheated at 500 and 700ºC suggests that a three-dimensional network of amorphous Si−O−Si units is formed, in agreement with other studies (Fernandez *et al.*, 2011; Foo *et al.*, 2011), demonstrating the production of amorphous phases at these temperatures. The SiO_2 content increase and that of Al_2O_3 decrease in the activated samples when the temperature before the reflux step increases (Table 2). These chemical results are in agreement with the structural data (XRD and FTIR), which indicated the disappearance of kaolinite and the presence of an amorphous phase rich in Si in samples preheated at a high temperature. These results are comparable with those of Okada *et al.* (1998) who produced metakaolinite by calcining kaolinite at 600ºC for 24 h and by treating it with 20% sulfuric acid at 90ºC for 0.5−5 h. Indeed, these authors reported that the SiO_2 content increased to more than

TABLE 2. Chemical compositions (wt.%) of the initial samples (unground and ground kaolin) and the activated samples.

	SiO_2	Al_2O_3	K_2O	Fe_2O_3	CaO	CuO	TiO_2	MnO	Al:Si
UGK	53.90	42.40	2.03	1.11	0.03	0.06	0.04	0.07	0.89
GK	54.10	42.00	2.07	1.03	0.04	0.06	0.05	0.07	0.88
100UG 2	60.50	35.80	1.95	0.69	0.19	0.05	0.07	0.04	0.67
300UG 2	61.5	35.2	2.22	0.72	0.10	0.05	0.04	0.05	0.65
500UG 2	89.20	7.31	2.31	0.63	0.07	0.05	0.05	0.05	0.09
700UG 2	92.70	4.90	1.44	0.47	0.04	0.05	0.04	0.03	0.06
100GR 2	80.20	16.60	1.97	0.55	0.10	0.05	0.03	0.04	0.23
300GR 2	84.4	12.7	2.02	0.44	0.06	0.05	0.04	0.03	0.17
500GR 2	91.40	5.68	1.91	0.42	0.06	0.05	0.06	0.03	0.07
700GR 2	94.40	3.48	1.27	0.31	0.06	0.05	0.04	n.d.	0.04
100GR 0.3	71.72	24.87	1.45	0.57	0.11	0.01	0.03	0.04	0.4
100GR 0.5	73.69	23.10	1.40	0.49	0.11	0.01	0.04	0.04	0.36
100GR 1	79.14	17.79	1.42	0.42	0.11	n.d	0.03	0.03	0.26
80GR 0.3	68.00	28.30	2.04	0.72	0.06	0.04	0.06	0.05	0.47
80GR 1	74.50	22.20	2.0	0.55	n.d	0.05	n.d.	0.04	0.34
80GR 2	80.70	16.20	1.84	0.54	0.09	0.05	0.06	0.04	0.23

n.d. = not detected

90 wt.% after 1.5 h of leaching. Finally, the extensive leaching of Al_2O_3 from the unground samples preheated at high temperatures (500 or 700ºC) before acidic refluxing, is in agreement with the drastic decrease of the relative proportion of kaolinite in these samples shown by XRD analyses (Table 2, Fig. 4a).

The SSA and total pore volumes of samples UGK and FUG 2 are listed in Table 3. The SSA and the pore volume (Vp) of unground kaolin preheated at 100ºC before acid reflux (100UG 2) is higher than those of samples without preheating (UGK). Indeed, the SSA of UGK and 100UG is ~42 and ~81 m^2/g respectively, and the pore volumes of

TABLE 3. Specific surface area (SSA), total pore volume (Vp), and bleaching capacities (BC) of the initial samples (unground and ground) and the activated samples.

Sample	SSA (m^2/g)	V_p (cc/g)	BC (%)
UGK	41.89	0.2	34.94±0.07
GK	60.69	0.28	49.7±0.12
100UG 2	81.25	0.28	38.5±0.03
300UG 2	74.13	0.2	33.95±0.03
500UG 2	304.49	0.27	28.74±0.05
700UG 2	456.22	0.42	15.08±0.05
100GR 2	372.10	0.91	67.12±0.03
300GR 2	369.4	0.89	34.6±0.05
500GR 2	294.90	0.47	20.36±0.05
700GR 2	304.80	0.30	13.34±0.04
100GR 0.3	244.80	0.42	78.96±0.07
100GR 0.5	257.20	0.46	79.79±0.03
100GR 1	299.60	0.57	77.74±0.04
80GR 0.3	223.61	0.37	81.41±0.03
80GR 1	271.38	0.44	78±0.12
80GR 2	293.92	0.76	66.9±0.05

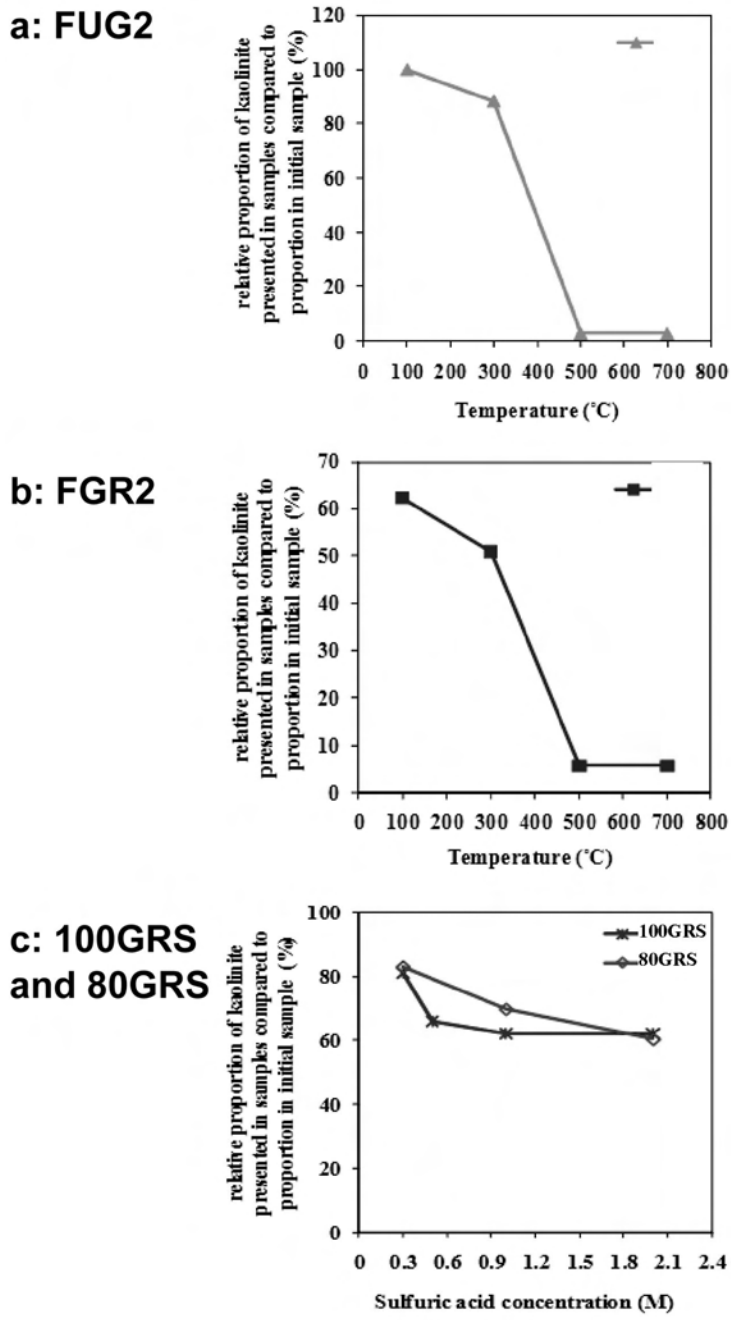

FIG. 4. Relative proportion of kaolinite present in the activated kaolins as a function of the temperature used for heating prior to refluxing in 2 M sulfuric acid for unground (a) and ground (b) kaolins. Data are also reported as a function of the sulfuric acid concentration used for refluxing ground kaolins dried at 100ºC and 80ºC before refluxing (c). See text for more details about calculations. (FUG 2 = samples heated at different temperatures and refluxed with 2 M sulfuric acid; FGR 2 = samples heated at different temperatures, ground, and refluxed with 2 M sulfuric acid; 100GRS = samples heated at 100ºC, ground, and refluxed with different concentrations of sulfuric acid; 80GRS = samples heated at 80ºC, ground, and refluxed with different concentrations of sulfuric acid).

these two samples are 0.2 and ~0.3 cc/g, respectively. Samples pre-heated at temperatures equal or higher than the dehydroxylation temperature (500ºC) have considerably higher SSA (~300 and ~450 m^2/g for 500UG 2 and 700UG 2 respectively). Preheating at 700ºC increases SSA and *V*p by a factor ~10 and a factor 2 respectively compared to the initial sample (UGK). Okada *et al.* (1998) also reported that the SSA and *V*p increased to ~340 m^2/g and ~0.2 cc/g respectively by calcining the kaolinite at 600ºC for 24 h prior to chemical treatment.

For GK samples preheated and activated with 2 M H_2SO_4 at temperatures between 100 and 700ºC, similar overall trends as those obtained for unground samples treated with the same preheating temperature and sulfuric acid concentration were observed (Fig. 2b, 3b). Indeed, in the FTIR spectra of ground GK activated kaolins (FGR 2) the kaolinite structure is preserved up to 300ºC and an amorphous phase rich in Si is observed for samples preheated at temperatures $\geqslant$500ºC before activation. These results are in agreement with SiO_2 and Al_2O_3 contents determined in these samples (see Table 2). The large decrease in the relative proportions of kaolinite in 500GR 2 and 700GR 2 samples calculated by assuming 100% kaolinite for the initial GK sample using XRD data is in good agreement with the extensive leaching of Al from these samples (Fig. 4b, Table 2). Furthermore, with thermal treatment at 100ºC (100GR 2), an approximately 6-fold increase in the SSA to ~372 m^2/g and a 3-fold increase in the total *V*p to ~0.9 cc/g are observed compared to the initial GK sample (Table 3). However, in contrast to the unground samples activated under 2 M H_2SO, both the SSA and *V*p of the ground activated samples preheated at a temperature higher than 100ºC are lower than those of the 100 GR, but higher than those of initial ground kaolin (GK). Such behaviour could be due to the acid attack, which induces intense leaching of Al from the kaolinite structure and opens the edges of the platelets (Bhattacharyya & Gupta, 2008).

Effect of the acid concentration used for reflux in samples preheated at 100ºC (100GRS) and at 80ºC (80GRS). The XRD patterns of activated kaolin samples (100GRS or 80GRS) were similar to the XRD patterns recorded for the FUG 2 and FGR 2 samples (data not shown). For samples preheated at 100ºC before acid refluxing, the kaolinite proportion decreased significantly from ~80% to ~62% when the acid concentration increased from 0.3m to 2 M (samples 100GR 0.3 and 100GR 2). The 80GRS sample also shows the same trend as the 100GRS sample (Fig. 4c). Note that the 80GR 0.3 and 80GR 2 samples have approximately the same relative proportions of kaolinite as the 100GR 0.3 and 100GR 2 samples, respectively. The FTIR bands at 1031 and 1008 cm^{-1}, which correspond to Si−O stretching vibrations of kaolinite in the 100GR 0.3 and 100GR 0.5 samples, are more intense than those of 100GR 1 and 100GR 2 (Fig. 3c-II), indicating that the kaolinite structure is only partially preserved in 100GR 1 and 100GR 2. The shoulder at 1090 cm^{-1} increased considerably with increasing acid concentration, and the most intense band was obtained for 100GR 2, suggesting the presence of a significant proportion of a Si-rich amorphous phase. The bands corresponding to Al−Al−OH bending vibrations at 938 and 912 cm^{-1} are also reduced after acid treatment.

The chemical compositions of the 100GRS and 80GRS samples are reported in Table 2. The SiO_2 content increases with increasing acid concentration. When the GK sample was treated with a 2 M sulfuric acid solution (100GR 2 and 80GR 2), the SiO_2 content increased to ~80% (54% in the initial GK sample), in agreement with the increase in the proportion of an amorphous phase rich in Si detected by FTIR for these two samples (Fig. 3c,d). The marked decrease in Al_2O_3 content in the acid-treated samples is attributed to the leaching of Al^{3+} ions from the octahedral sheet of kaolinite due to a strong hydrolysis under acidic conditions (Panda *et al.*, 2010). The SSA and *V*p of the samples 100GRS and 80GRS increase following acid treatment compared to the initial GK sample (Table 3). The maximum values of the SSA and the total pore volume were obtained for 100GR 2 (~372 m^2/g and 0.91 cc/g).

Relationship between the bleaching capacity of the activated samples and their physicochemical characteristics

The bleaching capacities of the unground and ground activated samples as a function of the temperature prior to reflux with 2 M sulfuric acid are presented in Fig. 5a. For the FUG 2 samples, 100UG 2 has a bleaching capacity of ~39% which is the maximum value for this series. The bleaching capacities decrease continuously with increasing preheating temperature. Furthermore, heating the

GK sample to 100ºC before acidic activation yielded a higher bleaching capacity (~67%; Fig. 5a) than the unground sample preheated at the same temperature and using the same acid concentration (2 M). The bleaching values of the ground FGR 2 samples decrease continuously with an increase of the preheating temperature. Thermal treatment of kaolins before acid activation, for bleaching edible oil, has not been tested before to the best of our knowledge. A previous study, with no preheating step, showed that the best bleaching capacity (~80%) of Ranong kaolin (the same material that the one used in this present study) was obtained for a ground sample refluxed with 2 M sulfuric acid (Worasith *et. al.*, 2011a). This information coupled with our results suggests that preheating samples at temperatures equal or higher than 100ºC prior to acidic reflux does not improve the removal efficiency of kaolins for pigments.

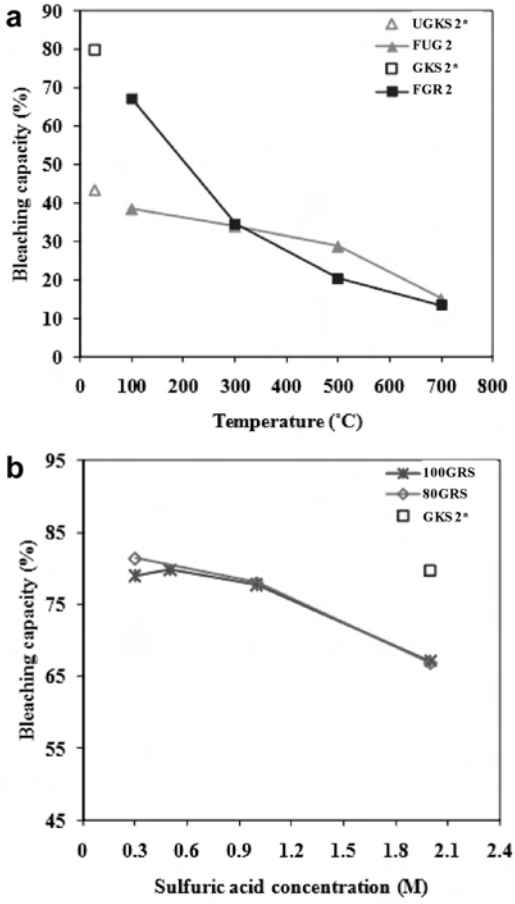

FIG. 5. Effect of various parameters on the bleaching capacities of activated kaolins. (a) Effect of the drying temperature used prior to the activation of unground and ground samples in 2 M sulfuric acid. (b) Effect of the sulfuric acid concentration used for refluxing ground samples heating at 100ºC or 80ºC. (UGKS 2* = unground kaolin refluxed with 2 M sulfuric acid; GKS 2* = ground kaolin refluxed with 2 M sulfuric acid). Captions for other sample names are reported in Fig. 4. * These results were reported in Worasith *et al.* (2011a).

Among the unground samples preheated at temperatures equal or higher than 100ºC before activation, 100UG 2, with Al_2O_3 content of ~36%, has the highest bleaching capacity, ~39%, whereas 700UG 2 with 5% Al_2O_3 content has a very low bleaching capacity of ~15% (Fig. 6a). Note that although 700UG 2 has the highest SSA and total pore volume, this sample also has the lowest bleaching capacity among the unground samples (Table 3). This behaviour suggests that a high SSA is not the sole parameter controlling the bleaching capacity, and that the preservation of the kaolinite structure seems to be a major factor for improving the removal efficiency for colour pigments. Among the ground samples, the highest bleaching capacity was obtained for 100GR 2, whereas the lowest bleaching capacity was obtained for 700GR 2. In contrast to sample 100UG 2, the rather high bleaching capacity value of ~67% obtained for 100GR 2 is probably due to the partial removal of Al. Indeed, it has been reported in montmorillonite that the acid activation partially leaches Al from ground samples, opens the edges of the clay platelets, and thus allows the maximum bleaching capacity to be obtained (Yang *et al.*, 2006).

The low bleaching capacities of all samples heated at temperatures higher than 300ºC prior to acidic reflux can be attributed to the complete destruction of the kaolinite structure. Indeed, kaolinite is characterized by the presence of aluminol sorption sites on its surface. Opposite to the silanol sites present on the surfaces of quartz and aluminosilicates (kaolinite, illite, and feldspar), which are generally neutral or negatively charged in the pH domain of the bleaching experiments ($7 < pH < \sim 3$), the aluminol sites located on the kaolinite surface can be positively charged in this pH domain (Tertre *et al.*, 2006, among others). The sorption of anionic pigments, such as chlorophyll-a, is then favoured when the kaolinite structure is partially preserved (i.e. low preheating temperature used before acid reflux).

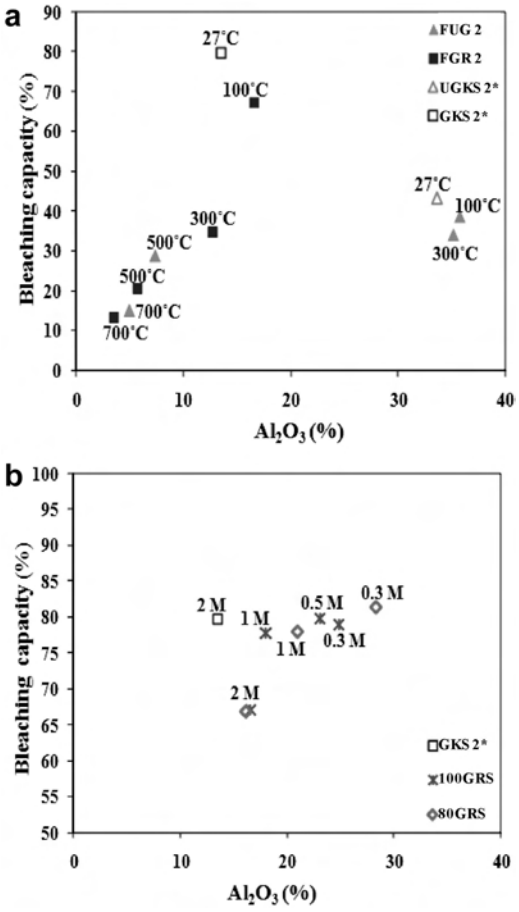

FIG. 6. Bleaching capacity values measured for activated kaolins as a function of the proportion of Al_2O_3 in the activated products. Data are reported for (a) unground and ground kaolin heated at different temperatures prior to refluxing in 2 M sulfuric acid and (b) ground kaolin dried at 100ºC or 80ºC prior to refluxing with different concentrations of sulfuric acid. Captions for sample names are reported for Fig. 5. * These results were reported from Worasith *et al.* (2011a).

The bleaching capacities of the ground samples preheated at 100ºC or 80ºC prior to acidic refluxing were plotted as a function of the concentration of sulfuric acid used during the reflux step (Fig. 5b). When a pre-heating step of 100ºC is used prior to refluxing (e.g. 100GRS samples), the optimum bleaching capacity (~80%) is obtained for 100GR 0.5; then bleaching capacity decreases to ~67% for 100GR 2. The slight decrease in the bleaching capacity observed between samples 100GR 0.5 and 100GR 2 is due to additional leaching of Al during acid activation when a high acid concentration was used (2 M), which in turn induces a more extensive destabilization of the kaolinite structure at 2 M than at 0.5 M (see Al_2O_3 contents in Table 2). This behaviour could result in a decrease in the number of aluminol sites available for the sorption of anionic pigments in samples activated at 2 M sulfuric acid concentrations. This is in agreement with the interpretation proposed above to explain the low bleaching capacity of the samples preheated at temperatures higher than 300ºC prior to refluxing with 2 M sulfuric acid solution.

Finally, in the 80GRS samples, the optimum bleaching capacity (~82%) is obtained for the sample activated with 0.3 M sulfuric acid solution (Fig. 5b). Further acid treatment reduces the Al content, and the bleaching capacity tends to decrease due to a lack of positive sorption sites at the surfaces of the mineral constituents of the activated samples. For example, the Al_2O_3 content is equal to ~28% for samples prepared at low sulfuric acid concentrations (80GR 0.3), but the content decreased significantly to ~16% in the sample 80GR 2 prepared with a higher sulfuric acid concentration (Fig. 6b). Kheok & Lim (1982) proposed that sulfuric acid treatment induced leaching of Al from the clay minerals and consequently caused a charge deficiency in the clay lattice and enhanced the clay's pigment sorption properties. However, extensive leaching of Al at high acid concentrations decreased the bleaching capacity of clays due to structural collapse.

Our results discussed in relation to data from literature obtained without a pre-heating step

Although thermal treatment of kaolins before acid activation has never been tested to the best of our knowledge in the context of bleaching edible oil, we have tried to discuss our results versus the literature data obtained without a pre-heating step before acidic refluxing. Many studies in the past have been focused on the decolourization of oil, particularly using sorption reactions onto clays (Stout *et al.*, 1949; Kheok & Lim, 1982; Falaras *et al.*, 1999; Hussein *et al.*, 2001; Temuujin *et al.*, 2006; James *et al.*, 2008; Nguetnkam *et al.*, 2008; Didi *et al.*, 2009). Most of these studies have demonstrated a good correlation between the bleaching capacity and the SSA of the activated samples (Falaras *et al.*, 1999; James *et al.*, 2008; Didi *et al.*, 2009). However, additional studies have also indicated that this

correlation is not systematic (Nguetnkam *et al.*, 2008; Worasith *et al.*, 2011a). Our results obtained with ground kaolin preheated at 100 or 80ºC prior to refluxing (samples 100GRS and 80GRS) are in agreement with the latter studies, as there is no clear relationship between our bleaching capacities and the SSA of these specific samples. This absence of correlation is also observed for unground samples that were preheated prior to refluxing with 2 M sulfuric acid (FUG 2 samples), except for the sample preheated at 300ºC. This absence of correlation at 300ºC could be attributed to experimental errors in SSA determination. Samples preheated at high temperatures (500 and 700ºC) before refluxing are characterized by high SSA and low Al_2O_3 content, due to the presence of an amorphous phase rich in Si for which a high proportion of functional groups (>SiOH) is not favourable for the sorption of anionic pigments. This is due to the neutral or negative charge of silanol groups in the pH domain at which the bleaching experiments were performed ($7 < pH < 3$). Pure SiO_2 phases are ineffective for the decolourization of palm oil (Nguetnkam *et al.*, 2005).

Grinding kaolins prior to refluxing with sulfuric acid induces more extensive leaching of Al from the samples compared to the procedure without grinding, in agreement with similar studies (Tang *et al.*, 2010; Worasith *et al.*, 2011b). Furthermore, previous studies have generally shown that there is an optimal concentration of acid for the reflux step to ensure best bleaching capacity (James *et al.*, 2008; Didi *et al.*, 2009). Beyond this optimum value, the bleaching capacity decreases due to the complete disruption of the crystal structure, in agreement with the present study. For example, the concentrations of sulfuric acid for maximum bleaching capacities were 0.3 and 0.5 M for samples 80GRS and 100GRS, respectively. The low bleaching capacities of kaolins activated with higher acid concentrations (e.g. 2 M) are due to the extensive leaching of Al_2O_3 (< 20%) which causes a strong decrease in the relative proportion of kaolinite (~60%; Fig. 4c).

MAIN CONCLUSIONS AND IMPLICATIONS FOR INDUSTRIAL APPLICATIONS

Preheating unground and ground kaolins before an activation step performed with 2 M sulfuric acid yielded activated samples with high SSA and pore volumes. However, the bleaching capacities are low due to the strong or complete destruction of the kaolinite present in the samples. Thus, the partial preservation of the kaolinite structure is a key factor for obtaining good bleaching capacity of kaolin, and this is directly related to the preservation of the aluminol sites at the kaolinite surface. These sites are likely to be involved in the sorption of anionic and organic pigments present in the crude rice bran oil, which are largely responsible for the undesired colour of edible oil. For a given temperature of preheating prior to refluxing, the optimum bleaching capacity is not necessarily obtained with the highest sulfuric acid concentration due to the formation of a Si-amorphous phase during dissolution, which is not favourable for bleaching.

For industrial applications, activated kaolin can be used as an effective adsorbent to remove colour pigments from rice bran oil. Low concentrations of sulfuric acid, such as 0.3 or 0.5 M, as well as a preheating temperature $\leqslant 100$ºC prior to acidic refluxing, are sufficient to activate kaolin and obtain maximum bleaching capacities. In addition, grinding of kaolin prior to acidic refluxing also enhances the bleaching capacity of the entire material. The use of low concentration (typically 0.3 or 0.5 M) of sulfuric acid after grinding limits leaching of Al from the activated sample and thus yields satisfactory bleaching capacities (~80%). The same optimal bleaching capacity (~80%) can be obtained with (1) ground sample refluxed with 2 M sulfuric acid and (2) ground sample preheated at 80ºC and refluxed with sulfuric acid of low concentration (0.3 M; this study).

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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