Journal of Oil Palm Research Vol. 19 June 2007 p. 373-380

OPTIMIZATION OF DEGUMMING WITH ATTAPULGITE AND ACID-ACTIVATED CLAYS IN REFINING PALM OIL

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ABSTRACT

Attapulgite clay was evaluated as adsorbent in palm oil refining with different dosages of degumming agent (phosphoric acid). Its adsorption of trace metals (iron and phosphorus), chlorophyll pigment and primary and secondary oxidation products, was compared with that by a commercial bleaching clay. Attapulgite clay showed its potential as adsorbent for refining palm oil. Commercial acid-activated clay W and attapulgite clay A responded differently to increase concentration of phosphoric acid during degumming. There was a direct correlation between the iron content and concentration of phosphoric acid. The results of the study are relevant to the earths with the properties shown in this paper and may differ from those of other clays. It is clear from the study that the efficiency of adsorption maybe not necessarily be related to the acid activation of the clay.

Keywords: degumming, bleaching clays, trace metals, chlorophylls, phosphorus.

Date received: 6 March 2006; **Sent for revision:** 14 August 2006; **Received in final form:** 16 November 2006; **Accepted:** 12 March 2007.

INTRODUCTION

Palm oil is physically refined with the crude oil degummed, bleached and deodorized to a light golden yellow. Crude palm oil contains carotenoids and other pigments. The carotenoids are removed at both the bleaching and the deodorization stages, while the other pigments generally at the bleaching stage. In the degumming stage, an acid such as phosphoric acid is added to condition gums together with the bleaching earth. The phospholipids, trace metals, oxidation products, some free fatty acids, pigments and their decomposition products are removed (Siew, 1987). Getting the conditions right is important for the efficient removal of the impurities, which, if retained, will cause darkening and other colour problems. Defining the actual content of gums has been discussed by Siew (1987).

The bleaching clays used in palm oil refining are mainly acid-activated and some non-acid-activated as well. Acid activation increases the surface of the clays, providing more area for adsorption. Natural clays, on the other hand, usually have a lower surface area, but yet may have sufficient pore volume and pore size for sufficient adsorption for the trace impurities. Attapulgite clays have been investigated as a natural product for refining vegetable oils (Cheah and Siew, 1999; Boki *et al*., 1994). This study analyses the clay adsorptive capabilities and evaluates the material for removal of undesirable compounds in palm oil vis-à-vis a commercial clay used at present by refineries in Malaysia. Since refining is a process that involves selection of a suitable degumming procedure and adsorbent to remove impurities from the crude oil, it is crucial to understand the influence of the degumming agent on the adsorbent properties. In Dijkstra's (1989) paper, the total degumming process is described involving an acid, followed by mixing with a base or sodium silicate to assist in removal of the gums. The factors found to be critical are the residual iron content which determines the finished oil quality, and the strength of the phosphoric acid used. While refining soyabean oil involves an additional alkali step which is perhaps better in removing the complexes of phospholipids and iron compounds, the refining of palm oil which, in general, does not include the alkali step, may need other critical evaluation on the different steps in the process. This

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paper also deals with the removal of these gums which include phosphorus materials, iron and other oxidation products.

In the experiment, a constant volume of phosphoric acid of different concentrations was added during dry degumming prior to bleaching, in order to have a better understanding of the effect of the degumming acid on performance of the clay during refining of palm oil. Attapulgite clay A from Hudson Resource and acid-activated commercial clay W from the Taiko Group, Malaysia were used as the bleaching clays.

MATERIALS AND METHODS

Materials

Crude palm oils were donated by FELDA Vegetables Oil Products Sdn Bhd, Port Klang, Selangor, Malaysia. The bleaching adsorbents employed were commercial acid-activated clay W (powder; Taiko Group of Companies, Malaysia) and attapulgite clay A (powder; Hudson Resources Ltd., Australia). All the chemicals used were of reagent grade.

Methods

Degumming and Bleaching

The procedures applied were modified from bleachability test in *MPOB Test Methods* (2005). Various concentrations of degumming acid (4%, 8%, 12%, 16% and 20% w/v) were prepared by diluting 85% phosphoric acid with distilled water. The 100 ± 0.1 g crude palm oil (CPO) were melted and weighed into the reaction vessel. The CPO was stirred with a magnetic stirrer under a nitrogen blanket throughout the degumming and bleaching processes. The CPO was heated to 90°C before 0.25 ml degumming acid (4% w/v phosphoric acid) was pipetted into the heated oil. The mixture was agitated for 10 min at 90ºC. After the degumming process, 1.0 g commercial acid activated clay W was added to the oil sample. The temperature was raised to 105°C and maintained for 15 min. After the bleaching, the hot oil/bleaching clay mixture was filtered using Whatman No. 1 filter paper. Then, deodorization was carried out under vacuum at 260°C for 20 min without agitation.

All the above steps were repeated with 0.25 ml degumming acid (8%, 12%, 16% and 20% w/v phosphoric acid) to obtain 0.02%, 0.03%, 0.04% and 0.05% w/w phosphoric acid in 100 g CPO, respectively.

Two controls were prepared for the purpose of comparison. The first was without adding any phosphoric acid during degumming. However, it was bleached with 1.0 g bleaching earth and deodorized. The second was without degumming acid and bleaching clay, and the oil deodorized. The experiment was repeated using clay A from Hudson Resources Ltd.

Specific extinction in UV light of 233 nm and 269 nm, and β-carotenes. These were analysed according to *MPOB Test Methods* (p2.14 and p2.6). Palm oil rich in carotenes was measured in a UV visible spectrophotometer, Lambda 12, Perkin Elmer using a 10 mm cell at 446 nm. The solvent was iso-octane. A sample of 0.1 g was weighed into a 25 ml volumetric flask and the solvent added. Measurement at 446 nm was taken and the results calculated as parts per million carotene. The same solution was also used for measurement of $E^{1\%}_{233}$ and $E^{1\%}_{269}$. Results were corrected for the carotene absorption.

Determination of colour **(MPOB Test Method, *p4.1*)**. The method consisted of matching the colour of light transmitted through a specified depth of refined, bleached and deodorized (RBD) palm oil to the colour of light, from the same source, transmitted through standard colour slides by a Lovibond Tintometer (Model E). The Lovibond scale includes white, red, yellow and blue colour. In the case where the red and yellow units did not render an acceptable match of the oil colour, a minimum level of blue unit was applied to obtain the best match.

Determination of chlorophyll content. A diode laser emitting at 630 nm was used as the exciting source for inducing fluorescence of the chlorophyll pigments in vegetable oils. The pulsed fluorescence intensity of the vegetable oil was then measured by a 1 cm^2 photodiode. A dual slope technique was used to estimate the intensity of the fluorescence signal, which was proportional to the chlorophyll content in the sample (Tan *et al.*, 1999).

A stock solution of dephotosensitised refined palm olein was prepared according to the method by Frankel *et al*. (1979). A column was packed with a *n*-hexane slurry of 1:1 (w/w) activated carbon black and diatomaceous earths to a height of 8 cm. The column was then topped with a 1 cm layer of silicic acid. The 100 ml *n*-hexane containing 25 g oil were then passed through the column. The oil was eluted with a further 100 ml *n*-hexane. The elutant was collected and the *n*-hexane evaporated off using a rotary evaporator followed by flushing with nitrogen. The resulting dephotosensitized oil was kept aside for preparation of the calibration standards.

Canola oil was used as the calibration standard with dilutions with dephotosensitized oil. The chlorophyll content of the diluted canola oil was then measured at 610 nm, 670 nm and 710 nm in a 10 mm glass cuvette against air instead of a reference cell. The content of chlorophyll pigment was expressed in mg Pheophytin *a*, the main chlorophyll pigment in crude vegetable oils. The calculation was as below:

$$C = 345.3\,(A_{670}\text{-}0.5A_{630}\text{-}0.5A_{710})\int^{-1}$$

where:

C = content of CHL pigments in mg PHY *a* in 1 kg oil
A = absorbance at the representative wavelengths (nm)
∫ = thickness of the spectrophotometer cell (mm)

The working standards with chlorophyll contents of 100, 500 and 1000 ppb were prepared by canola oil and dephotosensitized oil. The fluorescence intensities of the working standards were determined using a prototype laser-based fluorometer. A typical calibration curve was plotted from measurements of fluorescence signals of the working standards. The test sample was homogenized by heating to 60 ± 2°C in an oven. The liquid sample was then poured into a 10 mm glass cuvette, the cuvette inserted into the sample holder of the laser-based spectrofluorometer and the reading recorded. The same procedure was repeated twice to obtain triplicate readings.

Phosphorus and iron analysis. The phosphorus and iron contents were determined according to *MPOB Test Methods* (p2.8 and p2.10), respectively.

RESULTS AND DISCUSSION

Bleaching Clays

Naturally active clays possess some adsorptive properties. These minerals owe their high adsorption capacity due to their rather high surface area. Acid activated clays show much higher activity due to their large surface areas and acid sites. The two clays studied in this paper represented an acid-activated clay and a natural palygorskite. Their properties are given in *Table 1*. The surface area of clay W was 234 $m^2\ g^{-1}$ while that of the clay A only 139 $m^2\ g^{-1}$. The pore diameter of the acid-activated W was only 65 while that of clay A is higher. *Figures 1* and *2* show the morphology of the clays. Clay W was platelike with some needle-shape structures, somewhat similar to clay A. Clay A had clearly long needle-like structures as expected of the adsorbent.

TABLE. 1 PROPERTIES OF CLAYS USED IN EXPERIMENTS

Clay	BET surface area ($m^2\ g^{-1}$)	BET C value	r^2	BJH pore volume ($m^3\ g^{-1}$)	Average pore diameter (Å)
Clay W	234	125	0.9999	0.38	65
Clay A	139	255	0.9999	0.34	97

Notes: BET surface area = Brunaucer, Emmett and Teller surface area.
BET C value = Brunaucer, Emmett and Teller constant value.
R^2 = Brunaucer, Emmett and Teller correlation coefficient.
BJH = Barrett, Joyner and Halenda desorption cumulative pore volume.

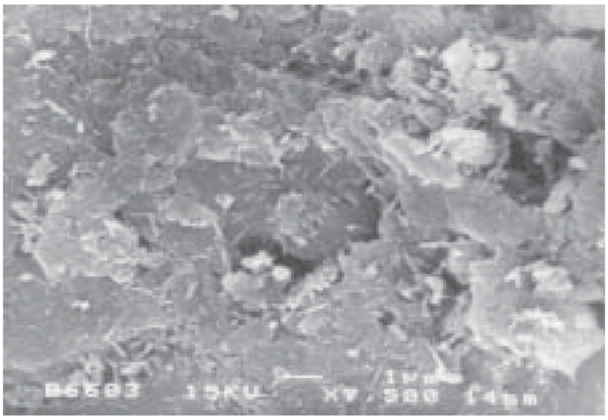

Figure 1. SEM morphology of acid-activated clay W.

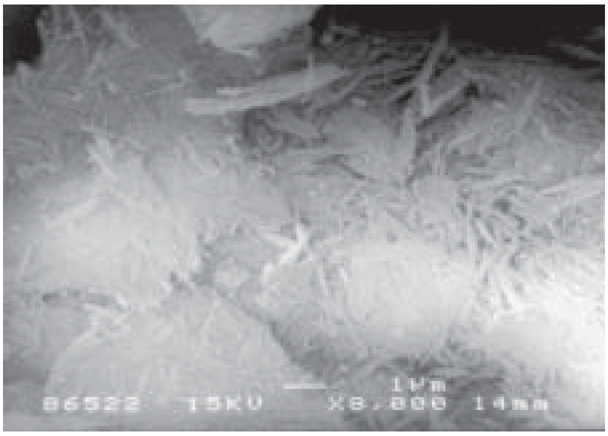

Figure 2. SEM morphology of natural clay A.

Gummy Materials in Crude Oil

The gums in CPO are a colloidal mixture of phospholipids, trace metals and some carbohydrate materials from the fruit bunch. These gums are usually measured as phosphorus compounds and are removed at the bleaching stage. They are conditioned by a degumming stage, so-called because the gums in colloidal form are precipitated by acid addition to the oil. The gums are precipitated with addition of acid or water as shown in *Figures 3* and *4*. The appearance of the gums from the water degumming process is lighter in colour and less compact than those from phosphoric acid treatment. Most probably, the dark colour from the latter

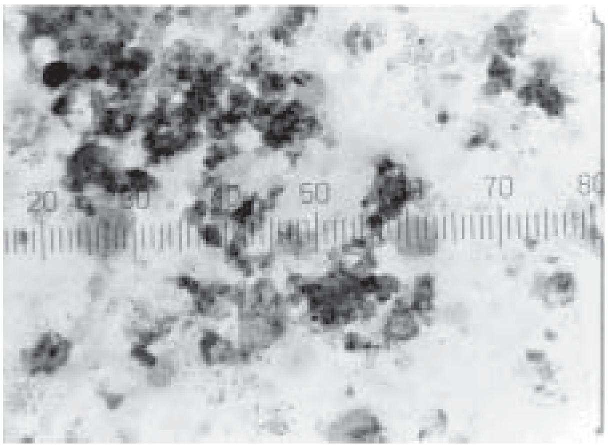

Figure 3. Gums precipitated with phosphoric acid.

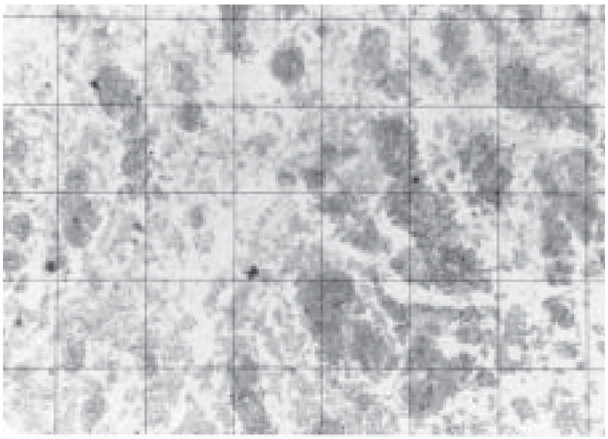

Figure 4. Gums precipitated with water degumming.

treatment is due to acidic conversion of the iron compounds into iron phosphates (Dijkstra, 1992), and darkening of the phospholipids. The use of acid is a more efficient process and is more common in the industry. After precipitation, the gums are only removed in the bleaching process with filtration by the earth. Dijkstra (1992) discussed the release of divalent ions in oils through degumming acids, thus requiring less bleaching earth. In this experiment, the use of different nature earths offers more insight into the need to carefully monitor the complexity of the earth's surface properties with those of the impurities being removed. In the following discussion, the focus is on the iron content, phosphorus compounds and oxidation products of glycerides.

Iron and Phosphorus Contents

Iron in CPO comes from the wear and tear of the extraction machinery. Degumming by phosphoric acid precipitates the iron as colloidal complexes, allowing them to be removed by filtration and the rest by adsorptive bleaching. The amount of iron retained in the refined oil is influenced by the concentration of phosphoric acid (*Figures 5* and *6*) used in the degumming process. The higher the concentration of phosphoric acid, the lower the iron content in the RBD oil. Pre-treatment by phosphoric acid will convert the metal complexes into a more easily adsorbed form (Shaw and Tribe, 1983). In fact, the degumming process in physical refining is very important because the stability of the oil is affected by the traces of metals and phosphorus left in it. The results showed that iron in the RBD palm oil bleached by clays A and W were 0.31 and 0.52 ppm, respectively. Thus, clay A was better at removing iron from the oil.

As expected, using the phosphoric acid as the degumming acid affected the phosphorus content in the RBD oil. Therefore, it is important to know the optimum concentration of phosphoric acid for different clay adsorbents. Too much phosphoric acid and too poor adsorption properties of the clay in removing the phosphate ions would leave the oil with too much phosphorus. Treatment with the right clay adsorbent should produce a lower phosphorus concentration than original by removing not only the phosphoric acid but the phospholipids in the crude oil as well. The acid-activated and natural clays responded differently to increase phosphoric acid used in degumming. The lowest phosphorus content (5.4 - 5.8 ppm) in the RBD palm oil was found using the optimum concentration of phosphoric acid (0.03%-0.04%) with clay W. When the concentration of phosphoric acid used exceeded or was below the optimum, phosphorus content was higher. Only a slight deviation from the optimum concentration sufficed to increase the residual phosphorus in the oil. The higher phosphorus level would then require more bleaching clay to reduce it to targeted level. Therefore, careful control of the concentration of phosphoric acid used in degumming must be stressed.

The phosphorus content remained unchanged (at about 5 ppm) in the RBD oil bleached with attapulgite clay, when 0.01% to 0.05% phosphoric acid was added for degumming.

The experimental controls were prepared by bleaching the crude oil with clays A and W, without adding any phosphoric acid for degumming. It is interesting to note that the phosphorus content in the RBD oil bleached with clay A was the lowest, at 4.5 ppm, from the initial 12.2 ppm in the CPO. Therefore, phosphorus was removed effectively by the adsorbent clay A without the recourse to phosphoric acid, which would have increased the phosphorus content of the oil. However, this phenomenon was not observed using acid-activated clay W. Therefore, generally, with or without using phosphoric acid for degumming, clay A possessed a better capacity for adsorbing phosphorus from oil than clay W.

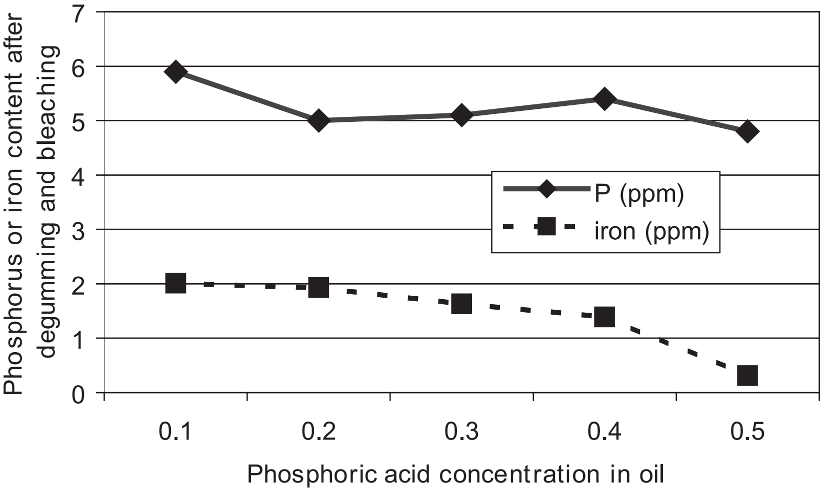

Figure 5. Effect of phosphoric acid concentration on phosphorus and iron removal with attapulgite clay.

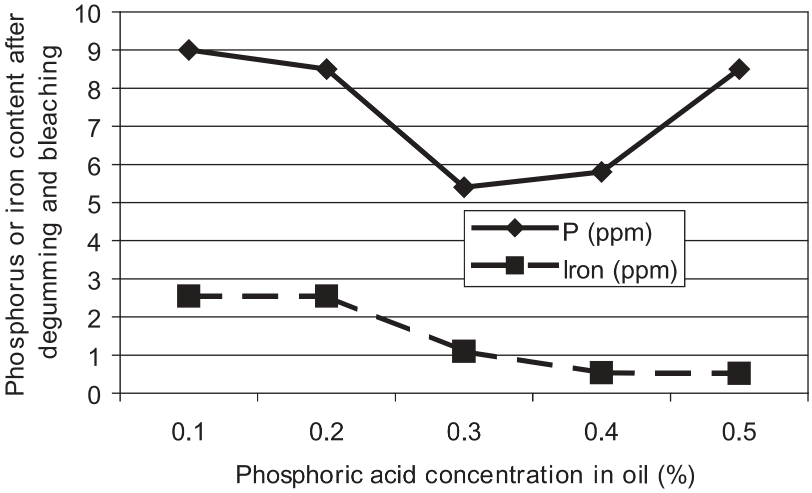

Figure 6. Effect of phosphoric acid concentration on phosphorus and iron removal with acid-activated clay.

Figure 5 implies a correlation between the phosphorus and iron contents in the RBD oil bleached with clay A. However, this was not observed using clay W, particularly at the high concentrations of added phosphoric acid, 0.04%-0.05% (*Figure 6*). This might be due to over-dosage of phosphoric acid. A plot of phosphorus content versus iron level in refined oils showed no correlation except at low levels (Dijkstra, 1992). According to Siew *et al.* (1990), the hydrolytic stability of refined palm oil is dependent on phosphorus and is also affected by its iron and water content.

Colour of RBD Palm Oil

Figure 7 shows the colour of RBD palm oil after degumming with phosphoric acid of different concentrations. The red colour decreased in RBD oil was observed with increasing concentration of phosphoric acid from 0.01% to 0.03%. The RBD palm oil showed 3.7 Red in 5.33 inch cuvette cell in the absence of phosphoric acid, dropping to 2.1 Red after addition of 0.03% phosphoric acid and bleaching with clay A. When phosphoric acid exceeded 0.03%, the colour of the RBD oil remained unchanged for both the bleaching clays. When lower colours are needed, it is necessary to increase the earth dosage.

Palm oil bleached with clay A was a lighter red colour and had lower phosphorus than the oil bleached with clay W. The result suggested that the colour of RBD palm oil was affected by the extent of removal of its phosphorus and iron contents. If phosphatides remained in the oil prior to deodorization, the refined oil would be darker in colour and poorer both in initial flavour and stability (Molik and Pokorny, 2000). Although one usually expects an acid-activated clay to perform better than a natural clay, it is clear that this is not always the case. Indeed, the performance of a clay is more complicated than just performanced based on its acidity, pore size and surface area.

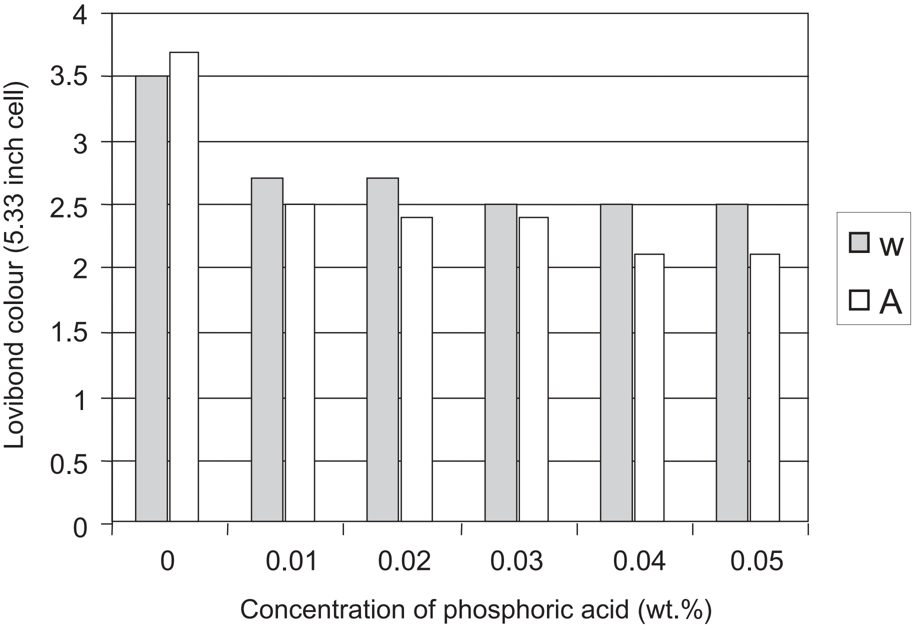

Figure 7. Colour of refined oil after degumming and bleaching with attapulgite (A) and acid-activated (W) clays.

Chlorophyll Content

Chlorophyll content in CPO is lower than compared in other vegetable oils such as rapeseed, canola and olive oils. As such, its removal from CPO is less of an issue. *Figure 8* shows that most of the chlorophyll in CPO is already decomposed with heat applied to the oil such as during bleaching and deodorization, where, a portion of chlorophyll was converted to pheophytin (Usuki, 1987). The experimental control revealed that heat degumming with phosphoric acid further decomposed more the chlorophyll in RBD oil than only heat degumming without phosphoric acid. Chlorophyll can also be converted to pheophytin by losing magnesium under acidic conditions, such as when phosphoric acid is used for degumming (Usuki, 1987). The two clays did not show much difference in their adsorption of chlorophyll, and addition of phosphoric acid at different concentrations had very little effect on the removal. This observation is not in line with general observations that acid-activated clays show better adsorption for chlorophylls. Pore volume and surface acidity are important factors in discussing chlorophyll adsorption. In this case, the acid-activated clay, with slightly higher pore volume and higher surface area, did not show very much more superior adsorption of chlorophyll. Perhaps, the larger pore diameter of clay A compensated for its inferior other physical properties.

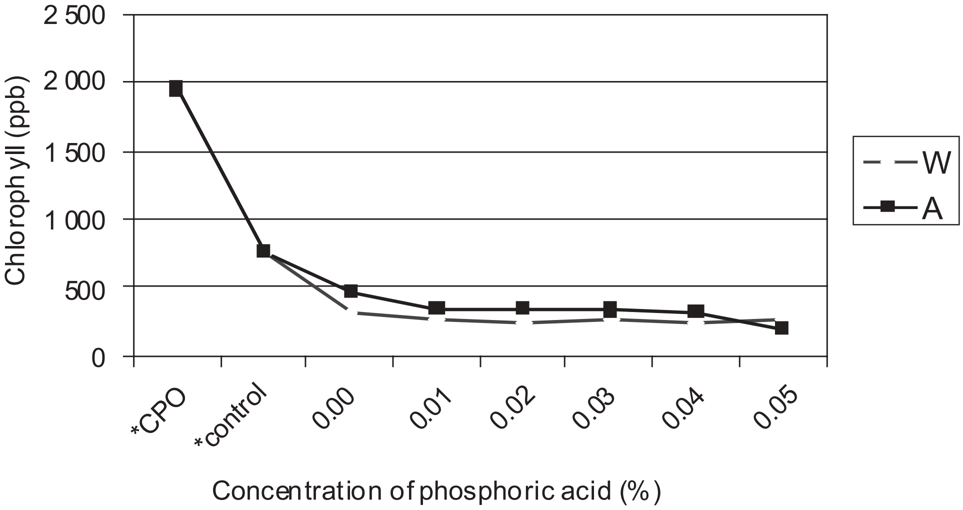

Figure 8. Chlorophyll contents in refined oil after degumming and bleaching with attapulgite (A) and acid-activated (W) clays.

3.6 $E^{1\%}_{233c}$ and $E^{1\%}_{269c}$

These parameters represented oxidation characteristics of an oil. *Figures 9* and *10* show $E^{1\%}_{233c}$ and $E^{1\%}_{269c}$ for RBD palm oil after degumming with phosphoric acid of different concentrations. The $E^{1\%}_{233c}$ is a measure of the conjugated dienes present, and is related to both primary oxidation and colour fixation. On the other hand, $E^{1\%}_{269c}$ is a measure of the conjugated trienes, and is related to the secondary oxidation level. The RBD oil after bleaching with clay A contained higher secondary oxidation products and lower primary oxidation products as the concentration of phosphoric acid was increased. However, this trend was not observed in the RBD oil after bleaching with clay W. Generally, with phosphoric acid, the $E^{1\%}_{269c}$ was higher for RBD oil after bleaching with clay W than with clay A. It is clear that the clays removed the primary oxidation products, as indicated by the lower $E^{1\%}_{233c}$ value. However, removal of the secondary oxidation products was not so clear, as these products continued to be formed even during the bleaching. It can be seen that using more acid-activated clay may result in higher secondary products evidenced by the higher values of $E^{1\%}_{269c}$.

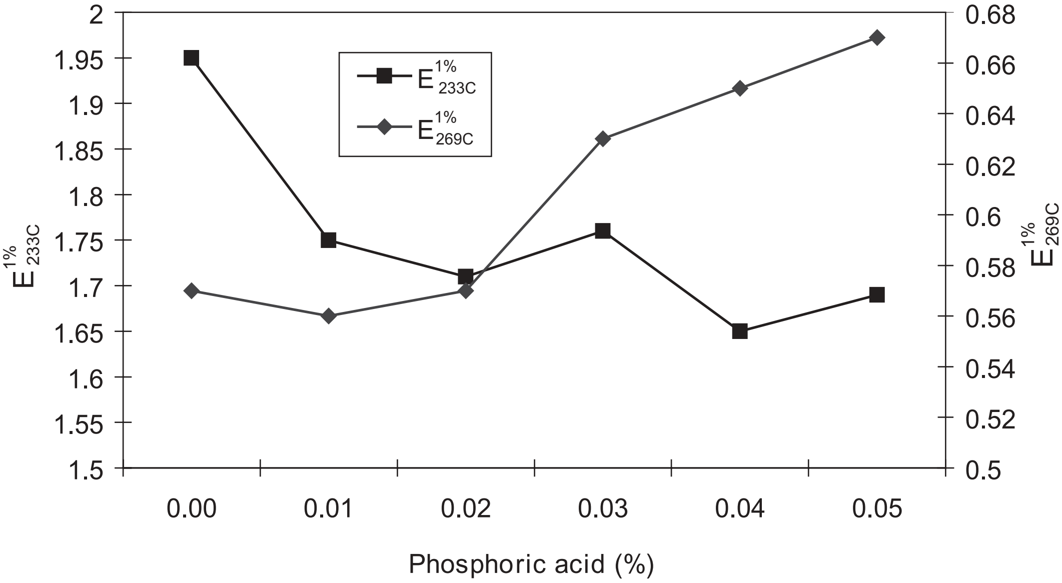

Figure 9. Effect of phosphoric acid concentration on $E^{1\%}_{233c}$ and $E^{1\%}_{269c}$ of palm oil using attapulgite clay.

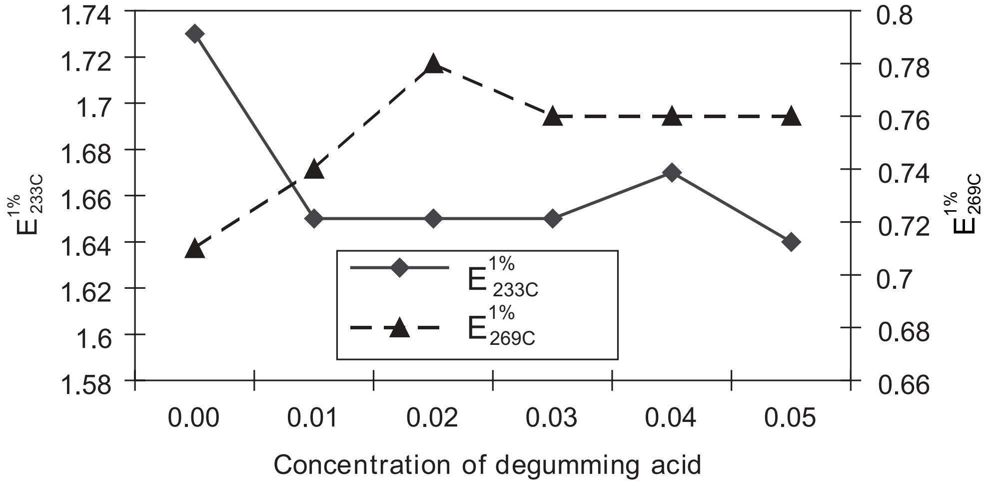

Figure 10. Effect of phosphoric acid concentration on $E^{1\%}_{233c}$ and $E^{1\%}_{269c}$ of palm oil using acid-activated clay.

CONCLUSION

Phosphoric acid degumming gives good results provided that optimum levels are used. Acid-activated clay W, and clay A responded differently to the increased concentration of phosphoric acid during degumming. Higher phosphoric acid used most probably resulted in it being carried into the oil, causing a high content of phosphorus in the deodorized oil. The results showed a direct correlation between the trace iron contents and concentration of phosphoric acid. An efficient degumming stage would improve oil stability by increasing the efficiency of phosphatide and iron removal.

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