J. Myanmar Acad. Arts Sci. 2020 **Vol. XVIII.No.1**B

REFINING OF WASTE FRIED PALM OIL BY MODIFIED BENTONITE CLAYS

Tha Zin Win[1], Kyi San Aye[2], Hlaing Hlaing Oo[3]

Abstract

Frying of foods is the most commonly used in the food preparation. Without any treatment, the fried oil can be used for a few days and must be discarded after such time. The useful life of fried palm oil can be increased by the refining with various adsorbents, natural adsorbents and modified adsorbents. In this paper, the natural bentonite clay and modified acid activated bentonite clay were used for refining of waste fried palm oils. The natural bentonite clay was collected from Kyaukpadaung Township. The essential parameters such as acid value, peroxide value, iodine value and saponification value of before and after refined fried oils were investigated. The completely refined fried oil showed the properties of the acid value, peroxide value, iodine value and saponification values were evenly spread between 1.39 to 1.54 mg g^{-1}, 2.28 to 2.62 meq kg^{-1}, 100.33 to 109.75 mg g^{-1} and 142.72 to 152.73 mg KOH g^{-1} respectively. These results were under permitted level for edible palm oil. Moreover, the determination of incremental adsorption capacity of acid activated bentonite clay sample using 3 % H_2SO_4, it can be resilient in refining process within 18h long frying time of waste fried palm oil. This experimental work found that locally available natural bentonite clay can be modified for the use of efficient and effective refining material to the waste fried palm oil.

Keywords: Fried palm oil, bentonite, activated bentonite, refining, adsorbent

Introduction

Bentonite clay is an aluminiumphyllosilicate, which consists mostly of the mineral montomorillonite. Bentonite clay enormously abundant in nature has been considered as a potential source of adsorbent for removing, colour pigments from edible oils. Surface modified the clay samples have high potential to provide an alternative to most widely used activated carbon (Chaisena and Rangsriwatananon, 2004). The surface modification of bentonite can be carried out by thermal activation and acid activation processes. Thermal processing change the structure and composition upon heating and largely depends on the particle size and the heating regime (Sennour *et al*., 2009).The another method by treating bentonite clay with inorganic acids at high temperature is termed acid activated clays. The cost of production of acid activated clays is low. The acid activation of the clays alters the physical properties, such as, enhancing the surface area and average pore volume (Lian *et al*., 2009).Palm oil is commonly used for cooking due to its high saturation (oxidative stability) of the refined product when it was frying. Palm oil is one of the few highly saturated vegetable fats and does not contain cholesterol, although saturated fat intake does increase a person's LDL (Low-density lipoprotein) and HDL (High-density lipoprotein) cholesterol. Refining of fried palm oil is done to remove unwanted minor components that make oils unappealing to consumers, while trying to cause the least possible damage to the neutral oil as well as minimum refining loss. The components to be removed are all those glyceridic and non-glyceridic compounds that are detrimental to the flavour, colour, stability or safety of the refined oils (Ruiz-Mendez and Dobarganes, 1999).

---

[1] Dr, Assistant Lecturer, Department of Chemistry, Yangon University of Distance Education
[2] Dr, Associate Professor, Department of Chemistry, Bago University
[3] Dr, Professor and Head, Department of Chemistry, West Yangon University

The aim of this research was to increase the usefulness of waste fried palm oil by refining process using natural and modified bentonite clay.

Materials and Methods

This experimental work concerned with the refining of waste fried palm oil by modified bentonite clays. In this work, the raw natural bentonite (NBN) clay was collected from the Kyaukpadaung Township, Mandalay Region and it was modified by acid modification and heat activation process. Waste fried palm oil used in this study was bought from local market. All chemicals used in this experiment were procured from British Drug House (BDH) Chemicals Ltd., Poole, England.

Preparation of Adsorbent Materials

(a) Natural bentonite clay sample preparation

Firstly, foreign matters were removed from raw natural bentonite clay sample and then soaked in distilled water and dried at 105 ºC for 4 h. The samples were ground and sieved with 125 µm mesh. The natural bentonite clay powders were stored in desiccators for further study of characterization and modification.

(b) Modification of Natural Bentonite Clay Sample

(i) Acid modification

The prepared natural bentonite clay sample (50 g) was treated with 500 mL of 1 to 5 % sulphuric acid (analytical grade) at 90 °C for 4 h in a stirred glass. After the acid treatment, the samples were filtered and washed with distilled water until neutral. The samples were dried at 105 °C for 5 h and ground to pass through a 75 µm sieve. The dried acid activated bentonite was kept in a desiccator containing silica gel for further study of characterization and modification oil bleaching.

(ii) Heat activation

The natural bentonite clay sample (50 g) was calcined in the range of temperature 100, 200, 300, 400 and 500 °C for 1 h. The heat activated bentonite clays sample was stored in desiccators for further study of characterization and modification.

Refining of Waste Fried Palm Oil

The refining process contains four steps. There are degumming process, neutralization process, bleaching process and deodorization process. For the degumming of waste fried palm oil, oil sample (300 mL) was placed in a conical flask and the flask was heated to 60-70 °C, and then 50 mL of water was added and mixed about for 30 min. The solution was taken out and removed the hydrated gums by centrifugal separation method. The sample was filtered off. Then, the resulted water degumming oil was continued for neutralization process. 1 M NaOH 20 mL was added in 300 mL degummed oil with a reaction time of around 30 min at slow stirring and temperature around 80 °C, the water phase is eliminated by centrifugation and the oil was with water to remove the remaining soap. Then, the resulted neutralized oil was carried on the bleaching process. In this process, 5 g each of natural and two modified bentonite clays were separately put in each conical flask and 50 mL of waste fried palm oil was added to each flask. The flasks were heated at 80, 100, 120, 140 ºC temperatures and 30, 45, 60, 75, 90 min bleaching time. The samples were filtered by vacuum flask using vacuum pump. Then, the quality of bleaching fried oil samples was analyzed. For deodorization process, the bleached oil 50 mL was added with 5 g of bamboo powder and stirred and filtered. Then finally, deodorized oil was obtained.

Determination of Incremental Adsorption Capacity of Acid Activated Bentonite Clay Sample

The experimental procedure of frying and refining were carried out repeatedly for 5 batches without changing acid activated bentonite clay. During the first refining process, (fried oil of first time refining process) designated as RFO 1. And then, this first refined oil (RFO 1) was fried again to obtain the colour like as first collected fried oil sample. The frying duration was as long as 5 h (FO 2). The obtained fried oil was refined again the same as above procedure and the resulted fried oil was designated as RFO 2 (fried oil of second time refining process). Similar procedure was made 5 h frying duration for RFO 2 designated as FO 3. Similarly, another 5 h frying duration for RFO 3 designated as FO 4 and the last frying duration 3 h for (RFO 4) and designated as FO 5 which was again refined (RFO 5). Finally, total 18 h frying durations were studied without changing acid activated bentonite clay adsorbent. The acid value, peroxide value, iodine value and saponification values of the oil samples were determined.

Characterization of Bentonite Clay Samples and Waste Fried Palm Oil

The characterization of natural bentonite (NBN) and modified bentonite clay samples were performed by XRD (Rigaku-D-Max-2200, Japan, URC, UY, Myanmar) and SEM (JOEL-JSM-5610 series, Japan, URC, UY, and Myanmar). In addition, XRD analysis of commercial bentonite clay and standard bentonite clay were carried out to compare with modified bentonite clay sample. Waste fried palm oil samples before and after refining process were analyzed conventional methods to determine the acid value, peroxide value, saponification value and iodine value.

Results and Discussion

In this research, natural bentonite clay sample, Kyaukpadaung Township, Mandalay Region, was used for the experimental work. From the XRD results, the particle size of natural bentonite clay sample compared with those of the commercial bentonite and standard bentonite are presented in Table 1. Because of the smallest particle size among these three, the natural bentonite clay sample was chosen to modify for the refining process.

Table 1 The Particle Size of Three Different Types of Bentonite Clay Samples

No.	Sample	Particle size (nm)	Source
1.	Natural bentonite clay	69.0063	Kyaukpadaung Township
2	Commercial bentonite clay	99.8983	Pyoneiyar Star Co. Ltd.
3	Standard bentonite clay	78.7160	Chemistry Department, UY

The natural bentonite clay sample was modified by acid activation method and heat activation method. The natural bentonite clays and acid activated bentonite clays at different sulphuric acid concentrations are presented in Table 2.

Table 2 Original Bentonite Clays and Acid Activated Bentonite Clays with Different Sulphuric Acid Concentrations

Sample	Concentration of H_2SO_4 % W/V	Code No.
Natural or untreated bentonite clay	-	NBN
Acid Activatied bentonite Clays	1	AABN 1
Acid Activatied bentonite Clays	2	AABN 2
Acid Activatied bentonite Clays	3	AABN 3
Acid Activatied bentonite Clays	4	AABN 4
Acid Activatied bentonite Clays	5	AABN 5

The natural bentonite clay sample is brown colour in nature. After acid treatment, the colour observations of acid activated bentonite clays were changed from brown, grey till the AABN 3 has whitish colour. The grey colour of bentonite could be due to the relatively some amount of cations such as Al^{3+} and Fe^{3+} which still remained after the activation The Whitish colour could be due to the replacement of metal ions such as Al^{3+}, Fe^{3+} and Ca^{2+} in the clay with H^+ (Lian *et al*., 2009).

Table 3 Heat Activated Bentonite Clays at Different Temperatures

Sample	Activated Temp °C	NBN
Natural or untreated bentonite clay	-	NBN
Heat activated bentonite clay	100	HABN 1
Heat activated bentonite clay	200	HABN 2
Heat activated bentonite clay	300	HABN 3
Heat activated bentonite clay	400	HABN 4
Heat activated bentonite clay	500	HABN 5

The heat activated bentonite clays at different temperatures are presented in Table 3. After thermal activation of natural bentonite clay, the colour changed from brown to dark colour. The heat activated bentonite clay is darker than acid activated bentonite clay. This is because of the clay minerals generally calcined prior to their use in order to remove any impurities or moisture attached to the clay particles. Consequently, the adsorbed and hydrated water, and impurities attached to bentonite clay were removed in the dehydration stage (Sennour *et al*., 2009).

From XRD pattern, the particle size of natural bentonite clay (NBN), acid modified and heat activated bentonite clay samples were determined by using Debye Scherrer equation (Yildiz *et al*., 2004). The resulted data are presented in Table 4. The particle size of natural bentonite clay is 69.0063 nm. After acid activation of natural bentonite clays, the particle sizes of AABN 1 to AABN 5 were in the range of 40.2970 to 46.5531 nm while HABN 1 to HABN 5 have in the particle size distribution range of 50.3280 to 60.2873 nm. The acid activated bentonite clay samples are more preferable to the refining process for the waste fried palm oil because of their smaller particle sizes than those of heat activated clay samples.

Table 4 Average Crystallite Grain Size of Bentonite Clay Samples by XRD

Sr. No.	Type of Bentonite	Average Crystallite Grain Size D (nm*)*
1.	NBN	69.0063
2.	AABN 1	46.5531
3.	AABN 2	44.0213
4.	AABN 3	40.2970
5.	AABN 4	41.8983
6.	AABN 5	42.1289
7.	HABN 1	60.2873
8.	HABN 2	50.3280
9.	HABN 3	57.4430
11	HABN 4	53.6349
11	HABN 5	52.1015

NBN = Natural Bentonite
AABN = Acid-Activated Bentonite
HABN = Heat-Activated Bentonite

Among acid activated samples, activated with 3 % H_2SO_4, AABN 3 gave the smallest average crystallite grain size (40.2970 nm). It can be explained that consolidation or agglomeration of smaller particles occurs by modification of bentonite with sulphuric acid. According to this trend, particles lose their clay mineral property due to both activation processes. The acid activation caused the creation of new pores having lower diameters than those of the original and heat activated bentonite clays (Yildiz *et al*., 2004). The particle size distributions of the original and activated bentonite clays showed that the acid activation strongly affected the particle size of the clays.

The surface morphologies of natural bentonite clay, acid activated bentonite clays and heat activated bentonite clays magnification using SEM are presented in Figures 1 and 2.

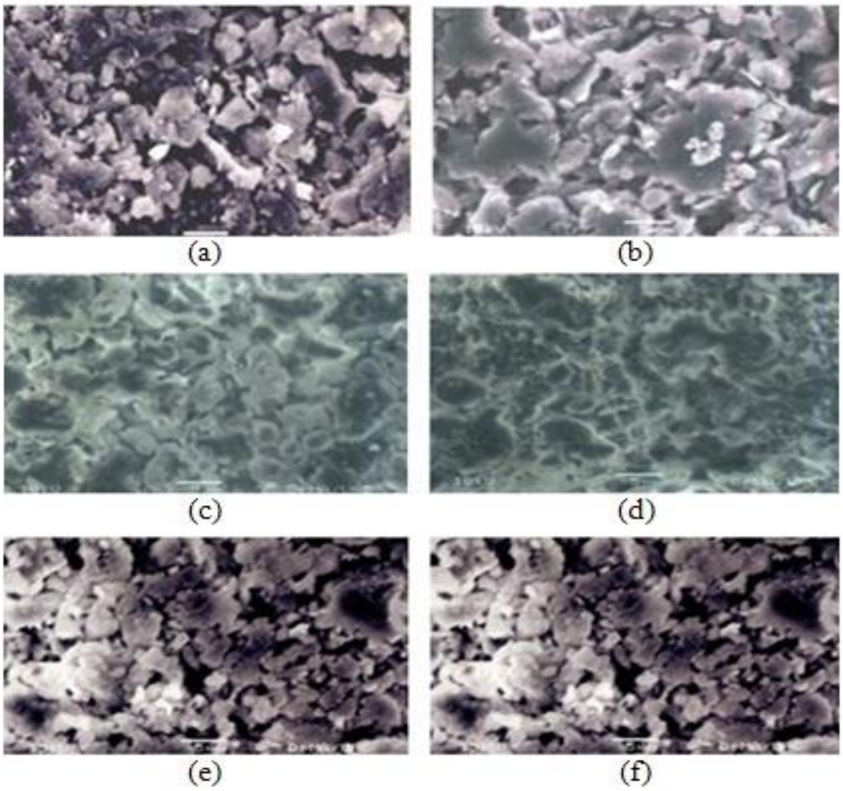

Figure 1 SEM Micrographs of (a) NBN (b) AABN 1 (c) AABN 2
(d) AABN 3 (e) AABN 4 (f) AABN 5

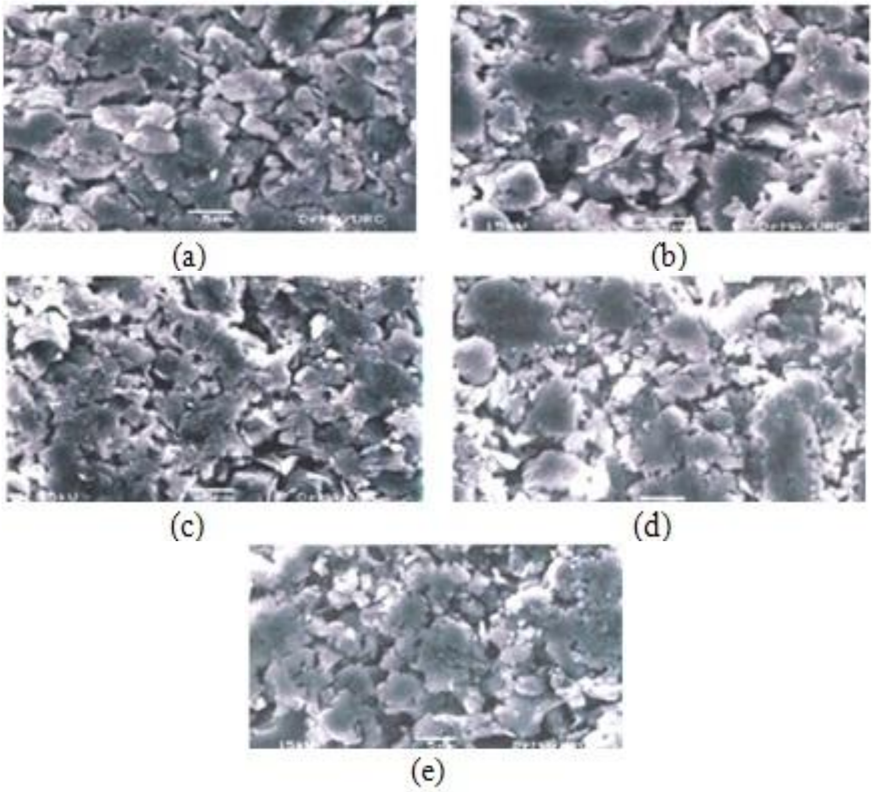

Figure 2 SEM Micrographs of (a) 100 °C (HABN 1) (b) 200 °C (HABN 2)
(c) 300 °C (HABN 3) (d) 400 °C (HABN 4)
(e) 500 °C (HABN 5)

According to these figures, an acid activation creates voids in the bentonite making the clay surface more porous as increase in acid concentration till the acid activation at 3 % H_2SO_4 and becomes highly porous. The formation of smaller pores takes place as the impurities are removed and the exchangeable cations are replaced by H^+ ions. Further increase in acid concentration (4 % H_2SO_4 and 5 % H_2SO_4) reduced the porosity rendering clay surface rather flat and clumps of uneven surface can be seen along with some that flakes of low porosity. Heating beyond 200 °C resulted in the gradual decrease in porous nature in heat activated bentonite and the interlayer spaces may have collapsed resulting in more tightly bound structure with reduction in porous structure at 500 °C. From XRD and SEM results, using acid activation 3 % H_2SO_4 for refining of waste fried palm oil gave the best results for this experiment.

In the refining procedure, the optimum temperature and duration time were studied for AABN 3 bentonite clay modified with 3 % H_2SO_4. The results are presented in Table 5 and Table 6. According to the literature, the higher the acid value found, the higher the level of free fatty acid which translates into decreased oil quality (Yang *et al.*, 2006). The peroxide value is a measure of oxidation during storage. The peroxide value determines the extent to which the oil has undergone rancidity, thus it could be used as an indication of the quality and stability of fats and oils.

From these observations, the optimum results for the refining process are 100 ºC temperature and 45 min time duration.

Table 5 Acid Values and Peroxide Values of the Fried Oil (F.O) Treated with AABN 3 at Different Treated Temperatures

Sr. No.	Treated Temperature (°C)	Acid Value (mg g^{-1})	Peroxide Value (meq kg^{-1})
1	80	2.26	10.80
2	100	1.80	3.60
3	120	2.36	18.00
4	140	2.14	21.60
5	F.O	16.83	39.60

(dosage 5 g, time 1h)

Table 6 Acid Values and Peroxide Values of the Fried Oil (F.O) Treated with AABN 3 at Different Treated Times

Sr. No.	Treated Time(min)	Acid Value (mg g^{-1})	Peroxide Value (meq kg^{-1})
1	30	1.80	3.90
2	45	1.52	3.60
3	60	1.73	7.20
4	75	1.94	10.80
5	90	2.68	18.00
6	F.O	16.83	39.60

(temperature 100 °C, dosage 5 g)

The step by step colour change of waste fried palm oil during refining process using 3 % H_2SO_4 (AABN 3) are presented in Table 7. Initial colour was dark brown and finally the decolourization of waste fried palm oil was observed. The overall refining process (4 steps) took 3.5 h for this experiment.

Table 7 The Colour Observation of Waste Fried Palm Oil in Refining Process

Steps No.	Refining Process	Colour	Time/ h
1	waste fried palm oil	dark brown	-
2	after degumming process	brown	½
3	after degumming and neutralizing process	yellow	1
4	after degumming, neutralizing and bleaching process	colourless	2

In the determination of incremental capacity of acid activated bentonite clay sample, the experimental procedure of repeatedly frying and refining without changing bentonite were carried out. The resiliency of AABN 3 with fried time is presented in Table 8.

Table 8 The Resiliency of Acid Activated Bentonite Clay Sample with Repeated Fried Time of Waste Palm Oil

Code No.	Fried time/h	Resiliency of acid activated bentonite clay/h
RFO1	-	-
RFO 2	5	5
RFO 3	5	10
RFO 4	5	15
RFO 5	3	18

Some essential parameters of oil samples after the repeated frying and refining with AABN 3. The result data are presented in Table 9.

According to Table 9, the acid value, peroxide value, iodine value and saponification value of waste fried palm oil (FO) sample were 16.38 mg g^{-1}, 39.6 meq kg^{-1}, 12.34 mg g^{-1} and 209.81 mg KOH g^{-1} respectively. Alternatively, the acid value, obtained for refined oil sample (RFO 1 to RFO 5) ranged from 1.39 to 1.54 mg g^{-1}, respectively.

Table 9 Some Essential Parameters of Oil Samples after the Repeated Frying and Refining with AABN 3

Properties	**Sample**							
	FO	**RFO 1**	**RFO 2**	**RFO 3**	**RFO 4**	**RFO 5**	**PO**	**Standard Range (Yang *et al*., 2006)**
Acid Value (mg g^{-1})	16.38	1.54	1.49	1.43	1.42	1.39	1.47	< 4
Peroxide Value (meq kg^{-1})	39.6	2.28	2.31	2.49	2.62	2.52	2.25	< 10
Iodine Value (mg g^{-1})	12.34	106.13	108.44	109.75	105.83	100.33	80.75	101-150
Saponification Value (mg $KOHg^{-1}$)	209.81	144.11	142.72	142.78	151.62	152.73	151.47	151-165

FO = Fried Oil PO = Palm Oil

The acid value of edible oil is lower than 4 mg g^{-1} (Yang *et al*., 2006). Therefore, the observed acid values were under allowable limit for edible oil after refining process.

The peroxide value of obtained refined oil sample ranged from (RFO 1 to RFO 5) 2.28 to 2.62 meq kg^{-1}. The lower peroxide value in the bleached fried oil suggests that the oil can be stored for a long time without deterioration. Oil with high peroxide value are unstable and become easily rancid oil having higher peroxide value (within 20-40 meq kg^{-1}).The iodine value obtained for RFO 1 to RFO 5 were between 100.33 and 109.75 mg g^{-1}. High iodine value in oil shows that the oil has good qualities of edible oils. The saponification values obtained for RFO 1 to RFO 5 were between 142.72 to 152.77 mg KOH g^{-1} respectively. The high saponi-fication value 209.81 for waste fried oil was significantly decreased to 142.72 mg KOH g^{-1} after refining process and it was under permitted level for edible palm oil. Therefore, it was found that refining of fried oil samples investigated were not contaminated until 18 h long frying time and were distributed under allowable limit for edible oil. Thus, the fried oil was extensively frying duration 18 h due to refining process including AABN 3 was used as adsorbent.

Conclusion

In the present research, modified bentonite material from Kyaukpadaung Township, Mandalay Region was evaluated in refining process to incremental frying time. In this study, two types of modification of natural bentonite clay, acid activation and heat activation were carried out. Acid modification of natural bentonite is preferred to the refining process for the waste fried palm oil. From XRD and SEM results, acid activated bentonite clay (AABN3) due to the smallest particle size and highly porous surface. The changes of surface properties of local bentonite clays after acid activation was observed that 3 % H_2SO_4 (AABN 3) gave the best results for the refining process. Moreover, the determination of incremental adsorption capacity of acid activated bentonite clay sample using 3 % H_2SO_4 can be resilient in refining process within 18 h long frying time. The degree of enhancement of frying time for fried palm oil greatly influenced by the use of acid activated bentonite clays. Thus, the acid modified bentonite from Kyaukpadaung, Mandalay Region can be a low cost adsorbent for refining of waste fried palm oil.

Acknowledgments

The authors would like to express their profound gratitude to the Department of Higher Education (Yangon Office), Ministry of Education, Myanmar, for provision of opportunity to do this research and Myanmar Academy of Arts and Science for allowing to present this paper.

References

Chaisena, A. and Rangsriwatananon, K. (2004). "Effects of Thermal and Acid Treatments on Some Physico-chemical Properties of Lampang Diatomite". *Suranaree Journal of Science and Technology*, vol.1(4), pp.289-299

Lian, L., Guo,L. and Guo, C.(2009). "Adsorption of Congo Red from Aqueous Solution on Ca-bentonite". *J. Hazardous Materials,* vol.161, pp.126-131

Ruiz-Mendez, M.V. and Dobarganes, M.C.(1999)."Olive Oil and Olive Pomace Oil Refining".*Oleagineux, Corps gras, Lipids,*vol.6, pp.56-60

Sennour, R., Mimane, G., Benghalem, A. and Taleb,S. (2009). "Removal of Persistent Pollutant Chlorobenzene by Adsorption onto Activated Montmorillonite". *Appl. Clay Sci.,* vol.43, pp.503-506

Yang, T., Wen, X.D., Li, J. and Yang, L. (2006). "Theoretical and Experimental Investigations on the Structures of Purified Clay and Acid-Activated Clay". *Appl. Surface Sci.*, vol.252, pp.6154-6161

Yildiz, N., Aktas, Z. and Calimli, A. (2004). "Sulphuric Acid Activation of Calcium Bentonite". *Particulate Sci. and Tech*., vol.22, pp.21-33.