values are close to the experimental ones. For trioleoylglycerol, the relative difference is only 12% and it is still lower for the others.

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Mechanism of Palm Oil Bleaching by Montmorillonite Clay Activated at Various Acid Concentrations

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ABSTRACT

The mechanism of bleaching by a nonswelling montmorillonite clay activated at various acid concentrations was studied in the bleaching of palm oil. Montmorillonite clay was activated by 2 parts of H_2SO_4 at concentrations of 10-40%. Chemical composition, bleaching ability, specific surface area and phosphorus content were studied. The study showed that an initial increase in bleaching ability by clay activated by an increasing addition of H_2SO_4 was due to acid leaching of organic matter and impurities in the clay. The consequence of acid leaching in this case tends to expose active sites for adsorption. Acid leaching also removed $A\ell^{3+}$, causing charge deficiency in the clay lattice and, hence, promoting the adsorption properties of the clay. A drop in bleaching efficiency at higher additions of H_2SO_4 was observed. This was due to excessive acid leaching of $A\ell^{3+}$, causing collapse of the clay lattice structure.

INTRODUCTION

Bleaching clays are produced by activating montmorillonite clay with either sulfuric or hydrochloric acid to increase its adsorbent properties.

The bleaching process, as commonly understood, is the removal of color bodies. In the case of plam oil, its objective is to change the oil from a red to pale yellow color. In contrast to the original oil, bleached oil is also more stable.

It is now recognized that bleaching clay performs not only color removal, but also the removal of trace metals, adsorbtion of phospholipids, soaps and decomposition of oxidation products such as peroxides (1). As a result, bleached oil is lighter in color and more stable.

It has been suggested that the activation process results in the replacement of aluminium by Mg and Fe ion (2). Its bleaching mechanism involves physical adsorption and chemisorption (1).

Results obtained by Zchau (1) showed that oil treated by bleaching clay tends to give a lower phosphorus content and anisidine value. Shaw and Tribe (2) reported that bleaching clay removes a portion of the trace metals in vegetable oil, in particular copper and iron, that are known to have deleterious effects on their oxidative stability and flavor. It is known that the red color in palm oil is mainly due to the presence of carotenoid compounds. Khoo et al. (3) suggested that the chemisorption of β-carotene occurs on aluminosilicate surfaces with some of the exchangeable cations acting as active sites.

The purpose of this study is to elucidate the physicochemical mechanism of bleaching by montmorillonite clay activated at various acid concentrations. The study is conducted with special reference to palm oil, which currently has the most rapid growth rates of the world export of oils and fats (4).

ACTIVATION OF CLAY

The clay used for bleaching is a nonswelling montmorillonite clay. They can be activated by either (a) natural process of acid leaching, or (b) sulfuric or hydrochloric acid activation.

Bleaching clays are predominantly aluminosilicate minerals. Such clay can be naturally activated by acid leaching, in which the aluminium present in the clay is removed. Hence, naturally activated clay is sometimes called "acid clay." Scheme I gives the structural formula for nonswelling montmorillonite clay.

$$\begin{array}{c} Ca \\ \uparrow \\ A\ell_2O_3\ 4SiO_2\ nH_2O \end{array}$$

SCHEME I

Clays which have low bleaching power can be increased by leaching with sulfuric or hydrochloric acid. In the experiment conducted, a nonswelling type of montmorillonite clay was added to 2 parts of sulfuric acid in which concentrations ranged from 10 to 40%.

After leaching by acid, the chemical composition of the dried clay sample was studied by X-ray fluorescence following the procedures outlined by Kheok and Thomas (5).

The results of the chemical composition of the natural and activated clays are given in Table I.

It can be seen that an increase in the concentration of the sulfuric acid tends to leach an increasing amount of $A\ell_2O_3$. This process tends to create net negative charges on the clay lattice structure and creates the cation adsorbtion properties of acid-activated montmorillonite clay.

DECOLORIZATION

To study decolorization by bleaching clay, experimental equipment was set up as shown in Figure 1.

Crude palm oil (400 g) was heated to 110 C before adding 2% by wt of bleaching clay. The mixture was then heated to 120 C and stirred for 15 min. A vacuum of 25-30 m Hg was maintained throughout the experiment. The hot oil and clay mixture was filtered and the color of the bleached oil was measured by Lovibond tintometer using a 1-in. cell.

The results of the color of oil bleached by clay activated at various sulfuric acid concentrations are shown in Figure 2.

It can be seen from Figure 2 that decolorization tends to improve with increasing acid concentration until at 20%, when the bleaching efficiency decreases.

Figure 3 shows a typical montmorillonite clay structure with aluminium ions, $A\ell^{3+}$, keying the clay lattice together. As the addition of sulfuric acid increases, more of the aluminium is removed. Eventually, the lattice structure of the clay presumably collapses due to a lack of $A\ell^{3+}$ needed to keep the lattice together.

It can therefore be explained that the initial increase in bleaching ability with increasing sulfuric acid addition is due to net charges in the clay. However, a drop in bleaching ability is observed at a higher addition of acid due to the collapse of the clay structure. This is a result of excessive leaching of $A\ell^{3+}$ by acid.

PHOSPHORUS CONTENT

The phosphorus content for crude palm oil is 350-450 ppm

TABLE I

Chemical Composition of Natural and Acid-Activated Clay

Sulfuric acid concentration	% wt				
	0	10	20	30	40
SiO_2	58.62	62.23	68.63	72.41	80.42
$A\ell_2O_3$	22.01	20.45	18.94	10.22	6.32
Fe_2O_3	4.51	4.01	3.64	3.02	2.64
MgO	4.98	4.12	3.98	3.42	2.96
CaO	2.25	1.89	1.43	1.02	0.94
K_2O	0.04	0.03	0.03	0.02	0.02
Na_2O	0.23	0.21	0.16	0.13	0.08
Ignition loss	8.94	8.04	6.39	5.89	5.12
Total	101.58	99.98	103.2	96.13	98.50

It can be seen that an increase in the concentration of the sulfuric acid tends to leach an increasing amount of $A\ell_2O_3$. This process tends to create net negative charges on the clay lattice structure and creates the cation adsorbtion properties of acid-activated montmorillonite clay.

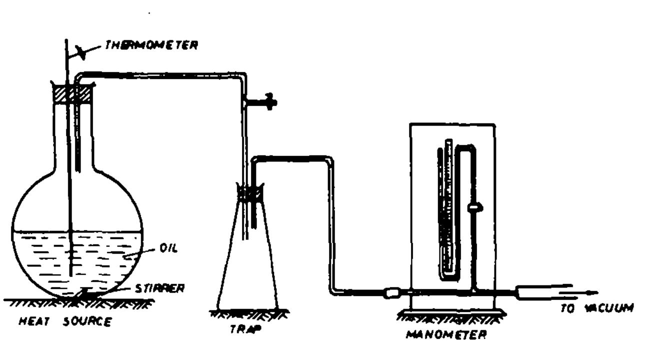

FIG. 1. Schematic diagram of laboratory set-up for oil bleaching.

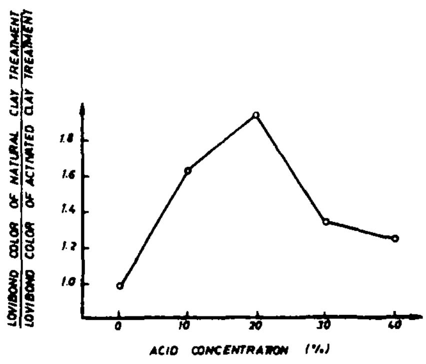

FIG. 2. Effects of acid concentration on color of bleached oil.

and drops to 127, 113, 118, 124 and 120 ppm for oil bleached by natural, 10, 20, 30 and 40% acid concentrations, respectively.

The drop in the phosphorus content indicates that some of the positively charged trace metals are adsorbed onto the clay lattice structure. Such behavior suggests chemisorption between metallic ions and the charge-deficient montmorillonite clay.

The results obtained so far show that bleaching clay assists not only in the removal of coloring matter, but also removal of phosphatides.

SPECIFIC SURFACE AREA

The specific surface area of clay particles can be used as a tool to assess its bleaching ability and this has been adopted widely by manufacturers of bleaching clay.

The procedures to measure specific surface area adopted in the current study follows ASTM (204-55) designation (6). The results of specific surface area with concentration are given in Figure 4.

It can be seen that the specific surface area increases with acid concentration up to an optimum, after which the surface area decreases. With reference to Figures 2 and 4, it can be suggested that the surface area gives an indication of its decolorization capability.

By acid leaching, some of the organic matter or impurities covering the active adsorption sites are leached. This increases the pore area and hence exposes more of the active adsorption sites. Furthermore, as discussed earlier, acid leaching creates a deficiency in charges in the clay due to removal of $A\ell^{3+}$. Thus, the initial increase in bleachability is the result of (a) increasing pore area and (2) leaching of $A\ell^{3+}$.

However, when the concentration of sulfuric acid passes the optimum, in this case, 20% acid concentration, the specific surface area decreases. The subsequent decrease in bleaching ability and surface area is a consequence of the collapse of the clay lattice structure.

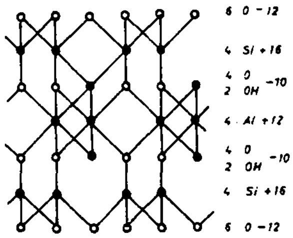

FIG. 3. Atomic structure of typical montmorillonite clay.

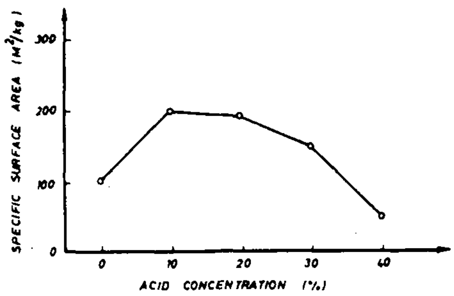

FIG. 4. Effects of acid concentration on specific surface area.

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