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Optimization of Natural Heat Treatment of Attapulgite: Effect on Rapeseed Oil Bleaching Process and Stability

Bakri A.Kareem[2, 3], Mohammed Dahir[2], Jin-Wei Li[1, 2, 3], Jiang Jiang[1, 2, 3], Pei-Rang Cao[1, 2, 3] & Y. Liu[1, 2, 3*]
1- The State Key Laboratory of Food Science and Technology, Jiangnan University
2- School of Food Science and Technology, Jiangnan University
3- Lipid & Vegetable protein science and technology Research Center, Jiangnan University, Wuxi, Jiangsu, 214122, CHINA
*Corresponding author: Yuan-Fa Liu

***Abstract* - This study was conducted to assess the potential activation of attapulgite and to obtain thermally activated samples to use as clarifying agents for rapeseed oil. The effect of changes in bleaching temperature 90˚C, 100˚C, 110˚C and 130˚C, and attapulgite dosage 1%, 2%, 3% and 4% by weight on free fatty acid, oxidation stability and color were investigated. Slight enhancement in FFA with an increase of bleaching temperature and clay dosages was seen due to the active catalyst and the partial losses of adsorbed and hydration water molecules which also increased the hydrophilicity and acidity of the surfaces. The effect on oxidation state was more complex and was related to both primary and secondary oxidation products. To gain adsorption curves from coloring compounds adsorbed into heat activated attapulgite, the attapulgite was exposed to different temperatures of 100˚C, 150˚C, 200˚C, 250˚C, 300˚C, and 350˚C. And with the rising temperature; the loss of total water increases. Moreover, the moisture and the zeolitic water were removed continuously till it reaches the elimination stage of coordinated water molecules. It was observed that with the increase of heat treated attapulgite dosage, the color intensity decreases. In addition, an increase in bleaching temperature seems to increase color adsorptions. More importantly; addition of 3% and 4% attapulgite sample activated at 250˚C exhibited greater potential for the clarification of rapeseed oil by the removal of pigments, and revealed higher efficiency compared with its counterparts.**

Key words: Attapulgite (Palygorskite), Thermal activation, Neutralized rapeseed oil, Bleaching, FFA, oil oxidation, Color.

1. INTRODUCTION

Bleaching is a crucial step in edible oil refining process where the removal of pigments and other undesirable impurities such as soaps, phospholipids, trace metals, oxidation products and polyaromatics takes place [1]. This improves the sensory quality, shelf life and the costumer acceptability of oil. Rapeseed oil is considered to be one of the most important vegetable oils around the globe due to its steady growth in production during the last 20 years with great anticipation to maintain its share in the vegetable oil market [2];[3]. It contains large amounts of chlorophylloid pigments which undergo auto oxidation and therefore more difficulties face the bleaching process compare to the other edible oils [4]. The increasing demand for higher quantities of activated bleaching earth to achieve complete removal of all chlorophyll derivatives and to reduce the carotenoid pigments from oil [5]. Activated clays are favored to other adsorbents such as activated carbon- and silica-based products due to its relatively high performance and lower cost to get a bright oil and more stability against oxidation due to the reducing the formation of primary and secondary oxidation products. Researchers have recently become involved in the significance and the complexity of the edible oil bleaching process; seven major clay groups and at least 33 different specific clay minerals had been used as adsorbents for oil bleaching stage. Bentonite clay is the most commonly used and also considered as standard in edible oil bleaching. However, there are other clays that are not well documented previously [6]; [7].

Palygorskite, previously named attapulgite, which is a special class of clay mineral under the 2:1 layer composition, It's a layered magnesium aluminum silicate which is present in nature usually as a fibrillar silicate clay mineral with reactive OH groups on the surface. Due to its high adsorption capacity, large specific surface area, rheological and catalytic properties, for palygorskite, four water molecules (zeolitic water) are present in the channels, and four others are bound to the octahedral edge inside the channels. Heat treatment is usually used to improve the adsorption capacity, cation exchange capacity and surface area of natural Attapulgite [7]; [8]; [9]. Heat treatment combined with acid addition, (acidification) was usually used to activate the bleaching earth. Nevertheless, no possible results have been revealed when heat treatment was used individually. The aim of this study was to investigate the influence of attapulgite on rapeseed oil bleaching when only the heat treatment was applied to activate it and also to determine the optimal heat treatment for clay. Furthermore, the effect of heat treated attapulgite on free fatty acid content, color characteristics and oxidation stability of rapeseed oil.

2. MATERIALS AND METHODS

2.1 Materials:

In this study natural attapulgite clay was supplied by OilBetter Clay Material Co. Ltd (Xuyi, China). Crude attapulgite was washed with distilled water to remove the contaminants. After drying in the oven at 105˚C, it was ground to pass through 200 mesh sieve. Neutralized rapeseed oil was supplied by JiaFeng edible oil Co.Ltd. (Jiangsu, China). The oil was kept in the controlled environment to avoid auto-oxidation. All other chemicals and solvents used were of analytical grade.

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2.2 Methods:

2.2.1 Oil Bleaching Process:

Neutralized rapeseed oil (100 g) was stirred and heated to a constant temperature (90˚C, 100˚C, 110˚C and 130˚C) for 5 min at 18 mmHg in a three-necked flask. When the desired temperature was reached, the final activated attapulgite clay was added to the heated oil in different dosages (1%, 2%, 3% and 4%) W/W and the mixture stirred with a mechanical stirrer at a constant speed (250 rpm). After bleaching for 30 min, the mixture was rapidly cooled to 30˚C under vacuum, and then filtered through a Buchner funnel [7]. Samples were stored at 4˚C in dark glass containers and purged with nitrogen gas after filling to prevent oxidation.

2.2.2 Preparation of heat treatment attapulgite:

150 g of clay was activated at 100˚C, 150˚C, 200˚C, 250˚C 300˚C and 350˚C for 4 h to constant weight, respectively, and then cooled to room temperature in a desiccator. All samples of activated clay were stored in polyethylene bags for characterization and bleaching studies.

2.2.3 Free fatty acids determination:

Free fatty acids of crude and refined oil were measured using the titration method with a sodium hydroxide solution (phenolphthalein as indicator), suitably diluted with an ethyl alcohol–ethyl ether mix. Results are expressed as% oleic acid [10].

2.2.4 Color determination:

Lovibond colors were determined in duplicate, using Lovibond PFX880-Tintometer according to the official AOCS method [10]. The optical path length of the glass cell was 1" for crude oil and 5.25" for refined oil.

2.2.5 Oxidative oil index determination:

Bleached rapeseed oil oxidative stability index (OSI) was measured by rancimat apparatus, model 743 (Metrohm Ω, Basel, Switzerland) according to [11]. Stability was expressed as the oxidation induction time (h), using an oil sample of 3.0 g heated up to 120˚C under constant air flow of 20 L/h. Official and Recommended Analysis Manual (AOCS Cd 12b-92) [12].

2.3 Statistical analysis:

All analyses were carried out in triplicate (n = 3) for each replicate which were reported as mean ± SD. The variance analysis was performed using ANOVA test. SPSS 16.0 (statistical software; SPSS Inc., Chicago, IL) was used to compare the mean values of each treatment. Significant differences between the means of the parameters were determined by using the Duncan test ($p < 0.05$).

3. RESULT AND DISCUSSION

3.1 Free fatty acids (FFA):

The effects of natural heat treated attapulgite (Palygorskite) on FFA content of rapeseed oil were summarized on Fig 1. Natural activated clays were reported to play an active role for the removal of soaps, phospholipids and pigments from oil, however these clays dramatically caused the increase of FFA content in oil due to their properties as active catalyst which accelerated the conversion reaction of peroxide formation where the O_2 attacks the unsaturated fatty acid chain. This evidently converted peroxides into small chained fatty acid molecules or again, by means of bleaching earth, to secondary oxidation products. Similarly, it was also reported that higher bleaching temperatures clearly promoted peroxide decomposition and triacylglycerol hydrolysis [13]. As the result, peroxide levels decline with rising the bleaching temperature, whereas free fatty acid level increased dramatically due to the enhance hydrolysis reactions of triacylglycerol. In this study, the augmentation of FFA content was observed while bleaching temperature and attapulgite dosage dependent manner. However, this increase did not necessarily reveal any significant differences between the different attapulgite dosages at different bleaching temperatures. When clay treated at 100˚C and 150˚C were used with the amount higher than 1% of attapulgite and at the higher bleaching temperature which was significantly different ($P<0.05$) with neutralized oil sample. Fig.1 (a, b). In contrast to this, a prolonged heat treatment of clay slightly rose the FFA content of oil along with the increase of the amount of clay; whereas a clear significant differences ($P<0.05$) were only observed among the neutralized and bleached oil under 130˚C.Fig.1(c, d, e, f). Possible explanation to the escalating FFA content in oil could be attributed to the loss of adsorbed water (moisture) and zeolitic water at earlier stages of heat treatment of clay (100˚C and 150˚C) followed by gradual loss of a first, second coordinated water and hydroxyl groups during the subsequent stages of heat treatment process (200˚C, 250˚C, 300˚C and 350˚C). The partial losses of adsorbed and hydration water molecules increased the hydrophilicity and acidity of the surfaces [14]. Resulting the increment of FFA content in the rapeseed oil. However; no data has been published on commercial scale applications of naturally heat treated attapulgite into vegetable oil bleaching process.

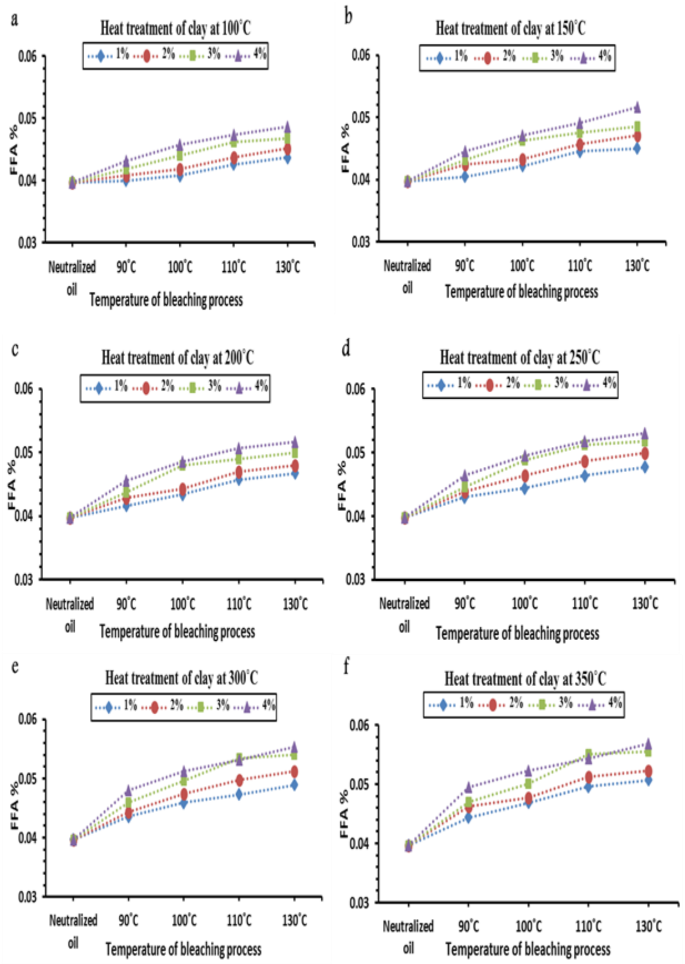

Figure 1.The Effect Of Attapulgite Dosage On FFA Content Of Rapeseed Oil At Different Heat Treatment And Bleaching Temperatures.

3.2 *Oil stability index (OSI):*

The oxidative stability is an important quality parameter for fats and oils. It is most commonly determined via the active oxygen method (AOM; AOCS Method Cd 12-57) but, for practical reasons, the simpler (and much faster) Rancimat method was used in this study .Figure.2 shows the influences of attapulgite heat treated with various temperature conditions with different dosage of attapulgite on the rapeseed oil stability. It's very clear that assorted temperature for heat treatment of attapulgite have effect on the water content of attapulgite. [15] showed that the water loss rate during the heating process have different stages that has a direct effect on attapulgite structure and its thermal behavior, accordingly the oxidation and peroxides formation during the oil bleaching was not stable where the water can take part in the oxidation reaction supported by the released oxygen during the bleaching process. From the graph (a, b, c, d), the bleaching process of rapeseed oil at 90˚C with 1% heat activated attapulgite strongly decreased the oil stability as compared to (2%, 3%, 4%). Whereas, the oxidative stability reduction rate was lower for figure.2 (e and f). In contrast, the bleaching process at 90˚C, 100˚C, 110˚C and 130˚C showed different performance and oxidative stability. If only attapulgite concentration and oxygen releasing reactions were present, a corresponding linear trend was expected for 1%, 2%, 3%, 4% attapulgite respectively due to more effective chlorophyll and tocopherols shielding by attapulgite active positions. Hence, there are more significantly contributing factors for this process. This behavior could be explained as the bleaching process at 90˚C was not enough to remove the moisture content in the attapulgite water content. The complete reaction took place at higher than 90˚C. In the other hand [16] showed that low clay content has no big effect on bleaching process. This result was in agreement with the color and FFA investigation in our study where 1% showed the lowest ability to improve those characters. Additionally, it is noted that attapulgite thermal treatment at higher than 250˚C had affected the bleaching efficiency. Many other researches established that the particle size and apparent bulk density of attapulgite, which are presumed to have a major impact on reduction of oil stability. The apparent bulk density value of clay depends on the amount of void space in the material. Since attapulgite has a finer particle size and lower apparent bulk density, the oxygen held in void spaces is released into

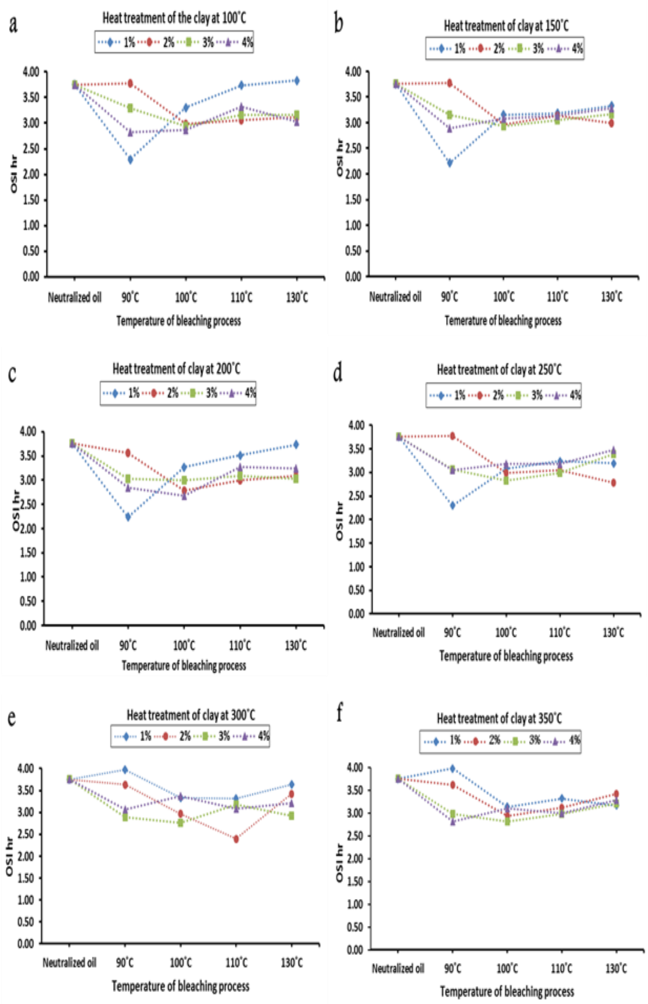

Figure 2. The effect of Attapulgite dosage on oxidation stability of rapeseed oil at different heat treatment and bleaching temperatures.

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the oil during the bleaching process and increases its peroxides. However, the observed escalations in the peroxides products of oil are reduced with the increase of the attapulgite concentration [17].

3.3 LCY and LCR:

The ability of attapulgite to bleach is mainly ascribed to its high surface area because the cation-exchange capacity is lower than that of montmorillonite-type clay minerals. It is thus, an alternative material to other sorbent in edible oil bleaching processes to remove the heavy metals, pigments, phenols and carotenoids that

		Bleached at 90°C		Bleached at 100°C		Bleached at 110°C		Bleached at 130°C	
Sample	Clay%	LCY	LCR	LCY	LCR	LCY	LCR	LCY	LCR
N.R		91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}
100°C		68.18± 1.22^{bc}	10.25± 0.07^{a}	72.33± 3.03^{b}	9.70± 0.56^{ab}	88.36± 1.58^{ab}	9.85± 0.07^{b}	72.17± 2.26^{b}	8.90± 0.14^{b}
150°C		75.32± 11.27^{ab}	9.80± 0.14^{bc}	70.66± 1.85^{b}	9.70± 0.14^{ab}	86.27± 1.28^{abc}	9.60± 0.14^{b}	65.34± 1.04^{c}	8.85± 0.07^{b}
200°C	1	61.71± 3.65^{bc}	9.65± 0.07^{bc}	71.44± 3.58^{b}	9.80± 0.28^{ab}	84.01± 0.39^{bcd}	9.55± 0.21^{b}	58.18± 1.80^{d}	8.45± 0.21^{c}
250°C		53.93± 0.92^{c}	9.55± 0.07^{c}	52.46± 0.87^{d}	9.55± 0.07^{b}	76.58± 4.39^{e}	8.40± 0.14^{d}	50.42± 1.25^{e}	7.65± 0.21^{d}
300°C		76.29± 14.93^{ab}	9.90± 0.14^{b}	59.50± 3.12^{c}	9.70± 0.14^{ab}	80.75± 4.53^{cde}	8.90± 0.14^{c}	59.86± 1.85^{d}	7.75± 0.21^{d}
350°C		68.55± 0.66^{bc}	9.90± 0.14^{b}	68.57± 0.90^{b}	9.80± 0.14^{ab}	79.93± 0.30^{de}	8.95± 0.21^{c}	49.77± 3.57^{e}	7.80± 0.14^{d}
N.R		91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}
100°C		79.18± 0.74^{b}	10.05± 0.07^{b}	59.14± 1.19^{b}	9.50± 0.56^{b}	61.83± 0.22^{b}	9.85± 0.07^{b}	36.61± 0.68^{b}	8.60± 0.14^{b}
150°C		40.82± 2.01^{cd}	9.95± 0.07^{b}	55.01± 0.23^{c}	9.35± 0.07^{b}	62.05± 1.50^{b}	9.50± 0.14^{c}	35.36± 3.94^{b}	7.90± 0.14^{c}
200°C	2	35.80± 1.54^{de}	9.05± 0.07^{c}	38.50± 1.61^{e}	8.00± 0.14^{c}	44.56± 0.31^{c}	7.55± 0.07^{de}	24.84± 0.00^{c}	7.10± 0.14^{d}
250°C		24.56± 2.34^{f}	8.65± 0.07^{c}	29.09± 0.37^{f}	7.70± 0.14^{c}	39.03± 1.19^{d}	7.45± 0.07^{e}	23.66± 1.34^{c}	6.35± 0.07^{e}
300°C		33.16± 5.49^{e}	8.85± 0.07^{cd}	36.67± 0.97^{e}	7.80± 0.14^{c}	35.22± 1.89^{e}	7.75± 0.21^{de}	15.58± 1.02^{d}	6.75± 0.21^{d}
350°C		42.51± 0.33^{c}	8.80± 0.14^{c}	44.85± 0.21^{d}	8.10± 0.14^{c}	35.76± 0.12^{e}	7.80± 0.14^{d}	15.88± 1.28^{d}	6.90± 0.14^{d}
N.R		91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}
100°C		42.43± 7.19^{b}	10.05± 0.07^{b}	35.59± 0.88^{b}	9.25± 0.07^{b}	39.66± 0.25^{b}	8.90± 0.14^{b}	16.65± 0.22^{b}	7.50± 0.14^{b}
150°C		25.76± 3.29^{c}	9.95± 0.07^{b}	33.06± 0.83^{c}	9.00± 0.14^{b}	27.52± 0.45^{c}	8.90± 0.14^{b}	14.73± 0.49^{c}	6.65± 0.35^{c}
200°C	3	20.61± 0.61^{cd}	9.05± 0.07^{c}	20.33± 0.32^{d}	7.85± 0.07^{c}	13.66± 0.45^{e}	7.55± 0.21^{c}	11.97± 0.08^{d}	6.25± 0.21^{c}
250°C		9.89± 1.95^{e}	8.65± 0.07^{c}	15.21± 0.75^{f}	7.25± 0.07^{d}	14.19± 0.83^{e}	7.40± 0.14^{c}	9.03± 1.67^{e}	5.60± 0.14^{d}
300°C		16.75 ± 3.25^{de}	8.85± 0.07^{cd}	9.37± 0.08^{de}	7.80± 0.14^{c}	16.11± 1.55^{d}	7.70± 0.14^{c}	11.68± 0.27^{d}	6.35± 0.21^{c}
350°C		15.59 ± 3.52^{de}	8.80± 0.14^{c}	18.35± 0.37^{e}	7.90± 0.14^{c}	17.30± 0.41^{d}	7.75± 0.21^{c}	9.52± 1.12^{e}	6.20± 0.28^{c}
N.R		91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}	91.90± 0.42^{a}	10.30± 0.14^{a}
100°C		19.82± 1.27^{b}	9.50± 0.14^{b}	21.66± 1.1^{b}	9.00± 0.14^{b}	24.14± 0.76^{b}	8.60± 0.14^{b}	10.96± 0.13^{b}	6.55± 0.07^{b}
150°C		16.61± 2.48^{b}	9.15± 0.21^{b}	19.14± 0.28^{c}	8.95± 0.21^{b}	17.33± 1.12^{c}	7.65± 0.07^{c}	10.01± 0.17^{b}	5.15± 0.21^{d}
200°C	4	9.71± 1.77^{c}	7.35± 0.21^{c}	13.19± 0.02^{e}	7.65± 0.07^{c}	12.58± 0.48^{d}	5.95± 0.21^{d}	8.17± 0.99^{cd}	5.00± 0.14^{d}
250°C		9.66± 1.7^{c}	7.30± 0.14^{c}	13.10± 0.25^{e}	7.20± 0.14^{d}	13.48± 0.80^{d}	6.10± 0.14^{d}	7.10± 0.49^{d}	4.20± 0.14^{f}
300°C		11.81± 0.06^{c}	7.35± 0.21^{c}	15.84± 0.31^{d}	7.45± 0.07^{cd}	12.33± 2.52^{d}	5.55± 0.07^{e}	7.56± 1.15^{d}	5.60± 0.14^{c}
350°C		10.86± 3.36^{c}	7.65± 0.21^{c}	18.87± 0.08^{c}	7.60± 0.14^{c}	12.83± 0.27^{d}	6.25± 0.21^{d}	9.48± 0.15^{bc}	4.60± 0.14^{e}

Table 1.The effect of Attapulgite dosage on the color LCR and LCY of rapeseed oil at different heat treatment and bleaching temperatures. N.R= Neutralized rapeseed oil. Thermal treatment of attapulgite at 100˚C, 150˚C, 200˚C, 250˚C, 300˚C and 350˚C, respectively.

responsible for undesired colors [8]. The effect of heat treated attapulgite and bleaching temperature on bleachability of neutralized rapeseed oil was studied to compare four different percentages of heat treated attapulgite. Table. 1 shows the bleaching of neutralized rapeseed oil with different percentage of heat treated attapulgite. The different dosage attapulgite treated at 250˚C showed the relatively best red and yellow colors adsorption efficiency at different bleaching temperature compare to the attapulgite treated at 100˚C, 150˚C, 200˚C, 300˚C, and 350˚C. In this study, the bleaching process activity for 1%, 2%, 3%, and 4% of heat treated attapulgite by measuring the red and yellow color to determine the effect of heat treated attapulgite dosages has been addresed. The evidence has been provided that the bleachability increases linearly with the addition of heat treated attapulgite. In agreement with our findings. [7]; [8] reported that the pigments removal is referring to the surface area and pore size distribution. However, the heat evolved for oil bleaching increased as the levels of activated attapulgite enlarged from 0.5% to 3%, due to the raise in active sites with increasing attapulgite levels as well as multilayer adsorption driven by van der Waals' forces at smaller amounts of adsorbents. There are enough adsorptive sites with 3% attapulgite to adsorb the pigments associated with soybean oil bleaching. The main reason of the best color improvement using heat treated attapulgite at 250˚C is supported by the findings reported that the specific surface area of the palygorskite increases to a maximum value with increasing the temperature to around 300˚C [18]. However, when thermal treatment temperature exceeds 400˚C the surface area of heat treated palygorskite would decrease due to the micropore demolition and structure folding [9]. This result also confirmed by [19];[20], They show a temperature rise over 300˚C causes irreversible dehydration and would change the structure of the clay mineral, due to loss of total water molecules that were coordinated to the metal of octahedral sheet.

4. CONCLUSIONS:

In the present study, heat activated attapulgite was used as a clarifying agent of rapeseed oils. The adsorption capacity of organic molecules, e.g., carotenoids, was proportionally increased for clay mineral samples treated at higher temperatures. Therefore, it showed significant changes within a temperature range of 200˚C–350˚C. That might be revealed structural and morphological changes associated with the partial and total loss of water molecules in the channels of the crystalline structure of the attapulgite as the thermal treatment temperature was increased. Activation attapulgite at 250˚C presented a maximum adsorption of pigments compared with the other heat activation. Water content of clay plays an important role for oxidation stability.

5. ACKNOWLODEGMENTS

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