Journal of Oil Palm Research Vol. 19 June 2007 p. 356-363

ADSORPTION ISOTHERMS FOR REMOVAL OF IRON, COPPER, PHOSPHORUS AND OXIDATION PRODUCTS FROM CRUDE PALM OIL USING NATURAL AND ACID-ACTIVATED CLAYS

SIEW WAI LIN* and CHEAH KIEN YOO*

ABSTRACT

A study was carried out on acid activated clay (W) and non-acid activated clays (P and A). Trace metal components and phosphorus compounds were monitored. The Langmuir isotherm was more applicable than the Freundlich isotherm for the adsorption of trace metals, copper and iron. Both the non-acid activated clays were better adsorbents of iron from degummed and bleached palm oil than the acid-activated clay, indicating that neutral and natural adsorbents (clays P and A) could be better for removal of iron in crude palm oil than the acid activated clay in spite of having lower surface areas. Clay P was the best adsorbent for most of the analysed components among the three tested clays. The degummed palm oil bleached with clay P had the lowest concentrations of phosphorus and copper. The removal of primary and secondary oxidation products did not follow the Freudlich and Langmuir equations, probably due to changing values effected by the adsorbent rather than by just mere adsorption.

The study shows that careful selection of clays for specific functions is very important for bleaching efficiency where minor impurities in palm oil are removed.

Keywords: phosphorus, iron, copper, oxidation products.

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

INTRODUCTION

Bleaching clays are used as adsorbents for the removal of pigments and other undesirable minor constituents which give off flavours and dark colours to vegetable oils. Adsorption is generally considered a chemical physical process since in the use of montmorrillonite acid-activated clays, the pigments removed, cannot be completely recovered by solvent extraction. In non-activated clays, physisorption is believed to predominate.

Crude oils contain impurities such as phosphorus from phospholipids, iron and copper either as inorganics or bound to organic compounds. In crude palm oil, the amounts of such impurities vary, depending on its quality. For example, phosphorus varies from 10 to 40 ppm, of which a portion is inorganic (Siew, 1987), and iron from 2 to 10 ppm (Tan *et al.*,1999). In general, such impurities are more difficult to remove from oil of poorer quality. The quality of crude palm oil is determined by its free fatty acids content, oxidative parameters such as peroxide values, anisidine value, DOBI (Swoboda,1982) and other oxidative measurements such as $E_{233}^{1\%}$ and $E_{269}^{1\%}$. The situation is complicated as no one parameter is able to predict oil quality sufficiently. The use of suitable adsorbents is crucial for removing as much as possible of the impurities which cause the poor stability and colour.

Acid-activated clays are commonly used in the industry being generally efficient for removal of such impurities. Non-activated clays are generally less

---

* Malaysian Palm Oil Board,
P. O. Box 10620,
50720 Kuala Lumpur,
Malaysia.
E-mail: siew@mpob.gov.my

efficient. The selection of suitable earths for the function is crucial to the success of refining. In this study, the common earths used in Malaysia for refining crude palm oil were evaluated for efficient removal of these impurities. In this article, the removal of phosphorus compounds, iron and oxidation products of lipids are discussed. Adsorption isotherms of chlorophyll and carotenes have already been discussed in another paper.

MATERIALS AND METHODS

Materials

Three clays, two attapulgite-based (P and RAL), and the other acid-activated (W), were used. They are commercial samples from the Taiko Group of Companies, Malaysia, Hudson Resources Ltd, Australia and Oil Dri, USA used for refining palm oil. They were tested on crude palm oil with FFA 3.9% and DOBI 2.2, 476 mg kg^{-1} carotene and 1987 µg kg^{-1} chlorophyll.

Methods

Bleaching test. The bleachability test in *MPOB Test Methods* was used. 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 $\pm$ 0.1 g crude palm oil (CPO) were melted and weighed into the reaction vessel. The CPO was stirred with a magnetic stirrer under nitrogen blanket throughout the degumming and bleaching process. 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 a further 10 min at the same temperature. After degumming, 1 g of the commercial acid-activated clay, W, was added. The temperature was raised to 105°C and maintained for 15 min. After the bleaching, the hot oil/bleaching clay mixture was filtered through a Whatman No. 1 filter paper. Then, deodorization was carried out under vacuum at 260°C for 20 min without agitation.

Phosphorus Measurements

Phosphorus compounds were measured by charring and ashing the oil in the presence of magnesium oxide followed by colorimetric measurement as phosphovanadate-molybdic complex. The yellow complex formed was measured at 400 nm. The test followed the procedure given in *IUPAC Seventh Edition* (2.421).

Iron and Copper Measurements

The test followed the procedure given in *MPOB Test Method* (p 2.10, 2005). A Perkin Elmer A Analyst 700 with AS-90 autosampler and graphite furnace were used.

RESULTS AND DISCUSSION

Adsorption of Iron and Copper

Traces of impurities such as these elements have to be removed as they cause deterioration of the oil quality. To avoid oxidation, it has been recommended that the iron content should be <0.1 mg kg^{-1}. In this study, three types of clays were evaluated. The acid-activated clay, W, displayed a high surface area of 234 m^2 g^{-1} while the other clays, P and RAL, exhibited low surface areas of 130 and 160 m^2 g^{-1}, respectively (*Table 1*). All the clays exhibited type IV isotherm with a hysteresis loop.

The applicability of the Langmuir isotherm can be examined from the plot of $X_e/(X/m)$ versus X_e for adsorption of the trace metals, iron and copper from the degummed palm oil. The results showed that the Langmuir equation was more applicable than the Freundlich equation for clay P (*Figures 1* and 2). However, clays W and RAL did not conform to the Langmuir model, although the R^2 values obtained were in range 0.7859 to 0.9309. Langmuir isotherm constants, *a* and *b* for iron are listed in *Table 2*. For the isotherms of copper, iron and phosphorus, the values of *a* did not correspond to the specific

TABLE 1. BET SURFACE AREA, PORE VOLUME AND PORE DIAMETER OF CLAYS

Clay	BET surface area (m^2 g^{-1})	BET (C value)	r^2	BJH pore volume (cm^3 g^{-1})	Average pore diameter (Å)
W	234	125	0.9999	0.38	65
P	157	336	0.9999	0.31	79
RAL	139	255	0.9999	0.34	97

Notes: BJH - Barett, Joyner and Halenda.
BET - Brunauer, Emmett and Teller.

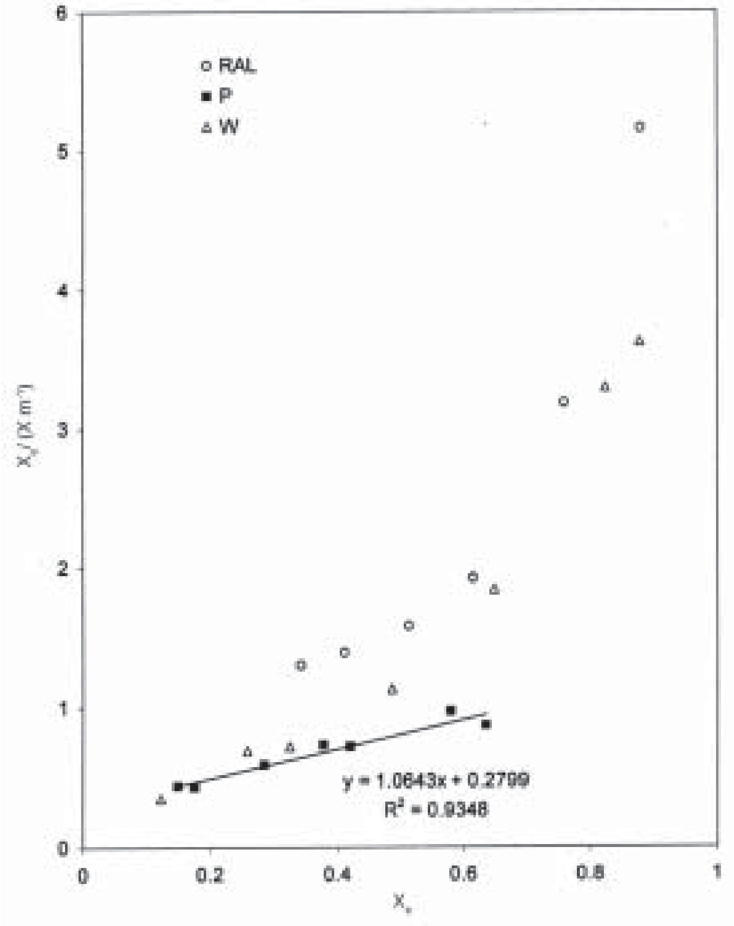

Figure 1. Langmuir isotherm for copper adsorption in crude palm oil.

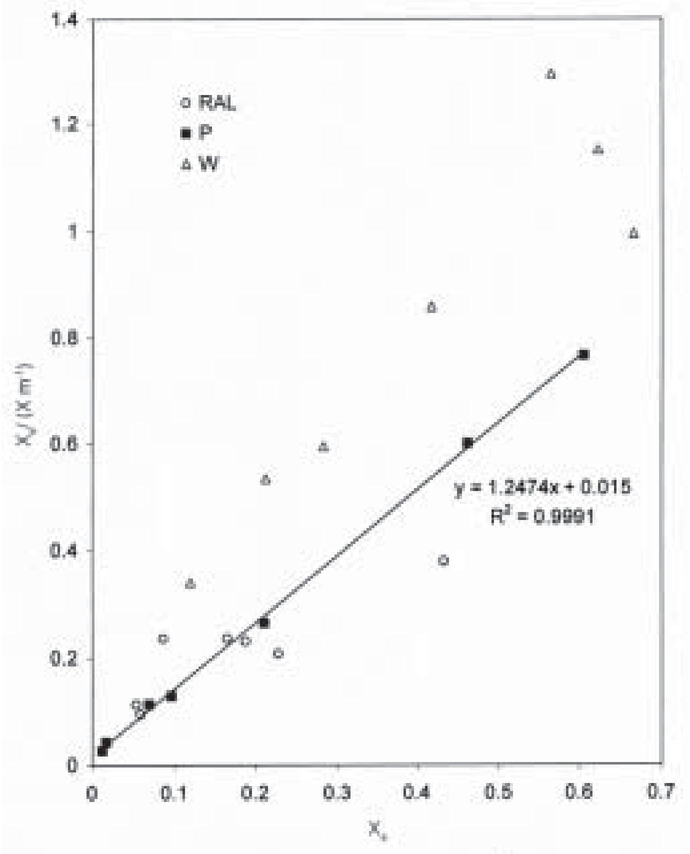

Figure 2. Langmuir isotherm for iron adsorption in crude palm oil.

TABLE 2. LANGMUIR AND FREUNDLICH CONSTANTS FOR IRON AND COPPER ADSORPTION FROM CRUDE PALM OIL BY DIFFERENT CLAYS

Iron Adsorption

Clay	Langmuir	r^2	*a*	*b*	
RAL	$y = 0.6339x + 0.1043$	0.7859	1.58	6.08	
P	$y = 1.2474x + 0.015$	0.9991	0.80	83.16	
W	$y = 1.507x + 0.2032$	0.8517	0.66	7.42	
Clay	**Freundlich**	r^2	*n*	*K*	1/n
RAL	$y = 0.4505x + 0.2324$	0.6860	2.22	1.71	0.45
P	$y = 0.1629x - 0.03$	0.7987	6.14	0.93	0.16
W	$y = 0.2745x - 0.204$	0.6925	3.64	0.63	0.27

Copper Adsorption

Clay	Langmuir	r^2	*a*	*b*	
RAL	$y = 6.7219x - 1.5254$	0.8550	0.15	-4.41	
P	$y = 1.0643x + 0.2799$	0.9348	0.94	3.80	
W	$y = 4.3642x - 0.5451$	0.9309	0.23	-8.01	
Clay	**Freundlich**	r^2	*n*	*K*	1/n
RAL	$y = -0.3965x - 0.6811$	0.3537	-2.52	0.21	-0.40
P	$y = 0.4385x - 0.0829$	0.9418	2.28	0.83	0.44
W	$y = -0.1836x - 0.536$	0.2974	-5.45	0.29	-0.18

surface areas of the clays with *a* (0.94) and *b* (3.80) for copper adsorption on clay P being the highest. The positive value of *b* also indicated that clay P gave the highest trace metals adsorption. On the other hand, negative values of *b* were obtained for copper adsorption on both clays RAL and W. In fact, clay P was the best adsorbent of copper and iron from the degummed-bleached oil, and clay W the worst.

Clays P and RAL were better adsorbents of iron from degummed and bleached palm oil than clay W. In refining, the acid functionality of the activated clay serves to enhance the binding of various trace constituents in the oil to the clay surface (Taylor and Jenkins, 1988). However, in this experiment, the neutral and natural adsorbents (clays P and RAL) removed iron more effectively than the acid-activated clay W. The amounts of adsorbed trace metals (iron and copper) and the specific area data also suggested that the amounts of trace metals adsorbed were not associated with the clay surface areas. On the other hand, increasing the dosage of bleaching clay, particularly P and W, from 0.5% to 2.5%, decreased the concentrations of trace metals in the bleached oil, implying higher surface area needed for greater removal of the trace metals. The Langmuir model is based on the assumption that adsorption proceeds only until a single layer is formed. The Langmuir isotherm was more applicable than the Freundlich isotherm for the adsorption of copper and iron.

Adsorption of Phosphorus

The observed linearity of the logarithm of the phosphorus retained versus logarithm of the phosphorus adsorbed/g of adsorbent (*Figures 3* and *4*), suggests the applicability of both the Langmuir and Freundlich isotherms to the adsorption of phosphorus on all the clays. However, a higher correlation coefficient was obtained for the Langmuir isotherm plot (*Table 3*). The Langmuir isotherms showed that the intensity of phosphorus adsorption on clay P (*b* = 48.45) and RAL (*b* = 34.09) was higher than that of clay W (*b* = 14.10). The adsorption isotherm studies also suggested that clays RAL and P were better adsorbents for phosphorus than clay W. The pore diameter was the smallest for clay W and largest for clay RAL. In addition to being a poor adsorbent for phosphorus, clay W was also unable to remove iron and secondary oxidation products effectively. The observation was in agreement with the finding of Taylor (1992) that phospholipid affected acid-activated clays adsorption of secondary oxidation products. Although clays RAL and P had lower surface areas, 139 $m^2 g^{-1}$ and 157 $m^2 g^{-1}$, respectively; they adsorbed more phosphorus than the acid-activated clay W, which possessed a higher surface area of 234 $m^2 g^{-1}$ (*Table 1*). The amounts of adsorbed phosphorus and the specific area data also suggested that adsorption on the clays were not associated with their surface areas. However, it is worth noting that increasing the dosage of bleaching clay, particularly of clay P and

W, from 0.5% to 2.5%, decreased the concentrations of chlorophyll and carotene pigments in the bleached oil. This was suggestive of the fact that with a higher clay dosage, there was more surface area of clay for the removal of chlorophyll and carotene pigments.

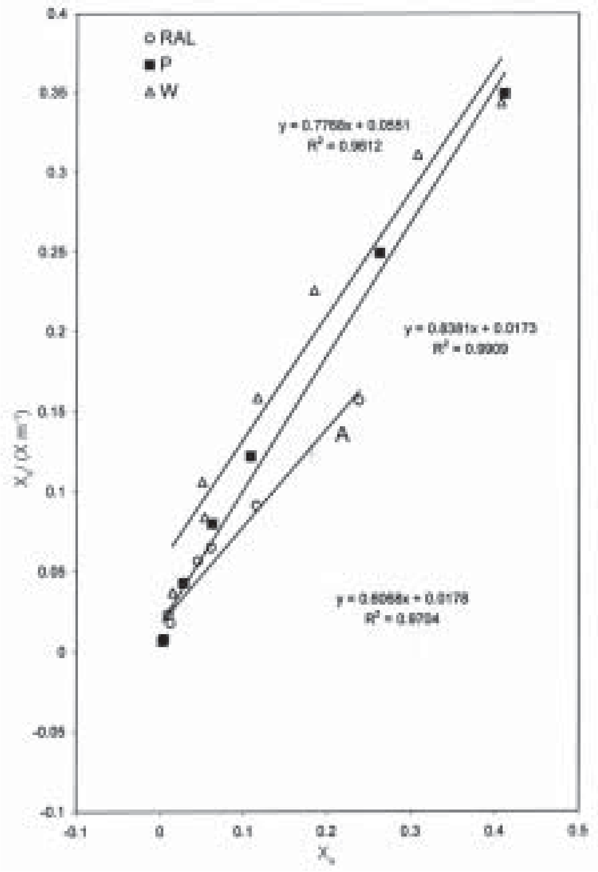

Figure 3. Langmuir isotherm for phosphorus adsorption in crude palm oil.

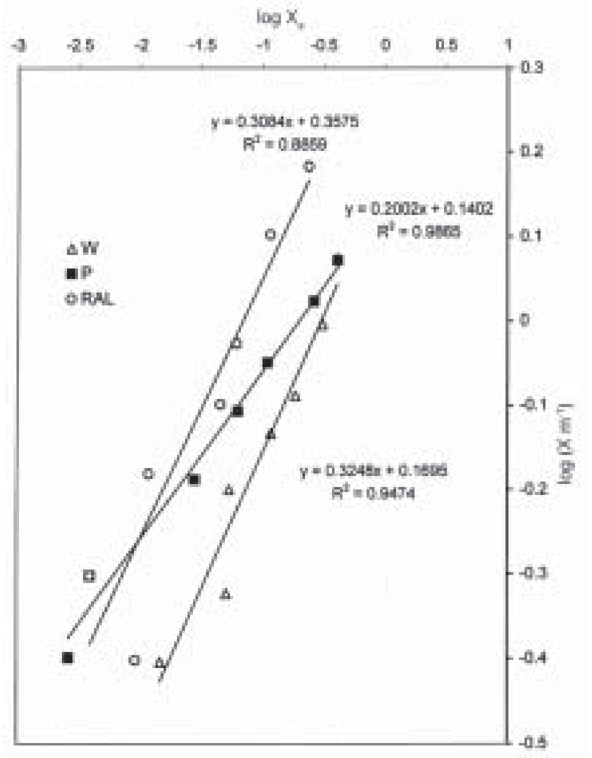

Figure 4. Freundlich isotherm for phosphorus adsorption in crude palm oil.

TABLE 3. LANGMUIR AND FREUNDLICH CONSTANTS FOR PHOSPHORUS AND OXIDATION PRODUCTS ADSORPTION FROM CRUDE PALM OIL BY DIFFERENT CLAYS

Phosphorus Adsorption					
Clay	Langmuir	r^2	*a*	*b*	
RAL	y = 0.6068x + 0.0178	0.9704	1.65	34.09	
P	y = 0.8381x + 0.0173	0.9909	1.19	48.45	
W	y = 0.7768x + 0.0551	0.9612	1.29	14.10	
Phosphorus	Freundlich	r^2	*n*	*K*	1/n
A	y = 0.3084x + 0.3575	0.8859	3.24	2.28	0.31
P	y = 0.2002x + 0.1402	0.9865	5.00	1.38	0.20
W	y = 0.3248x + 0.1695	0.9474	3.08	1.48	0.32
$E^{1\%}_{233c}$					
Clay	Langmuir	r^2	*a*	*b*	
RAL	y = -71.637x + 65.503	0.6216	-0.01	-1.09	
P	y = -84.134x + 76.287	0.8047	-0.01	-1.10	
W	y = -8.0606x +12.88	0.7838	-0.12	-0.63	
Clay	Freundlich	r^2	*n*	*K*	1/n
RAL	y = 11.365x + 0.0882	0.7822	0.09	1.23	11.37
P	y = 12.768x + 0.1711	0.8840	0.08	1.48	12.77
W	y = 7.4314x + 0.2098	0.6495	0.13	1.62	7.43
$E^{1\%}_{269c}$					
Clay	Langmuir	r^2	*a*	*b*	
RAL	y = -22.155x + 33.468	0.5405	-0.05	-0.66	
P	y = -6.8561x + 9.5611	0.7134	-0.15	-0.72	
W	y = -5.0898x + 7.1143	0.2791	-0.20	-0.72	

Adsorption of Primary and Secondary Oxidation Products

The adsorption isotherms of primary and secondary oxidation products from degummed palm oils for the three tested clays did not obey both the Freundlich and Langmuir equations. Little change in the primary oxidation products was observed with the increase in clay dosage. A control oil was prepared by heat bleaching without use of any clay. It showed that clays during bleaching effectively reduce the primary oxidation products but increased the secondary oxidation products. The primary oxidation products were converted to the secondary products in the degumming and bleaching processes, thus the higher results obtained upon higher usage of bleaching clays. From *Figure 5*, removal of the primary oxidation products by clay RAL appeared to level off at 1.5% dosage. On the other hand, the other two earths continued to reduce the primary oxidation products. From *Figure 6*, clay RAL gave an oil with a lower secondary oxidative value than the oil refined with the acid-activated clay. It is clear that the two characteristics are linked when bleaching earths are utilized in the purification of oils. It is, however, not clear whether lower primary oxidative products are essential for better oil stability since the results showed that more secondary products are then formed.

Further research is suggested to analyse and correlate the levels of secondary oxidation products in oil from bleaching with different clays and their effects on the storage stability of RBD oil.

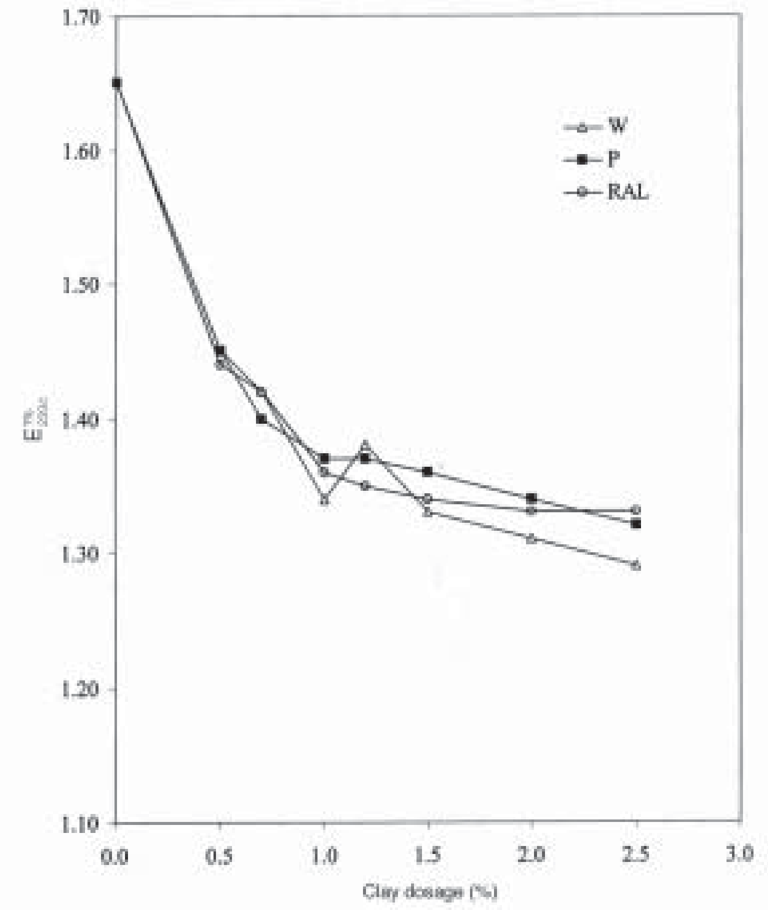

Figure 5. Removal of primary oxidation products from crude palm oil by different clays.

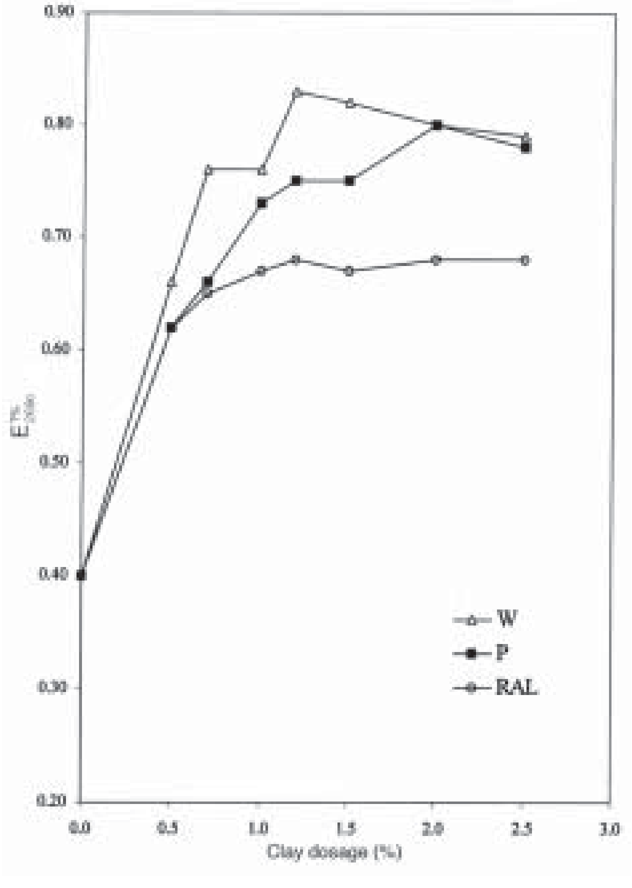

Figure 6. Removal of secondary oxidation products in crude palm oil by different clays.

CONCLUSION

Clay P was the best adsorbent for most of the analysed components in crude palm oil among the three tested clays. The degummed palm oil bleached with clay P had the lowest concentrations of phosphorus and copper. It is interesting to note that clay RAL was a better adsorbent of phosphorus and iron at low doses (1.0% - 1.5%) than clay P. Increasing the dosage did not increase the bleaching efficiency greatly. The lowest concentration of secondary oxidation products was obtained from bleaching with clay RAL. However, this degummed-bleached oil had the highest concentration of copper. Generally, clay W was a poor adsorbent of phosphorus, iron and secondary oxidation products but this acid -activated clay removed copper more effectively than clay RAL.

REFERENCES

IUPAC. *International Union of Pure and Applied Chemistry Standard Methods for Analysis of Oils Fats and other derivatives, 6th Edition.*

PORIM (1995). *PORIM Test Methods.* PORIM, Bangi.

SIEW, W L (1981). *Phosphorus Compounds in Palm Oil*. M. Sc. thesis. University of Salford, UK.

SWOBODA, P A T (1982). Bleachability and the DOBI. *PORIM Bulletin No. 5*: 28-38.

TAN, Y A; KUNTOM, A; SIEW, W L; YUSOF, M and CHONG, C L (1999). Present status of crude palm oil quality in Malaysia. *Proc. of the 1999 PORIM International Palm Oil Congress - Chemistry and Technology Conference*. PORIM, Bangi. p. 205-211.

TAYLOR, D R (1992). Adsorptive purification. *Proc. of the World Conference on Oilseed Technology and Utilization* (H A, Thomas ed.). American Oil Chemists' Society Press, Champaign, Illinois. p. 138-151.

TAYLOR, D R and JENKINS, D B (1988) Acid activated clays. *Society of Mining Engineering of the American Institute of Mechanical Engineers, Trans., 282*: 1901-1910.