

## CHAPTER 5

### CONCLUSIONS

Although rice bran oil contains several components that are considered beneficial to health, its color is unattractive to consumers, and in addition the natural oil has problems of limited stability. Thus it is common practice for such oils to be bleached (decolored) before sale. Currently, the bleaching process is normally performed using a commercial bleaching clay, typically acid activated bentonite, although the use of other aluminosilicate minerals, such as sepiolite, or attapulgite, has been investigated. Prior to use for bleaching vegetable oils such minerals are normally acid activated to improve their adsorption properties.

Thailand has limited reserves of bentonite, and consequently most bleaching clays need to be imported. However, it has large deposits of kaolin, a group of closely related 1:1 aluminosilicate minerals, and the objective of this project was to investigate whether kaolin could be modified to produce a material that could be used as a substitute for the bentonite-derived bleaching clays. It focused on the Ranong kaolin, which is the major deposit in the south of Thailand, and for which some basic physical characterisation had been published previously.

Results on the bleaching of rice bran oil by acid-activated kaolin were disappointing, and the performance of the kaolin was vastly inferior to that of a similarly-treated commercial bleaching clay. Physical investigations indicated that this was probably the result of the strong hydrogen bonds which hold together adjacent layers in the kaolin structure, and as a result experiments were performed to investigate the effects of disruption of the structure by extensive grinding. Although the bleaching properties of the kaolin were improved by grinding, they were still inadequate for commercial consideration, but acid activation of the ground material produced mineral samples with bleaching capacities comparable to those of a commercial bleaching clay.

The work in this thesis shows that the Ranong kaolin can be modified for use as a bleaching material for decolorisation of rice bran oil by combined physical and chemical treatments, and thus it meets the main objective of the project by

demonstrating that kaolin can be treated to produce a material that can be used as a substitute for conventional bleaching clays. Some preliminary steps were then taken towards refining the physical and chemical conditions used for modification of the mineral with the objective of improving its practical performance.

The first stage of the modification was the physical treatment to disrupt the kaolin mineral structures. With the equipment available in the university laboratory, this was achieved using a ball mill operating at 300 rpm for 1 h. These conditions were found to be adequate for production of a disordered structure, which could then be more easily attacked in subsequent acid activation treatments.

The 2<sup>nd</sup> stage of the modification was the acid activation treatment, and the use of sulfuric and oxalic acids was investigated. With both acids treatment of the rice bran oil at 90 °C for 4 h was found to produce acceptable results, and these conditions were subsequently used for the majority of the measurements performed in this project. The effects of various concentrations of the acids were investigated, and it was found that the highest bleaching capacities were achieved using 2 M sulfuric acid, or 0.7 M oxalic acid. Poorer performance was observed with higher and lower concentrations of each acid. Furthermore, the performance of sulfuric acid was somewhat better than that of oxalic acid, a result which suggests that further improvements in bleaching capacity might be achievable with the use of some other acid for activation.

Various physical and spectroscopic characterisations were then performed on the kaolin samples in an attempt to develop an understanding of the underlying scientific reasons for the different performance of the samples produced by different modification treatments.

XRD and SEM measurements demonstrated that halloysite is the major mineral in the Ranong kaolin, and that it is accompanied by appreciable amounts of kaolinite, with illite and quartz as the major impurity phases. The XRD technique confirmed that major structural damage resulted from the physical treatment, and this result was supported by measurements using spectroscopic techniques; The EPR spectra indicated the generation of a more disordered structure and FTIR showed that this was accompanied by the loss of hydroxyl groups from the surface of the octahedral sheet.

Acid activation of the ground kaolin resulted in the loss of Al from the structure and the generation of a Si-rich phase, which may be amorphous silica.

The new material generated by the combined physical and 2 M sulfuric acid treatments had a specific surface area of  $\sim 244 \text{ m}^2/\text{g}$  compared to about  $\sim 13 \text{ m}^2/\text{g}$  in the untreated kaolin. The combined treatments also resulted in an increase in the total pore volume from  $0.0647 \text{ cm}^3/\text{g}$  to  $0.4280 \text{ cm}^3/\text{g}$ . At the same time, the average pore diameter decreased from  $\sim 20.0 \text{ nm}$  to  $\sim 7.0 \text{ nm}$ , these physical changes are, therefore, the main reasons for the improved adsorption of pigment molecules for rice bran oil by the treated kaolin sample.

The next objective of the project was to investigate the processes through which colored materials from crude rice bran oil are adsorbed on the modified kaolin minerals. This was done by analysing the adsorption isotherm, which was found to be able to be described by both the Freundlich and Langmuir models. FTIR spectroscopy showed that adsorption involved interactions between pigment molecules and acidic sites on the clay surface, and desorption studies suggested that this interaction was mainly electrostatic in nature.

The EPR technique showed that, although stable free radical centres associated with the colored pigments were removed from the rice bran oil using modified kaolins as bleaching materials, new free radicals were formed as a result of oxidation of  $\alpha$ -tocopherol and related tocopherols. However, unlike in biological systems, these radicals were quite stable and persisted for several weeks, indicating the presence of antioxidant molecules in the bleached oil that prevent their further oxidation. The rice bran oil after bleaching with modified kaolin was slightly yellow in color, the peroxide value decreased from  $18.8 \text{ meq/kg}$  to  $5.3 \text{ meq/kg}$ , but the free fatty acid remained constant at  $0.14\%$ . Thus the bleaching treatment should lead to a substantially improved shelf life for the rice bran oil.

Finally, although it can be concluded that the kaolin from the Ranong deposit can be used as an alternative material to conventional bleaching clays for the decolorisation of vegetable oils, this is only possible after extensive modification by a combination of physical and chemical treatments. Furthermore, because of major structural and

compositional differences between different kaolin samples, the results from samples from one deposit will not necessarily be equivalent to those from another, and extensive physical and chemical characterisation should be performed in order to evaluate the potential uses of minerals from different kaolin deposits.