Surface and Pore Structure of Deoiled Acid- and Heat-Treated Spent Bleaching Clays

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ABSTRACT: Samples of spent bleaching clay were deoiled by hexane, methanol, hexane–methanol, and supercritical CO_2 extractions. The deoiled clays were regenerated by acid and heat treatments. Nitrogen adsorption isotherms for these samples are type IV with hysteresis loops corresponding to type H3, indicating slit-shaped pores. Used deoiled and dried samples have smaller surface areas and pore volumes than unused clay. The surface areas and pore volumes increased after heat treatment. Acidified heat-treated deoiled samples have smaller surface areas and greater pore volumes than unused clay, except for the methanol-deoiled sample. Thus, heat and acid treatments removed substances adsorbed in the pores that were not removed by solvents or CO_2 extraction. This was confirmed from the ratios of the cumulative surface area/BET surface area, as well as analysis of the pore size distributions, which indicated an increase in mesopores with radii of between 25 and 100 Å. The *t*-plots showed that smaller pores with sizes between 7 and 25 Å, present originally in the unused clays, were closed by heat treatment. These pores were absent in the deoiled and the heat-treated samples except for the heat-treated sample that was deoiled by hexane followed by methanol. Smaller pores, accompanied by an increase in surface area, were also observed for all deoiled samples after acid and heat treatments.
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KEY WORDS: Acid-heat treatment, pore structure, spent bleaching clay, surface.

Bleaching with activated clay is an essential step in refining vegetable oils. At a dosage of 0.5–1.0% clay, the current world production of >60 million tons of oils is accompanied by production of solid spent clay, containing 30–40% oil, estimated at 600,000 tons worldwide. Malaysia produced 7.8 million tons of palm oil in 1995. This was accompanied by about 70,000 tons of spent clay, which was disposed untreated. This disposal constituted a significant economic waste and an environmental burden.

Methods for oil recovery by solvent extraction from spent bleaching clays and other adsorbents resulting from edible oil refining are well known (1), and oil recovery facilities have been installed in some refineries. No palm oil refiners are known to have such a facility, perhaps because operation of an oil recovery facility alone without clay regeneration may not be financially profitable although environmentally essential. Laboratory methods for clay regeneration have been studied and reviewed (2,3) and include a combination of steam pretreatment, acid and heat activations, as well as wet oxidation under medium pressure (3–5). Regeneration after supercritical CO_2 extraction has also been investigated (6). For example, synthetic silica-containing alumina has been successfully regenerated by thermal treatment at 540°C in air or nitrogen for repeated use in producing contaminant-free oil (7). A commercially viable method involving a multistep all-aqueous process has been reported to yield 100% efficiency, measured in terms of chlorophyll removal (8). Pilot-plant regeneration has also been described (9). However, no detailed study on regeneration of spent clays from palm oil refining has been reported in the open literature. The objective of our study was to examine the surface and pore structures of deoiled and acid- and heat-treated spent bleaching clays from palm oil refining.

EXPERIMENTAL PROCEDURES

Activated bleaching clays and fresh spent clay were obtained from Palmco Ind. Sdn. Bhd, Prai, Malaysia. The spent clay (~10 g) was deoiled by solvent extraction in a modified Soxhlet extractor or by supercritical CO_2 at a temperature of 60°C and pressure of 300 bar. The extraction was carried out until no further increase in weight of the extracted materials was detectable. For samples deoiled by hexane–methanol, the sample deoiled by hexane was further extracted with methanol. Deoiled samples were dried at 120°C in an oven for 24 h and stored in a stoppered bottle. The deoiled clays were divided into three portions. Two were subjected to further treatment. Of these two, one portion was heat-treated at 400°C for 10 h in a muffle furnance in air. The other portion was treated with 20% H_2SO_4 at room temperature for 5 h, washed with distilled water until the pH of the filtrate was neutral, and then subjected to heat treatment at 400°C for 10 h. These samples are designated dried, heat-, and acid-heat-treated samples.

Nitrogen adsorption experiments were carried out at 77 K by a volumetric method with an automated accelerated surface area and porosimetry system, Model ASAP 2000, manufactured by Micromeritics Instrument Corporation (Norcross,

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GA). Sample weights were 0.2–0.3 g. Heat-treated and acid-heat-treated samples were degassed at 350°C, and the dried nonactivated samples were degassed at 125°C for 3 h prior to the adsorption experiments.

The BET surface areas, the monolayer values, and the BET constants, *C*, were determined from the slopes and intercepts of the plots of $P/V(P_o - P)$ vs. P/P_o according to the BET equation. The pores of the samples were assumed to be slit-shaped, and the pore distribution curves of all samples were calculated from the desorption branch of the hysteresis loop by the Kelvin equation, $(P/P_o) = -2\,\gamma\,V/r_m\,RT$, where r_m is the width of the slit core, γ is the surface tension, and V is the molar volume of liquid nitrogen. A procedure described by Gregg and Sing (10) was adopted for calculating the pore size distribution. The cumulative surface area, S_{cum}, and the cumulative pore volume, V_{cum}, were calculated from the desorption branch of the hysteresis loop from $P/P_o = 0.95$ to hysteresis inception.

Analysis of the retained substances after deoiling was carried out as follows: 50 g of the spent clay, deoiled with hexane, was heated in a tube furnace from room temperature to 400°C under a flow of helium. Volatilized substances were collected in an ice-cooled trap. The samples, as well as the standards, were derivatized prior to analysis by gas chromatography. Five mL of 0.1 M NaOH in methanol was added to 0.3 g of the sample and refluxed gently. When the sample was dissolved, 7 mL of BF_3-methanol was added, and the solution was refluxed for a further 2 min. Finally, 3 mL heptane was added, and the solution was refluxed for 1 min. The solution was cooled to room temperature, and a saturated aqueous solution of NaCl was added. The mixture was swirled until two layers were obtained. A 0.4-μL aliquot of the top layer was injected into a Hewlett-Packard HP 5880A gas chromatograph (Palo Alto, CA), equipped with a flame-ionization detector. The stationary phase was a DB23 (J&W Scientific, Folsom, CA) fused-silica capillary column 30 m × 0.25 mm (i.d.) The carrier gas was helium at a flow rate of 1 mL min^{-1} with a split ratio of 1:100. The temperatures of the injector, column oven, and detector were 290, 180, and 290°C, respectively.

RESULTS AND DISCUSSION

The adsorption isotherms. The nitrogen adsorption isotherms for the three different types of samples were determined, with the unused clay serving as the control. These are (i) the deoiled, (ii) heat-treated, and (iii) acid- and heat-treated samples. The isotherms of all samples were reproducible when the adsorption and desorption cycles were repeated. The isotherms are shown in Figure 1. The shapes of the isotherms of all samples, except the methanol-deoiled, acid- and heat-treated sample, are similar. These isotherms are type IV, according to the BET classification, with the hysteresis loops corresponding to type H3 of the International Union of Pure and Applied Chemistry classification.

Type IV isotherms are characteristic of mesoporous solids. According to de Boer (11), specific pore structures can be deduced from certain shapes of the hysteresis loops. Type H3 hysteresis loops are associated with adsorbents having slit-shaped pores. Such pores occur because the adsorbent is mainly composed of plate-like particles or of a layer structure that is typical of clay structures. Because the isotherms of the different samples are largely similar to each other as well as to the isotherms of the control unused clays, we concluded that deoiling by solvent as well as by supercritical fluid extraction, with or without subsequent treatment, did not substantially alter the layer structures of the clays.

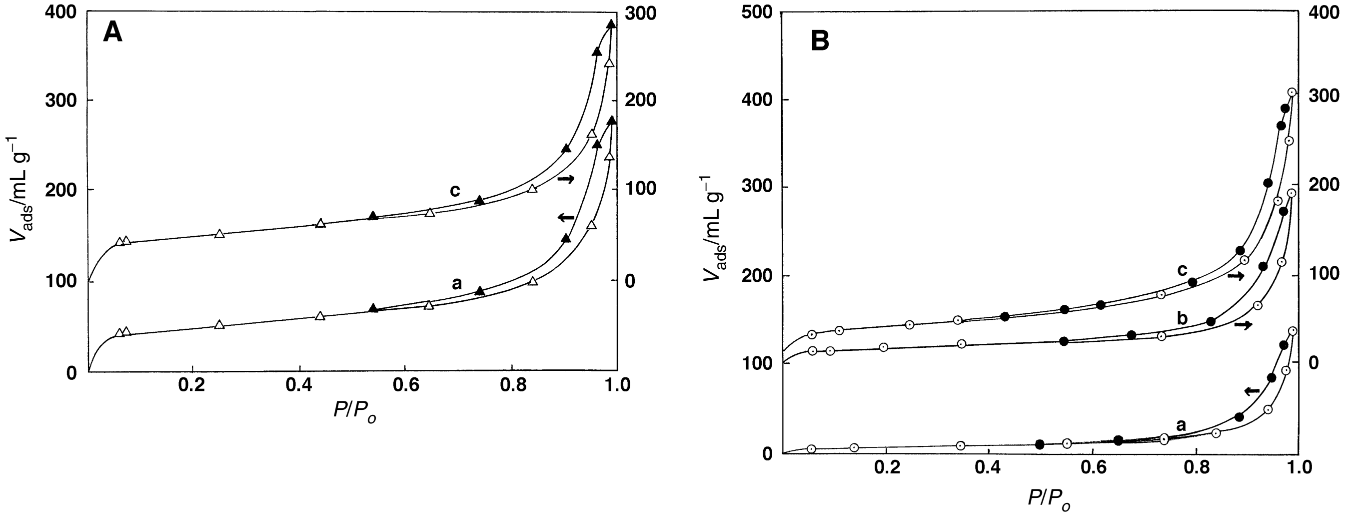
From the isotherms, the total pore volumes (V_p), in terms of volume of N_2 adsorbed at standard temperature and pressure by the adsorbents, were calculated by assuming that the region of the isotherms near $P/P_o = 0.95$ represents the filling of all pores with adsorbate in ordinary liquid form. The V_p values in Table 1 show that all samples that were acid- and heat-treated had a greater pore volume than the unused (control) clay sample, indicating that acid treatment resulted in the creation of additional pore space within the samples. With the exception of samples deoiled by supercritical CO_2 and methanol followed by heat activation, the V_p values of all heat-treated samples were similar to that of the unused clay, implying that no significant structural changes had taken place upon heat treatment at 400°C. However, compared with the V_p values of the dried deoiled samples, $\mathrm{V_p}$ values of heat-treated samples were substantially increased, presumably caused by the removal of substances that were adsorbed in the pores during bleaching and that could not be removed by simple deoiling.

Figure 2 shows the gas chromatogram of the derivatized solution of the volatilized substances from the hexane-deoiled clay sample. The three peaks were identified by comparing the retention times with those of a derivatized mixture of palmitic, oleic, and stearic acids and of the individual fatty acids. The results show that substances present in crude palm oil are still retained in the pores after deoiling the clay.

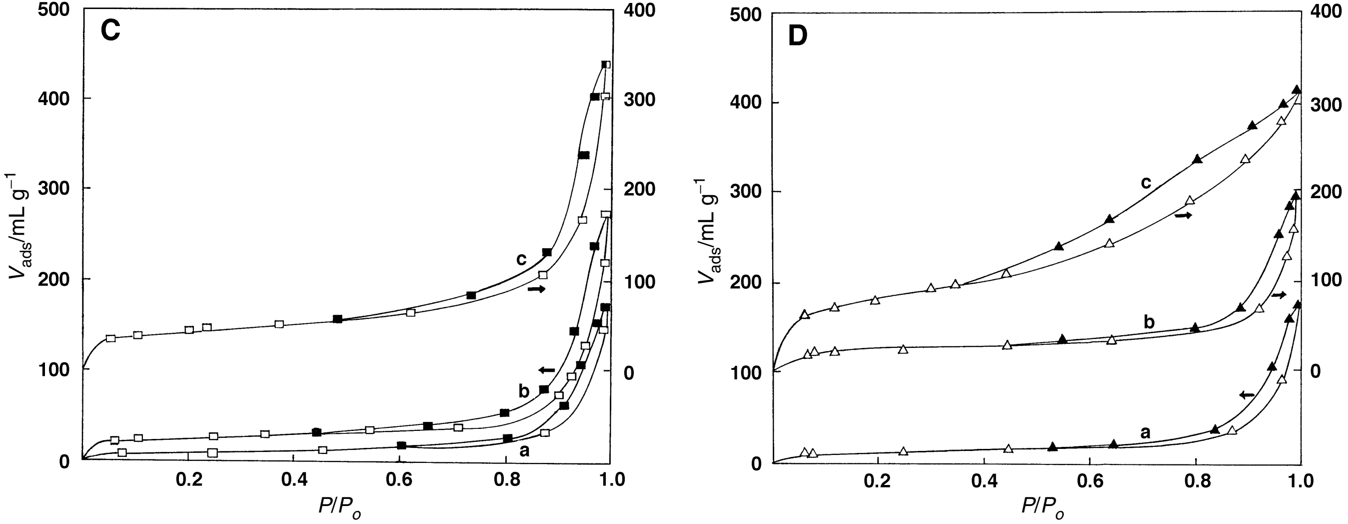
Specific surface area. All samples yielded linear BET plots with a range of linearity up to P/P_o values of 0.20 to 0.30. The BET constants, *C* and the monolayer volumes V_m, are shown in Table 1. The BET surface areas, S_{BET}, were calculated by using the cross-sectional area of a nitrogen molecule 16.2 Å^2.

According to the BET theory, the constant *C* gives an estimate of the magnitude of the adsorbent–adsorbate interaction because it is directly related to the heat of adsorption of the first layer. Table 1 shows that the *C* values of the deoiled samples were between 24 and 53, which increased to between 120 and 340 on heat or acid-heat treatments. Thus, the *C* values indicate that the surface was modified after the samples had been deoiled by the various solvents. Subsequent treatments enhanced the adsorbent–adsorbate interaction because the remaining traces of retained substances were removed by the treatments.

Similar to the *C* values, the deoiled samples showed a substantial decrease in specific surface area when compared to that of the dried nonactivated unused clay. The surface area of these samples was only about 20% that of the unused clay.



On heat treatment, these areas increased substantially to



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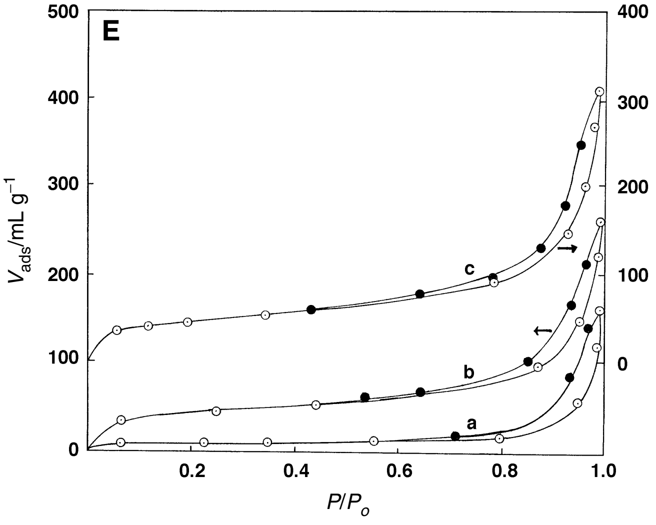

FIG. 1. Adsorption isotherms of volume V_{ads} of N_2 at standard temperature and pressure adsorbed per gram of sample at 77 K vs. relative pressure (P/P_o) for (A) unused clay and for spent clay deoiled with (B) supercritical CO_2 at 300 atm and 60°C, (C) hexane, (D) methanol, and (E) hexane followed by methanol. Isotherms (a) sample dried at 120°C for 24 h; (b) sample heat-treated at 400°C for 10 h; and (c) sample acid-treated with 20% H_2SO_4 and heat-treated at 400°C for 10 h.

TABLE 1
Parameters for Surface and Pores of Clays[a]

Sample	C	V_m	r_1	S_{BET}	S_{cum}	S_w	V_p	V_{cum}	V_n	S_{cum}/S_{BET}	V_p'
Nonactivated											
Montmorillonite	792	41.03	25	179	77	115	279	247	18	0.43	0.435
300/60	24	6.36	26	28	32	—	136	139	—	1.14	0.212
Hexane	40	8.48	32	37	36	—	171	172	—	0.97	0.267
Methanol	53	9.95	26	43	39	—	179	177	—	0.91	0.279
Hex > MeOH	40	7.89	30	34	34	—	166	168	—	1.00	0.259
Heat-treated											
Montmorillonite	151	30.56	27	133	76	113	267	249	9	0.57	0.417
300/60	171	15.41	26	67	50	43	201	197	6	0.75	0.314
Hexane	239	20.05	29	87	66	52	279	277	11	0.76	0.435
Methanol	341	17.25	31	75	50	56	194	187	8	0.67	0.303
Hex > MeOH	165	36.37	27	158	76	120	275	249	10	0.49	0.429
Acid- and heat-treated											
Montmorillonite	190	32.62	28	142	83	106	345	338	27	0.58	0.538
300/60	165	34.67	27	151	82	112	300	280	8	0.54	0.468
Hexane	264	31.83	28	139	92	110	344	327	10	0.66	0.537
Methanol	120	66.45	25	289	184	260	313	278	2	0.64	0.488
Hex > MeOH	132	37.50	27	163	86	138	303	278	6	0.53	0.473

[a] C: BET constant; V_m: monolayer volume at standard temperature and pressure (STP), in mL g^{-1}; r_1: pore radius at hysteresis inception in Å; S_{BET}: BET surface area, in $m^2\ g^{-1}$; S_{cum}: cumulative surface area, in $m^2\ g^{-1}$; S_w: surface area of pores with width greater than 3.5 Å, in $m^2\ g^{-1}$; V_p: total volume of N_2 adsorbed at STP in pores at $P/P_o = 0.95$, in mL g^{-1}; V_{cum}: cumulative volumes of gas adsorbed between hysteresis inception and $P/P_o = 0.95$; V_n: volume of gas adsorbed in micropores at STP, in mL g^{-1}; V_p': total volume of N_2 adsorbed as liquid, in mL g^{-1}; 300/60: SFC at 300 bar and 60°C; Hex > MeOH: Hexane followed by methanol.

deoiled clay, heat treatment caused some regeneration of the smaller pores, except for the sample deoiled with hexane–methanol, in which the heat treatment caused restoration of the pores to a distribution resembling that of the unused clay. In these deoiled and heated samples, the pore width of the larger pores, between 100–200 Å, shifted to slightly lower values. Upon acid and heat treatment, a pronounced increase in the number of pores with small width was observed, and the pore size distribution was restored to a pattern similar to the unused original clay, except for the methanol-deoiled sample. In contrast, a distinct decrease of pores with width ~25 Å in the unused clay was observed. Presumably, the acid and heat treatments caused more damage to the smaller bare pores in the unused clay relative to the deoiled samples with retained substances in those pores. For the clay deoiled with methanol, acid-heat treatment caused the larger pores to disappear and they were replaced by pores smaller than 100 Å, with a mean between 25 and 60 Å.

The foregoing observations were confirmed by the following analysis. The specific area calculated according to the BET theory, which takes into account all surfaces present in the solid, is generally larger than the cumulative surface area, which only accounts for the surface due to the large pores; thus, values of S_{cum}/S_{BET} within the range 0.5–0.8 are considered to indicate the presence of micropores. On this basis, the heat-treated and acid-heat-treated deoiled clays possessed micropores, whereas the deoiled samples without further treatment did not show the presence of micropores. The presence of micropores is also indicated for all samples of unused bleaching clays.

The t-*plots—estimation of micropores and mesopores*. The *t*-plot of a test sample is usually in the form of the total amount of adsorbate adsorbed per gram of adsorbent vs. thickness *t* of the adsorbed layer, which is obtained from the reference *t*-curve. If multilayers can be formed unhindered on all parts of the surface of the sample, the initial region of the *t*-plots should be a straight line that passes through the origin, and the total surface can be estimated from the slope.

The *t*-plots of the nonactivated deoiled samples, as well as the activated samples, are shown in Figure 4, utilizing the reference *t*-curve of Lippens *et al.* (9). The *t*-plots of the deoiled nonactivated samples do not pass through the origin but intersect the *V* axis with a negative intercept. Such behavior has been attributed to an incorrect choice of the reference *t*-curve. However, similar behavior was also observed when utilizing other reference *t*-curves (12–14). Thus, the *t*-plots of the deoiled samples also indicated that residual adsorbed substances from the oil were still retained on the surfaces after deoiling with various solvents. In contrast, the deoiled, heat-treated and the deoiled, acid-heat-treated samples, as well as the various unused samples, intersect the *V*-axis with a positive intercept, indicating the presence of micropores in these samples. If adsorbed nitrogen is assumed to have a close-packed structure like liquid nitrogen, then the adsorbed layer would be 3.54 Å thick. Thus, the micropores that caused the positive intercept are less than 7 Å because they would permit only one adsorbed layer to be formed on each side of the slit.

Because the deviations of the *t*-plots of the samples at low relative pressure regions are not well defined, the total specific areas were not calculated. Instead, the areas due to the wider pores ($r > 7$ Å), S_w, were estimated from the slopes of

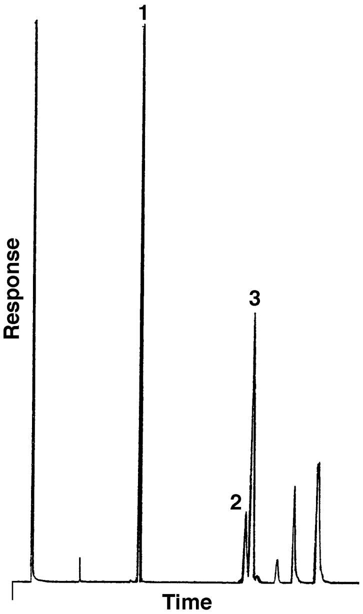

FIG. 2. Gas chromatogram of derivatized solution of volatilized substances from hexane-deoiled clay. See the Experimental Procedures section for conditions. 1 = palmitic acid; 2 = stearic acid; 3 = oleic acid.

the initial linear regions of the plots. The difference, $S_w - S_{cum}$, was thus used to estimate the specific area of pores whose sizes were between 7 and ~25 Å; the latter value corresponds to the relative pressure at the point of inception of the hysteresis loop. These values are shown in Table 1. For the nonactivated unused bleaching clay, the pores with dimensions between 7 and 25 Å constituted a specific surface area of ~38 m^2/g. On heat treatment, the surface area of the unused clay decreased by about 25%, but its $S_w - S_{cum}$ value remained relatively unchanged, indicating a closure of some pores with dimensions less than 7 Å. As indicated earlier, the deoiled samples did not contain micropores. On heat treatment, the samples, with the exception of the hexane–methanol-deoiled samples, have similar S_w and S_{cum} values. For these samples, pores with dimensions between 7 and 25 Å were closed compared to the unused heat-treated clay, indicating that some adsorbates were still retained. In contrast, the samples deoiled by hexane–methanol had the retained material removed on heat treatment, as indicated by the $S_w - S_{cum}$ value. Pores with widths at this range were also observed. By comparing the various surface areas, calculated by the different methods discussed, it is estimated that contributions to the surface area by pores with dimensions >7 Å are in the range of 24 to 40% for the heat-treated deoiled sample and in the range of 10 to 26% for the acid- and heat-treated deoiled samples.

Except for the heat-treated hexane–methanol-deoiled samples, the other heat-treated samples did not contain pores in the range of 7 to 25 Å, but for the acid- and heat-treated deoiled samples, the contributions to the area by pores of this range are in the range of 14 to 25%. These data are also shown in Table 1.

In summary, the results indicate that simple deoiling with hexane, methanol, hexane–methanol, or supercritical CO_2 extractions resulted in clays with much reduced surface areas and pore volumes and that were devoid of micropores owing to blockage by retained substances.

Heat treatment at 400°C for 10 h, followed by evacuation at 350°C, increased the surface areas and pore volumes compared to the nonactivated deoiled samples. Micropores were also regenerated, presumably because some of the retained materials were removed. Compared to the unused clay, the surface areas were still reduced, except for the sample that was deoiled with hexane–methanol.

The surface areas of samples that were deoiled, acid- and heat-treated were restored to similar or slightly higher values, and the pore volumes were restored to similar or slightly lower values compared to the similarly treated unused clay. The sample that was deoiled with methanol, followed by acid and heat treatments, exhibits a high surface area, which was double the value of the similarly treated unused clay and 60% higher than the nonactivated unused clay. Because the pore volume of this sample was only 10.2% lower than the similarly treated and 10.8% higher than the untreated unused clay, the increase in surface area of this sample, as shown from its pore size distribution curve, is due to the creation of mesopores, which replaced the large pores that had collapsed or been plugged. The mechanism for these observed changes is outside the scope of this investigation. A plausible explanation for the increase in mesopore volume may be that some of the lattice aluminium ions, along with other metallic oxides, may have been leached out by the acid treatment. However, acid and heat treatment of samples deoiled by hexane–methanol did not exhibit similar changes in pore size distribution and surface area. In a separate experiment, we found that, after 18 h of methanol extraction, the total amount of extractables was 32.3% of the initial weight of the spent clay, whereas extraction for 4 h with hexane, followed by 18 h with methanol, yielded 37.4% of extractables. The amount of retained substances in the methanol-deoiled samples is considerably higher than in the hexane–methanol-deoiled samples. It is likely that the amount and nature of the retained substances after deoiling may have altered the effect of the acid treatment and subsequent heat treatment.

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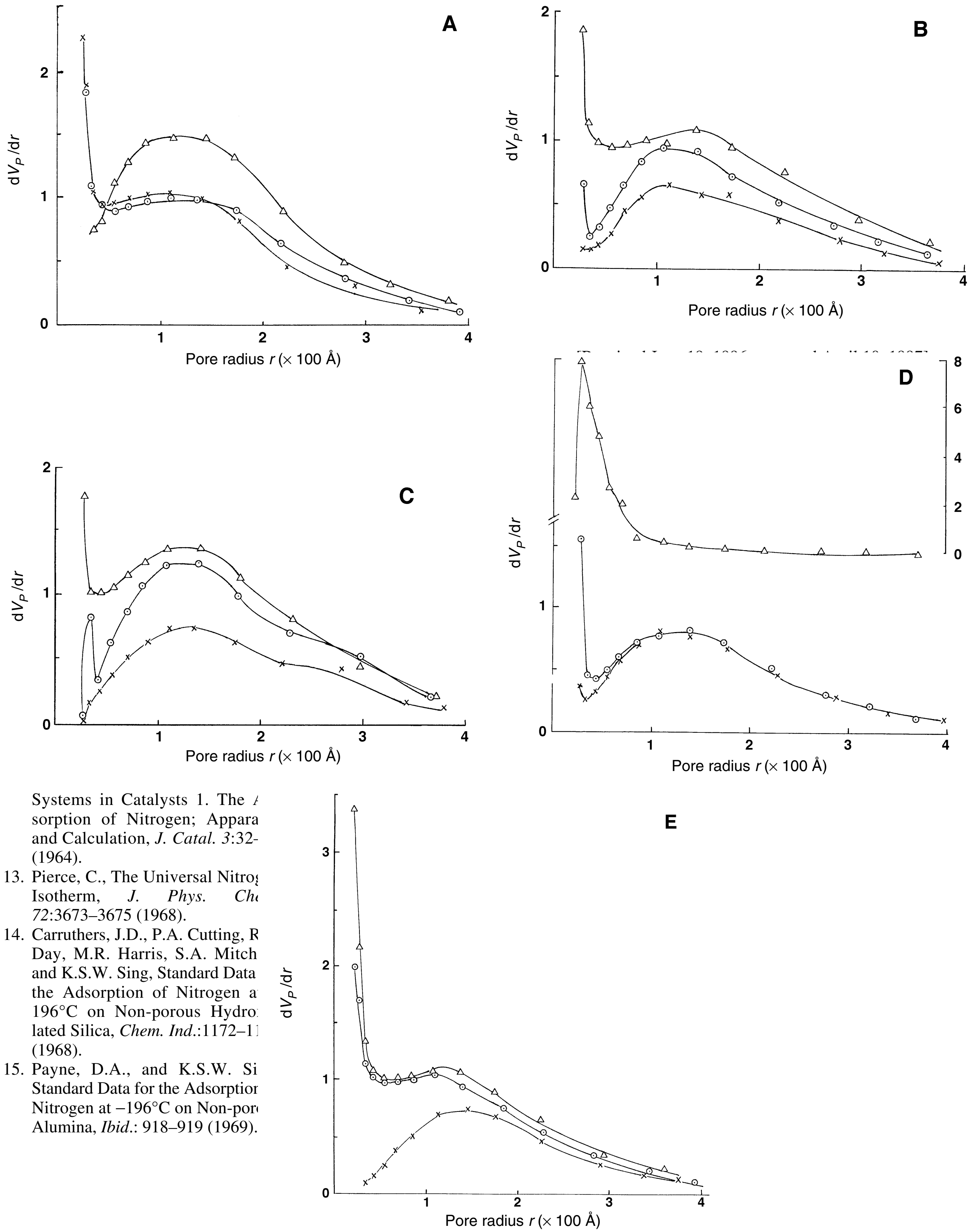

FIG. 3. Pore size distributions of pore volume $\mathrm{d}V_p$ at dimension interval d*r* vs. pore dimension, *r*, for (A) unused clay and for spent clay deoiled with (B) supercritical CO_2 at 300 atm and 60°C, (C) hexane, (D) methanol, and (E) hexane followed by methanol. Dried samples, X. Heat-treated samples, ⊙. Acid-treated followed by heat-treated samples, △.

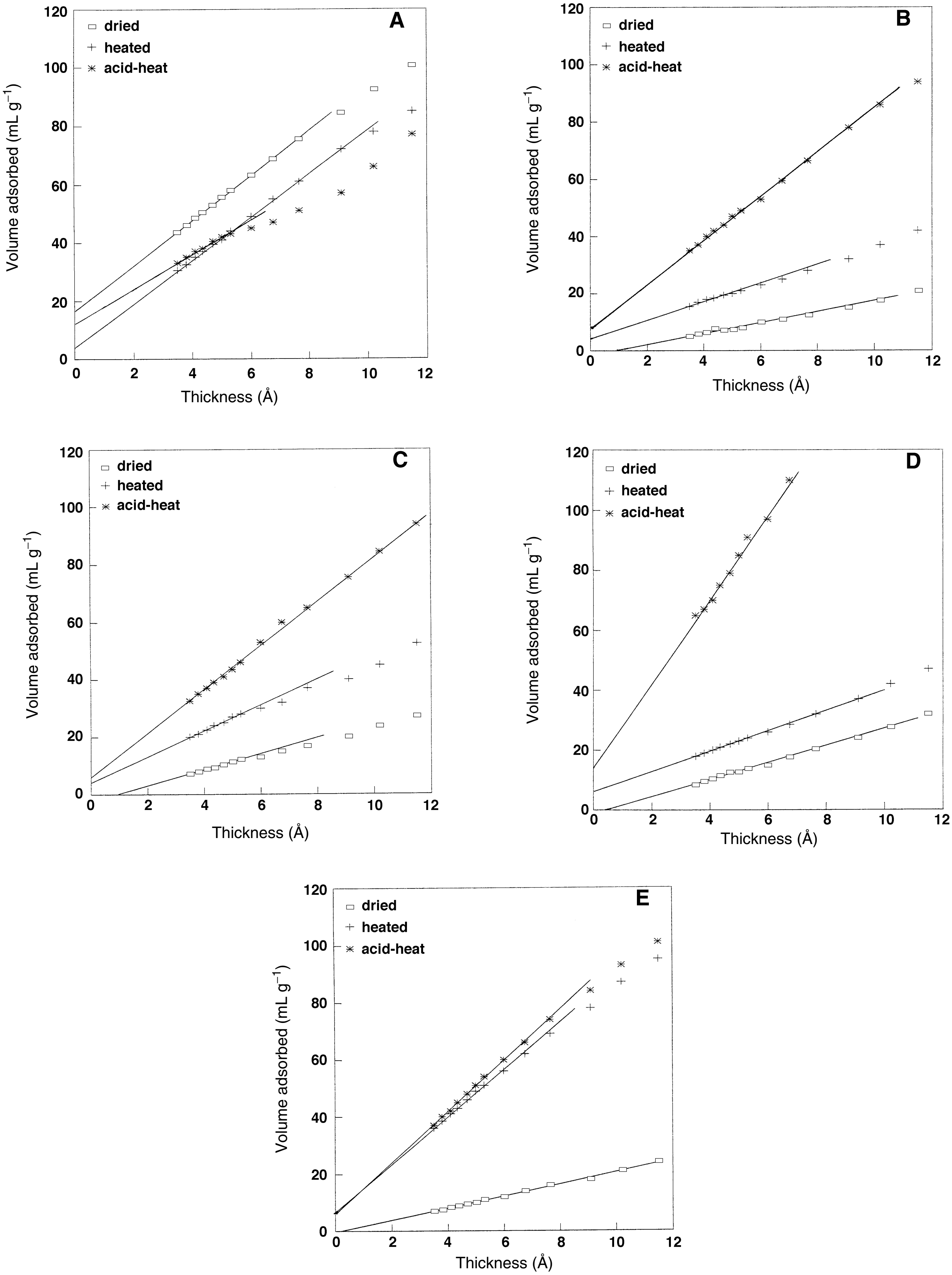

FIG. 4. *t*-Plots based on Lippens' reference *t*-curve for (A) sample unused clay, and for spent clay deoiled with (B) supercritical CO_2, (C) hexane, (D) methanol, and (E) hexane followed by methanol. Dried, □; heated, +; acid-heat, ∗.