



**SCREENING THE ALKALI-NEUTRALIZED SUNFLOWER SEED OIL  
BLEACHING ABILITY OF SOME NATURAL AND ACID-ACTIVATED  
NATURAL CLAYS, SYNTHETIC ADSORBENTS, AND METAL-ORGANIC  
FRAMEWORKS**

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**ABSTRACT**

The aim of this study was to search vegetable oil bleaching abilities of 30 different adsorbent materials placed into four groups (natural clay, acid-activated natural clay, synthetic adsorbent, metal-organic frames). After oil treatment against control sample, oil color (L, a\*, b\* values), oil weight loss (%), free fatty acidity (FFA), peroxide value (PV), and the specific extinctions of K<sub>232</sub> and K<sub>270</sub> were measured. Based on the data analysis, natural montmorillonite, acid-activated halloysite, Dowex, and Ti-MOF were selected, and tested in the same way against two commercial bleaching earth (C.B.E.) samples. Finally, an equal weight portion mixture of the four selected adsorbents were prepared and tested against C.B.Es. Results indicated that acid activated halloysite and Dowex had certain potentials to be implemented in oil bleaching. In conclusion, some other clay modification techniques suggested being applied to those potential adsorbents to improve their bleaching activity for potential commercial applications.

**Keywords:** Natural clays, synthetic adsorbents, MOF, bleaching, screening

**BAZI NATURAL VE ASİT-AKTİVE NATURAL KİLLERİN, SENTETİK  
ADSORBANLARIN VE METAL-ORGANİK ÇERÇEVELERİN ALKALİ-  
NÖTRALİZE AYIÇIĞI YAĞI AĞARTMA YETENEKLERİNİN İNCELENMESİ**

**ÖZ**

Bu çalışmanın amacı dört grup altında (natürel kil, asit-aktif natürel kil, sentetik adsorban, metal-organik kafes) toplanmış 30 farklı adsorbentin bitkisel yağ ağartma kapasitelerinin araştırılmasıdır. Ağartma işlemi sonrasında yağlarda, yağ rengi (L, a\*, b\* değerleri), yağ ağırlık kaybı (%), serbest yağ asitliği (SYA), peroksit değeri (PD), ve K<sub>232</sub> ile K<sub>270</sub> özgül sönümlenme katsayıları ölçülmüştür. Veri analizi sonucunda, doğal montmorillonit, asit-aktif halloysit, Dowex ve Ti-MOF seçilmiş, ve aynı yolla ticari ağartma topraklarına karşı test edilmiştir. Nihayet, seçilmiş adsorbanların eşit ağırlıklı bir karışımı hazırlanmış ve yine ticari örneklerle karşı test edilmiştir. Asit-aktif halloysit ve Dowex'in

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diğerlerinden daha yüksek ağartma potansiyeli olduğu görülmüştür. Sonuç olarak, bazı kil modifikasyon tekniklerinin bu potansiyel adsorbanlara uygulanarak ticari uygulamalar için kapasitelerinin artırılabilceği değerlendirilmiştir.

**Anahtar kelimeler:** Doğal killer, sentetik adsorbanlar, MOF, ağartma, tarama

## INTRODUCTION

The massive edible vegetable oil production system relies on extraction of crude oils from the oil seeds by pressing, solvent extraction or combination of both techniques. The generated crude oils contain some impurities (residual solvents, pesticides, Maillard products, etc.) which prevent their immediate acceptance by the consumers due to their health risk and sensory taints. Consequently, the crude oils have been refined by classical processes or physical refining operations. Usually classical refining involves consequent unit operations of degumming, alkali neutralization, bleaching, deodorization, winterization and polishing. Sometimes, one or two of these processes could be omitted depending on the condition of the crude oil being refined (Anderson, 1996; O'Brien, 2004).

Bleaching is the adsorptive removal of color pigments from the crude vegetable oils by adsorbent clays. The oil mixed with selected adsorbents (natural clays, activated clays and carbons, synthetic silicates, silica gel and others) at around 75-110 °C, mixed for 15-30 min under vacuum, and filtered. By this process not only color pigments (carotenoids, chlorophylls, gossipol, Maillard compounds etc.), but also some residual soaps and phosphatides, oxidation products, trace metals, the polyaromatic hydrocarbons (PAH) if present, and some pesticides were removed by adsorption principle onto and inside the adsorbent material used, and removed by filtration. The ratio of oil and adsorbent clay, efficient mixing, duration of mixing, process temperature, efficiency of the filters are the most important factors in addition to the adsorptive capacity and affinity of the clays used (Hodgson, 1996; Zschau, 2001).

Thereby, one research challenge is to find effective new adsorbents and/or modify them for the best bleaching with affordable feasibility. Further, minimization of neutral oil losses and highest possible retention of minor nutrients like

phytosterols and tocopherols were anticipated. Activated carbon, natural and activated clays (bentonite, palygorskite, sepiolite, montmorillonite, alumina and magnesium silicates, Fuller's earth, silica gel, etc.), and filter aids like kieselguhr, perlite, pulp, and organic powders have been implemented in oil bleaching industry (Boki et al., 1992; Zschau, 2001; O'Brien, 2004). Further, acid modified bentonite (Didi et al., 2009), modified kaolin (Worasith et al., 2011), and sepiolite (Sabah et al., 2007), active carbon (Zhang et al., 2018), silica gel and silicates (Gil et al., 2014), Magnesol XL (Srimiati et al., 2015), chitin (Samonin et al., 2021), and amberlite (Jamal and Boulanger, 2010) have searched for crude oil bleaching abilities. New adsorbent materials like synthetic porous materials, the metal-organic frameworks (MOFs), have tested for crude oil bleaching (Vlasova et al., 2016; Yılmaz et al., 2019). Since the material scientists and mining engineers develop new clays and adsorbents, more research will be done for better crude edible oil bleaching.

In this study, selected natural clays (halloysite, zeolite, bentonite, sepiolite, kaolin, montmorillonite) and their acid modified versions, some selected synthetic adsorbents (molecular sieve Å, Magnesol XL, amberlites IR400, IR120, and XAD7, silica gel blue, silica gel 60, Dowex, chitin, and active carbon), and some selected metal-organic frameworks (Ti-MOF,  $\gamma$ -CD-MOF, Cr-MOF, Al-MOF, Zn-MOF, Mg-MOF, HKUST-MOF, MIL-53-MOF) were screened for edible oil bleaching ability. As far as we searched, the halloysite, molecular sieve Å, the amberlites selected, silica gel blue, Dowex, HKUST-MOF, and MIL-53-MOF were screened for bleaching purpose for the first time in this study. Further, others were included together with two different commercial bleaching earths for comparison purpose.

The aims of this study were to screen various potential adsorbent materials for their ability for

crude vegetable oil bleaching, and compare them among themselves and with commercial bleaching earths to select the best performing candidates under laboratory experimental conditions for further studies.

## MATERIALS AND METHODS

### Materials

Degummed and alkali-neutralized, unbleached crude sunflower seed oil was provided by the Trakya Birlik Oil Co. (Çorlu, Türkiye). The adsorbent materials used in this study with their source firms were following: Halloysite (Esan Co., Eskişehir, Türkiye), Zeolite (Türkzeolit Mining Co., Balıkesir, Türkiye), Bentonite (Rota Mining Co., İstanbul), Sepiolite (Madkim Mining and Chem. Co., İstanbul), Kaolin (Kaolin Industrial Mines Co., İstanbul), Montmorillonite (Rota Mining Co., İstanbul), Molecular Sieve Å (Sigma, St. Louis, USA), Magnesol XL (The Dallas Group of America, Inc., Jeffersonville, IN, USA), Amberlite IR-400, Amberlite IR-120, and Amberlite XAD-7 (Sigma, St. Louis, USA), Silica Gel Blue and Silica Gel 60 (Merck, Darmstadt, Germany), Dowex (Sigma, St. Louis, USA),

Chitin (Jinan Qinmu Fine Chem. Co. Ltd., China), and Active Carbon (Zag Kimya, İstanbul). In addition, the 8 different MOFs were synthesized in our laboratory following the procedure given in the references. The Ti-MOF (Vlasova et al., 2016),  $\gamma$ -CD-MOF (Smaldone et al., 2010), Cr-MOF (Li et al., 2014), Al-MOF (Ma et al., 2014), Zn-MOF (Bu et al., 2012), Mg-MOF (Spanopoulos et al., 2015), HKUST-MOF (Naeimi and Faghihian, 2017), and MIL-53-MOF (Pu et al., 2018) were synthesized. Lastly, two commercial bleaching earths, the Amcol 930 (from Trakya Birlik Oil Co.) and Pure-Flo Supreme B81 (from Ata Endüstriyel Prod. Industry and Trade Ltd. Co., İstanbul) were provided. The adsorbent materials used in this study could be observed from Figure 1. The adsorbents were used as they received from the firms or synthesized in our laboratory. Their particle size were not measured, but they were ranged from fine dust to gritty small spheres. All other chemicals, standards and solvent used in the analyses were of analytical grade, and purchased from Sigma Chem Co. (St. Louis, USA) and Merck (Darmstadt, Germany).

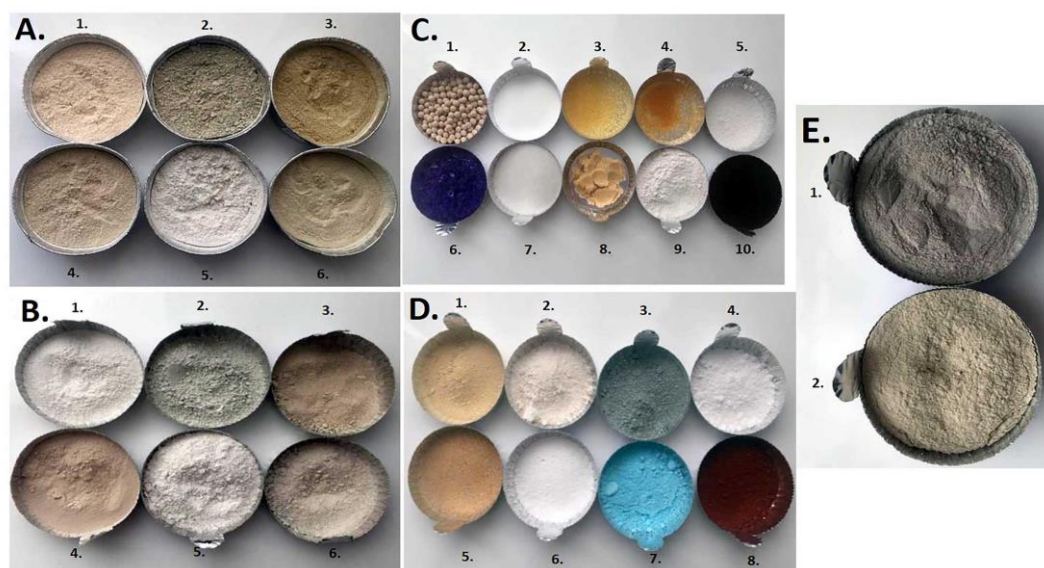


Figure 1. The natural (A) and acid-modified natural (B) adsorbents (1.Halloysite, 2.Zeolite, 3.Bentonite, 4.Sepiolite, 5.Kaolin, 6.Montmorillonite), synthetic (C) adsorbents (1.Molecular Sieve Å, 2.Magnesol XL, 3.Amberlite IR400, 4.Amberlite IR120, 5.Amberlite XAD7, 6.Silica Gel Blue, 7.Silica Gel 60, 8.Dowex, 9.Kitin, 10.Aktive Carbon), metal-organic frameworks (D) (1.Ti-MOF, 2. $\gamma$ -CD-MOF, 3.Cr-MOF, 4.Al-MOF, 5.Zn-MOF, 6.Mg-MOF, 7.HKUST-MOF, 8.MIL 53-MOF), and commercial bleaching earths (E, 1. Amcol 930, 2. Pure-Flo Supreme B81) used in this study.

### **Activation of the Natural Clays and Amberlites**

The acid-activation of the six natural clays were completed by first mixing each clay with 30% HCl at 1:5 (w/v) ratio and mixing under vacuum hood for 30 min. After that, the clay slurry were decanted, and washed with 10-fold pure water as many times as required to reach a decantation liquid with neutral pH. Finally, activated clays were dried at 150 °C for 5 h inside a vacuum incubator. These six clays were grouped as acid-activated natural clays.

The three amberlite resins studied under the synthetic adsorbents group were also activated before applications. The Amberlite IR400 were placed in 4 N HCl, and slowly mixed for 24 h, before filtration and washing until the collected washing liquid reached to pH 7.0. Finally, it was dried in the same way explained above (Mishra and Kar, 2003). The Amberlite IR120 was activated in a similar procedure but in 4 N NaOH solution (Mishra and Kar, 2003). Lastly, the Amberlite XAD7 was activated by washing it with plenty of pure water at room temperature for 4 times before drying it at 40 °C under vacuum for 48 h (Ribeiro et al., 2002).

### **Treatment of the Crude Sunflower Oil with the Adsorbents**

There were 4 treatment groups; the first group was named the natural clays, and included natural halloysite, zeolite, bentonite, sepiolite, kaolin, and montmorillonite. The second group was the acid-activated natural clays and included the same six clays after the modifications. The third group included 10 adsorbents (molecular sieve Å, Magnesol XL, Amberlites IR400, IR120, XAD7, silica gel blue, silica gel 60, Dowex, chitin, and active carbon), and named the synthetic adsorbents group. Lastly 8 MOFs (Ti-MOF,  $\gamma$ -CD-MOF, Cr-MOF, Al-MOF, Zn-MOF, Mg-MOF, HKUST-MOF, MIL-53-MOF) included the metal-organic frameworks group. In addition, there were two commercial bleaching earth (Amcol 930 and Pure-Flo Supreme B81), one adsorbent mixture prepared after the first part of this study, and one control sample treated in the same way.

The adsorbent treatment procedure briefly was as following; 10 g of crude oil was weighed into a glass beaker, and 0.3 g of the adsorbent was weighed and added into the oil. The mixture was stirred at 280 rpm at room temperature for 1 h. Finally, the oil-adsorbent slurry was filtered through Whatman no. 40 filter paper under natural gravity. The collected oil was placed into tubes, flashed with nitrogen gas before tightly capping. Finally, the tubes stored in refrigerator during the analyses. The effect of treatment temperatures were not studied in this study, and temperature as a factor could be considered in future studies.

### **Selection of the Best Performing Adsorbents and Preparation of the Adsorbent Mixture**

After the treatments, the oils were analyzed for instrumental color, weight loss, free fatty acidity (FFA), peroxide value (PV), and specific extinction ( $K_{232}$  and  $K_{270}$ ) values. All treatments were compared with control sample (no adsorbent treatment) and among themselves within each group to select the best one adsorbent from each of the 4 treatment groups. Selection was based on judgement of the analyses results yielding the best bleaching activity with minimal oil loss and lowest possible free fatty acidity and oxidation values. Consequently, montmorillonite from natural clays group, halloysite-AA from acid-activated natural clays group, Dowex from synthetic adsorbents group, and Ti-MOF from the MOF group were selected. These selected 4 adsorbents and the two commercial bleaching earths (C.B.E.-I and C.B.E.-II) were treated in the same way against control sample (no adsorbent treatment) to get a comparison among themselves. Finally, the 4 selected adsorbents were mixed in 1:1 weight ratio to prepare the 'adsorbent mixture' as a new adsorbent. This new adsorbent was also compared with the C.B.E.s and control sample in the same way.

### **Analyses of the Treated Oil Samples**

After each treatment, the oil was weighed by a Sartorius ED2245 scale (Sartorius, Germany), before placing it into glass tubes, and the weight loss (%) values were calculated, since the initial weight was known. The color of the treated oil

samples was assessed with a Minolta CR-400 colorimeter (Minolta Camera Co., Osaka, Japan). The oil sample was placed into the liquid sample holder of the instrument and several readings of color values (CIE standards) were recorded. The L value indicating brightness/darkness,  $a^*$  value indicating redness (+) / greenness (-), and  $b^*$  value indicating yellowness (+) / blueness (-) were measured.

The FFA of oil samples was measured following American Oil Chemists' Society (AOCS) method Ca 5a-40, and the PV was measured following AOCS method Cd 8-53 (AOCS, 1998), respectively. Finally, the specific extinction values of  $K_{232}$  and  $K_{270}$  were measured according to AOCS method Ch 5-91 (1998) with a UV-Vis spectrophotometer (Shimadzu UV-1800, Shimadzu Co., Japan).

### Statistical Analysis

In this study all experimental layouts were completed two times as two replicates. Within each replicate the analyses were done for three times. The data were reported as the mean with standard deviation of the six measurements. Comparison of the samples were accomplished by means of one-way ANOVA and Tukey's test at  $P \leq 0.05$ . The Minitab v.16.1 software (Minitab, 2010) was used for the statistical analyses.

## RESULTS AND DISCUSSIONS

### The Oil Bleaching Ability of the Natural Clays

Analytical values of the crude oils treated with the six natural adsorbents against control sample are presented in Table 1. The treated oil samples could be observed in Figure 2. The CIE color dimension of the L value indicates the brightness level of a sample and takes values from 0 (full dark or black) to 100 (full bright or white) (Pomeranz and Meloan, 1994). Compared with the control sample (30.28), zeolite (31.78) and kaolin (31.25) treated samples showed some improvements (lightening), but most importantly the other natural clays (halloysite, bentonite, sepiolite, and montmorillonite) yielded small decreases of brightness after treatment. This is an unexpected finding, but might be due to inefficient filtering of

the very fine clay dusts at the laboratory conditions (Whatman no. 40 filter paper). Some small particles of the clays could not be separated from oil, and hence may caused little increments of the L values. The  $a^*$  value shows the level of redness in the positive number direction, and greenness in the negative number direction (Pomeranz and Meloan, 1994). Compared with control sample (- 1.35), all samples had a little higher  $a^*$  values. Green tone was dominant in montmorillonite and bentonite treated samples. In vegetable oils, green color is caused by the presence of chlorophyll, while red-yellow tones are resulted from various carotenoids (O'Brien, 2004). Generally, decrease in one class pigments causes enhancement of the visibility of the other group, if both have not decreased together. It could be concluded that montmorillonite and bentonite removed most of the red color pigments, but not the green color pigments. Similarly, the  $b^*$  color value shows yellow (+  $b^*$ ) and blue (-  $b^*$ ) colors. Clearly, all samples had some yellowness, but treatments with bentonite, kaolin, and montmorillonite yielded higher yellowness, and treatment with sepiolite resulted significantly lower yellowness. This might be due to their inefficiency to remove the yellow colored pigments or most possibly their efficient removal ability for the red pigments. Contrarily, sepiolite was quite efficient to remove yellow colored pigments. Overall, as long as pigment removal ability considered, the most efficient natural clays were montmorillonite, bentonite and sepiolite. It was indicated that natural clays with layers of silicates such as bentonite, palygorskite, and sepiolite had high surface area, and could be used for oil decolorization, but also it was indicated that highest surface area was not yielded the highest bleaching (Zschau, 2001). In an early study (Boki et al., 1992), natural bentonites, sepiolites and montmorillonites were compared and sepiolites were suggested as the best adsorbents.

After the treatment, the total oil weight loss (%) values was also calculated (Table 1). The halloysite, bentonite and montmorillonite had lower weight loss values than zeolite, sepiolite and kaolin treatments. Generally, all weight loss values

were above 18%. This is an important quantity, which cause economical losses. Weight loss of bleached oils has been indicated as an important factor in selecting optimum bleaching technique, and numbers ranging from 5% to 40% have been

reported. It was also indicated that weight loss was related with the adsorbents affinity to bind neutral oil as well as to adsorbent addition level, process duration and filter efficiency (Hodgson, 1996; Zschau, 2001; O'Brien, 2004).

Table 1. The color and weight loss values, and chemical parameters measured for the oil samples treated with the natural clays.

	L Value	a* Value	b* Value	Weight Loss (%)
Control	30.28±0.44 <sup>a*</sup>	-1.35±0.07 <sup>c</sup>	6.23±0.27 <sup>b</sup>	—
Halloysite	29.73±0.63 <sup>b</sup>	-1.51±0.13 <sup>c</sup>	6.37±1.04 <sup>b</sup>	18.86±0.21 <sup>c</sup>
Zeolite	31.78±0.75 <sup>a</sup>	-1.47±0.05 <sup>d</sup>	6.53±0.35 <sup>b</sup>	19.06±0.33 <sup>b</sup>
Bentonite	28.10±0.29 <sup>b</sup>	-1.70±0.06 <sup>b</sup>	7.69±0.50 <sup>a</sup>	18.21±0.21 <sup>c</sup>
Sepiolite	29.43±0.04 <sup>b</sup>	-1.44±0.08 <sup>d</sup>	4.41±0.19 <sup>c</sup>	20.08±0.38 <sup>a</sup>
Kaolin	31.25±1.33 <sup>a</sup>	-1.45±0.08 <sup>d</sup>	7.05±0.29 <sup>a</sup>	19.01±0.27 <sup>b</sup>
Montmorillonite	28.30±1.11 <sup>b</sup>	-1.76±0.15 <sup>a</sup>	7.97±0.76 <sup>a</sup>	18.19±0.15 <sup>c</sup>
	Free Fatty Acidity (% Linoleic)	Peroxide Value (meqO <sub>2</sub> /kg)	Specific Extinction (K <sub>232</sub> )	Specific Extinction (K <sub>270</sub> )
Control	1.01±0.00 <sup>a†</sup>	17.73±0.20 <sup>c</sup>	2.49±0.00 <sup>f</sup>	0.41±0.00 <sup>d</sup>
Halloysite	0.62±0.05 <sup>d</sup>	17.74±0.28 <sup>c</sup>	3.51±0.01 <sup>a</sup>	0.83±0.00 <sup>a</sup>
Zeolite	0.96±0.05 <sup>b</sup>	20.65±0.74 <sup>a</sup>	3.18±0.02 <sup>c</sup>	0.48±0.00 <sup>b</sup>
Bentonite	0.89±0.01 <sup>c</sup>	19.44±0.45 <sup>b</sup>	3.20±0.01 <sup>c</sup>	0.44±0.00 <sup>c</sup>
Sepiolite	0.50±0.05 <sup>e</sup>	18.63±0.29 <sup>b</sup>	3.33±0.02 <sup>b</sup>	0.50±0.00 <sup>b</sup>
Kaolin	0.96±0.05 <sup>b</sup>	20.15±0.21 <sup>a</sup>	3.15±0.02 <sup>d</sup>	0.41±0.00 <sup>d</sup>
Montmorillonite	0.44±0.01 <sup>f</sup>	19.38±0.35 <sup>b</sup>	3.02±0.02 <sup>e</sup>	0.31±0.00 <sup>e</sup>

\*Small uppercase letters indicate the statistically significant differences within each column for the mean±SD values calculated from four determinations by one-way ANOVA and Tukey's test ( $p \leq 0.05$ ).

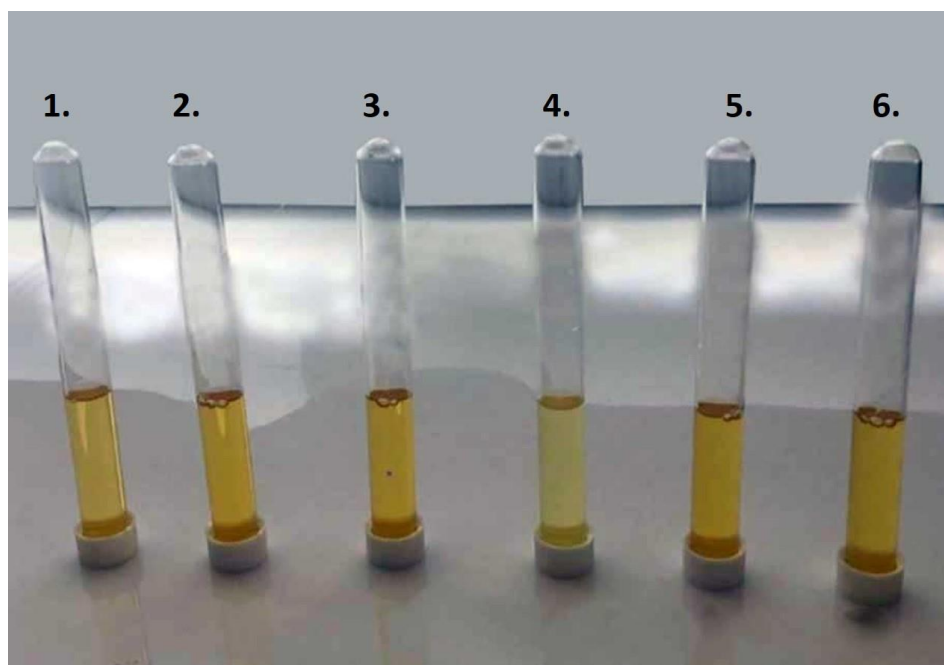


Figure 2. The oil samples treated with natural adsorbents (1. Halloysite, 2. Zeolite, 3. Bentonite, 4. Sepiolite, 5. Kaolin, 6. Montmorillonite).



Some chemical quality parameters of the treated oil samples were also measured (Table 1). The free fatty acidity (FFA) of control sample was 1.01% linoleate, and all treated samples had lower FFA values than the control sample. FFA reduction was the most with montmorillonite treated sample (0.44%) followed by sepiolite (0.505), and halloysite (0.62%) treated samples, respectively. Since the control oil sample was alkali-neutralized one, its low FFA was expected, and further reduction after adsorbent treatments could be accounted a good side benefit. Generally natural clays were found good adsorbents in terms of adsorbing the free fatty acids. Similar findings were reported previously for various natural adsorbents (Zschau, 2001; O'Brien, 2004). The peroxide values (PV) indicated a different trend, and all treated samples had PVs higher than that of the control sample (Table 1). PV indicates the level of active oxygen compounds in an oil sample, and it is limited in refined vegetable oils to a max value of 10 meq O<sub>2</sub>/kg oil sample (TGK, 2012). All treated samples and the control sample had PVs higher than the codex limit for refined oils. Since we used alkali-neutralized crude sunflower oil, this finding is quite expected. After all adsorbent treatments, the PV of samples enhanced compared to control sample (17.73 meq O<sub>2</sub>/kg oil) possibly due to long duration of the treatments including filtration time open to atmosphere. Since it was not possible to use a closed vacuum vessel in laboratory, the treatments were completed under atmospheric pressure, and consequently some oxidation were occurred. Among the treatments, some enhanced PV more than the others, and this might be due to some catalytic effect for oxidation or some physical effect of oxygen distribution in the oil. It is well known that under industrial conditions, bleaching process is always done under hermetic condition with full vacuum. Consequently, one adsorbent with the best quality parameters and the lowest oil loss value could be selected omitting the PV, since in real applications PV will not be a problem because of the full vacuum application. The specific extinctions of K<sub>232</sub> and K<sub>270</sub> were also measured (Table 1). These parameters indicate the level of dienoid (hydroperoxides and conjugated dienes) and trienoic (carbonyl compounds and

conjugates) acids as the primary and secondary oxidation compounds. These parameters were defined for virgin olive oil as acceptable limits of 2.5-2.6 for K<sub>232</sub> and 0.22-0.25 for K<sub>270</sub>, respectively (TGK, 2017). Clearly, there are some primary oxidation products present in the treated samples in accordance with PV data. Further, secondary oxidation products were also present in the treated samples. Overall, for any adsorbent treatment or bleaching process, vacuum seems inevitable. When all findings were considered together (Table 1), montmorillonite was selected as the best one among the natural clays for bleaching treatment.

### **The Oil Bleaching Ability of the Acid-Activated Natural Clays**

The six natural clays were acid-activated as explained in the method section, and oil treatments were done in the same way. The analytical results of the oil samples are presented in Table 2, and the oils could be observed from Figure 3. Evaluation of the data will be in the same way as completed above to select one best adsorbent among the samples. All acid-activated natural clays enhanced the brightness level of the oil, but the highest brightness (L value) was observed in zeolite (34.79) treatment followed by halloysite (34.76). Similarly, green tones reduced most by sepiolite (- 0.92 a\* value) followed by halloysite (- 1.13 a\* value) treatment. The same trend was evident for yellowness, and b\* value was 2.61 for sepiolite and 3.88 for halloysite treatments. Clearly acid-activated sepiolite, halloysite and zeolite were better in color correction among others. The lowest weight loss value (12.08%) was with halloysite, and the highest (19.51%) was with sepiolite treatment. Further, if the acid-activated clays (Table 2) were compared to their natural forms (Table 1), it could be observed that acid activation enhanced their oil brightening ability and reduced oil loss values. Generally, acid activation could be accepted as a good strategy for natural clays to be used as oil bleaching agents. In this study, one type acid-activation treatment was applied to all clays, but in literature acid-activation with different factors were studied for individual clays. For example, the optimum activation process for bentonite was

determined as 31% acid concentration, 10 h contact time, and solid to acid ratio of 320 g/L for sulfuric acid (Didi et al., 2009). Likewise, 1 N 65%

HNO<sub>3</sub> acid-activation at room temperature for 1 h with 1:10 solid: liquid ratio yielded a significantly better sepiolite (Sabah et al., 2007).

Table 2. The color and weight loss values, and chemical parameters measured for the oil samples treated with the acid-activated natural clays.

	L Value	a* Value	b* Value	Weight Loss (%)
Control	30.28±0.44 <sup>d*</sup>	-1.35±0.07 <sup>d</sup>	6.23±0.27 <sup>c</sup>	—
Halloysite-AA	34.76±1.44 <sup>a</sup>	-1.13±0.07 <sup>e</sup>	3.88±0.18 <sup>d</sup>	12.08±0.21 <sup>d</sup>
Zeolite-AA	34.79±2.47 <sup>a</sup>	-1.63±0.24 <sup>c</sup>	7.14±0.32 <sup>b</sup>	13.57±0.19 <sup>c</sup>
Bentonite-AA	31.59±0.54 <sup>c</sup>	-1.95±0.08 <sup>a</sup>	8.71±0.39 <sup>a</sup>	12.88±0.20 <sup>c</sup>
Sepiolite-AA	33.62±0.65 <sup>a</sup>	-0.92±0.07 <sup>f</sup>	2.61±0.02 <sup>e</sup>	19.51±0.49 <sup>a</sup>
Kaolin-AA	33.42±0.62 <sup>a</sup>	-1.77±0.03 <sup>b</sup>	7.55±0.52 <sup>a</sup>	16.64±0.24 <sup>b</sup>
Montmorillonite-AA	32.13±1.09 <sup>b</sup>	-1.78±0.13 <sup>b</sup>	7.87±0.46 <sup>a</sup>	13.73±0.16 <sup>c</sup>
	Free Fatty Acidity (% Linoleic)	Peroxide Value (meqO <sub>2</sub> /kg)	Specific Extinction (K <sub>232</sub> )	Specific Extinction (K <sub>270</sub> )
Control	1.01±0.00 <sup>at</sup>	17.73±0.20 <sup>a</sup>	2.49±0.00 <sup>f</sup>	0.41±0.00 <sup>g</sup>
Halloysite-AA	0.92±0.00 <sup>b</sup>	7.83±0.35 <sup>f</sup>	3.99±0.00 <sup>b</sup>	1.68±0.00 <sup>d</sup>
Zeolite-AA	0.99±0.04 <sup>a</sup>	11.07±0.33 <sup>c</sup>	4.00±0.00 <sup>a</sup>	2.18±0.00 <sup>b</sup>
Bentonite-AA	0.91±0.01 <sup>c</sup>	10.25±0.39 <sup>d</sup>	3.16±0.00 <sup>e</sup>	0.57±0.00 <sup>f</sup>
Sepiolite-AA	0.92±0.00 <sup>b</sup>	13.94±0.12 <sup>b</sup>	3.51±0.01 <sup>d</sup>	1.40±0.00 <sup>e</sup>
Kaolin-AA	0.92±0.00 <sup>b</sup>	11.20±0.43 <sup>c</sup>	4.00±0.01 <sup>a</sup>	2.07±0.00 <sup>c</sup>
Montmorillonite-AA	0.92±0.01 <sup>b</sup>	9.43±0.35 <sup>e</sup>	3.75±0.02 <sup>c</sup>	2.47±0.00 <sup>a</sup>

\*Small uppercase letters indicate the statistically significant differences within each column for the mean±SD values calculated from four determinations by one-way ANOVA and Tukey's test ( $p \leq 0.05$ ).

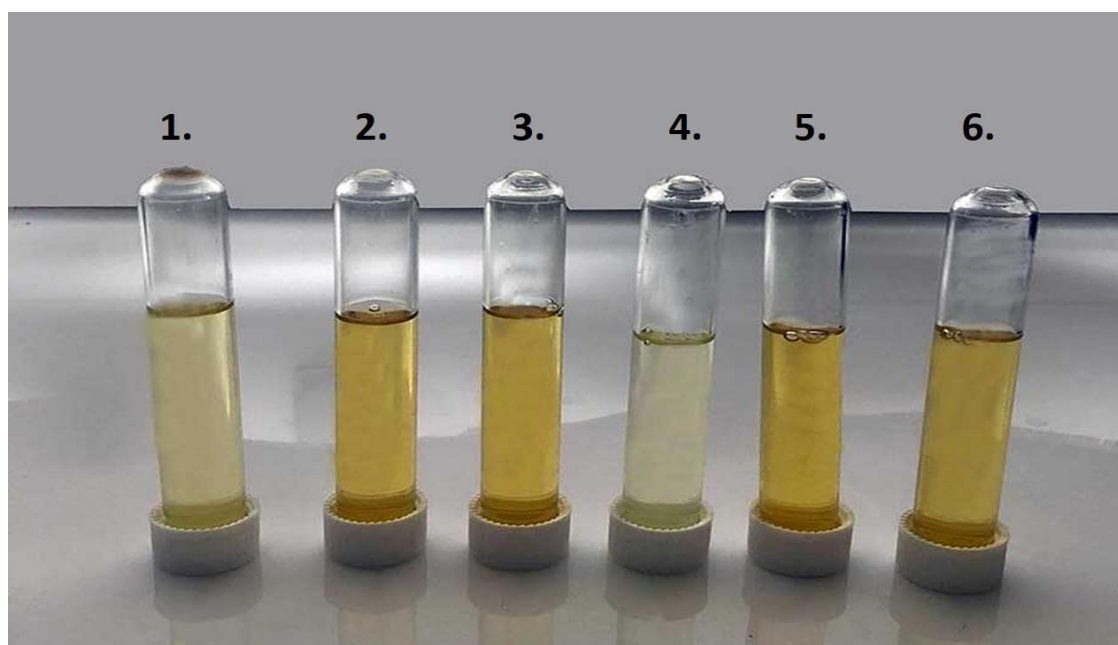


Figure 3. The oil samples treated with acid-activated natural adsorbents (1. Halloysit-AA, 2. Zeolite-AA, 3. Bentonite-AA, 4. Sepiolite-AA, 5. Kaolin-AA, 6. Montmorillonite-AA).



After the treatments, all FFA values were reduced compared to control sample (Table 2). There were small differences among the treatments, and FFA adsorption capacity was highest with bentonite treatment. The PV of all treated samples were lower than that of the control sample (Table 2), indicating that acid-activated clays were able to adsorb some peroxides. This was not evident with the natural clays (Table 1). PV reduction was highest with halloysite (8.83 meqO<sub>2</sub>/kg) treatment. This situation was not confirmed with the specific extinction values. There were some enhancement in both K<sub>232</sub> and K<sub>270</sub> values for the treatments compared with control sample. Consequently, some secondary oxidation must have taken place during the treatment duration. Similarly, vacuum or neutral gas atmosphere must be present during oil bleaching treatment.

After considering all findings together, the acid-activated halloysite was selected the best one among this group for further evaluation. Since there is no study in literature for halloysite for oil bleaching purpose, this finding could be important for further studies.

#### The Oil Bleaching Ability of the Synthetic Adsorbents

Ten different synthetic adsorbent were tested for oil bleaching purpose and the results of the

treated oil samples are summarized in Table 3. The treated oil samples are shown in Figure 4. Compared to control sample, some treatments enhanced oil brightness (Amberlite IR120, Amberlite XAD7, Dowex, Amberlite IR400 and molecular sieve Å), while some others (active carbon, chitin, silica gel 60, silica gel blue, Magnesol XL) decreased it. The negative a\* value in control sample (- 1.35) were increased in all treated samples. The highest a\* values were measured with Amberlite XAD, Amberlite IR400 and Dowex treated samples. In these samples, the level of greenness increased. This might be due to proportional decrease of pigments giving red color. The level of yellowness (b\* value) were mostly increased, only active carbon treatment decreased it. This is unexpected because adsorbents usually remove the yellow carotenoid pigments. It must be remembered that the carotenoid pigments yield colors from yellow to dark red and even to brown-red. Consequently, proportional decrease of a pigment could result a higher color value reading of the other pigment. For color correction activity, it seems that amberlites and Dowex were better among others. The oil weight loss values were also varied (Table 3). The lower weight loss values were in the order of Amberlite IR120 < Dowex < Amberlite IR400, respectively.

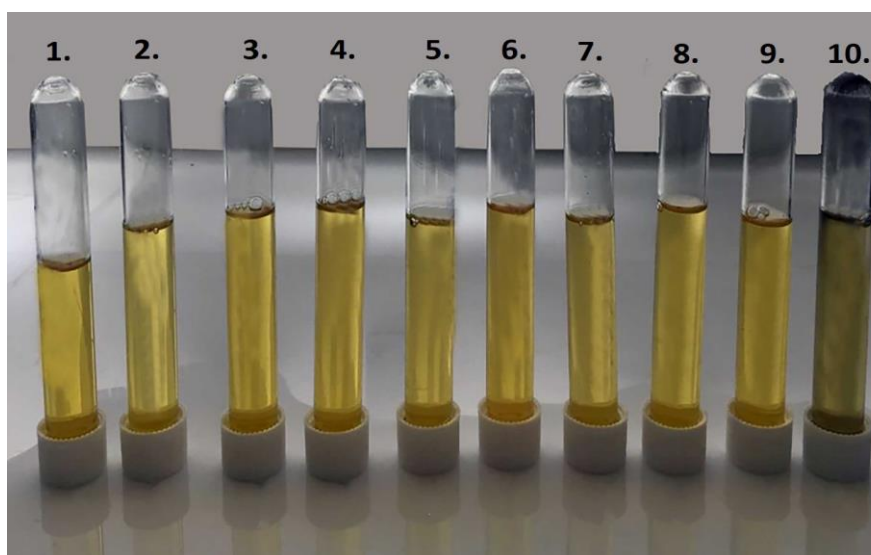


Figure 4. The oil samples treated with synthetic adsorbents (1. Molecular Sieve Å, 2. Magnesol XL, 3. Amberlite IR400, 4. Amberlite IR120, 5. Amberlite XAD7, 6. Silica Gel Blue, 7. Silica Gel 60, 8. Dowex, 9. Kitin, 10. Aktive Carbon).

Table 3. The color and weight loss values, and chemical parameters measured for the oil samples treated with the synthetic adsorbents.

	L Value	a* Value	b* Value	Weight Loss (%)
Control	30.28±0.44 <sup>c*</sup>	-1.35±0.07 <sup>f</sup>	6.23±0.27 <sup>d</sup>	–
Molecular Sieve Å	30.57±0.95 <sup>c</sup>	-1.76±0.19 <sup>d</sup>	7.27±0.28 <sup>c</sup>	16.91±0.24 <sup>b</sup>
Magnesol XL	29.45±0.83 <sup>d</sup>	-1.80±0.13 <sup>c</sup>	6.73±0.58 <sup>d</sup>	16.77±0.11 <sup>b</sup>
Amberlite IR400	31.46±0.80 <sup>b</sup>	-2.10±0.15 <sup>a</sup>	9.42±0.71 <sup>a</sup>	11.99±0.16 <sup>e</sup>
Amberlite IR120	33.19±0.61 <sup>a</sup>	-2.01±0.04 <sup>b</sup>	9.19±0.25 <sup>a</sup>	11.08±0.09 <sup>e</sup>
Amberlite XAD7	32.68±0.88 <sup>a</sup>	-2.13±0.11 <sup>a</sup>	8.30±0.61 <sup>b</sup>	16.36±0.28 <sup>b</sup>
Silica Gel Blue	27.77±0.35 <sup>c</sup>	-1.81±0.05 <sup>c</sup>	7.78±0.35 <sup>c</sup>	15.15±0.30 <sup>c</sup>
Silica Gel 60	27.77±0.36 <sup>c</sup>	-1.67±0.09 <sup>d</sup>	6.70±0.68 <sup>d</sup>	14.98±0.66 <sup>c</sup>
Dowex	32.28±0.20 <sup>b</sup>	-2.03±0.07 <sup>b</sup>	8.44±0.38 <sup>b</sup>	11.88±0.19 <sup>e</sup>
Chitin	27.39±0.04 <sup>e</sup>	-1.97±0.09 <sup>b</sup>	7.92±0.17 <sup>c</sup>	17.44±0.21 <sup>a</sup>
Active Carbon	27.41±0.31 <sup>e</sup>	-1.48±0.03 <sup>e</sup>	5.21±0.20 <sup>e</sup>	13.46±1.03 <sup>d</sup>
	Free Fatty Acidity (% Linoleic)	Peroxide Value (meqO <sub>2</sub> /kg)	Specific Extinction (K <sub>232</sub> )	Specific Extinction (K <sub>270</sub> )
Control	1.01±0.00 <sup>a*</sup>	17.73±0.20 <sup>g</sup>	2.49±0.00 <sup>f</sup>	0.41±0.00 <sup>f</sup>
Molecular Sieve Å	0.87±0.06 <sup>c</sup>	26.30±0.47 <sup>a</sup>	3.25±0.02 <sup>e</sup>	0.35±0.00 <sup>b</sup>
Magnesol XL	0.86±0.05 <sup>c</sup>	22.70±0.22 <sup>d</sup>	3.48±0.00 <sup>d</sup>	0.38±0.00 <sup>g</sup>
Amberlite IR400	0.97±0.06 <sup>a</sup>	24.21±0.01 <sup>c</sup>	3.93±0.01 <sup>b</sup>	0.49±0.00 <sup>e</sup>
Amberlite IR120	1.03±0.01 <sup>a</sup>	21.79±0.47 <sup>f</sup>	4.00±0.00 <sup>a</sup>	0.56±0.00 <sup>c</sup>
Amberlite XAD7	0.95±0.03 <sup>b</sup>	26.10±0.06 <sup>b</sup>	4.00±0.00 <sup>a</sup>	0.52±0.00 <sup>d</sup>
Silica Gel Blue	0.92±0.01 <sup>b</sup>	21.56±0.19 <sup>f</sup>	3.93±0.07 <sup>b</sup>	0.41±0.00 <sup>f</sup>
Silica Gel 60	0.96±0.05 <sup>a</sup>	22.18±0.44 <sup>e</sup>	4.00±0.00 <sup>a</sup>	0.44±0.00 <sup>e</sup>
Dowex	0.80±0.00 <sup>d</sup>	8.47±0.33 <sup>i</sup>	3.98±0.00 <sup>a</sup>	0.49±0.00 <sup>e</sup>
Chitin	0.91±0.00 <sup>b</sup>	12.58±0.32 <sup>h</sup>	3.56±0.04 <sup>c</sup>	0.59±0.00 <sup>b</sup>
Active Carbon	0.91±0.00 <sup>b</sup>	10.71±0.04 <sup>i</sup>	3.42±0.04 <sup>d</sup>	0.79±0.00 <sup>a</sup>

\*Small uppercase letters indicate the statistically significant differences within each column for the mean±SD values calculated from four determinations by one-way ANOVA and Tukey's test ( $p \leq 0.05$ ).

Compared to the control sample (1.01%), the lowest FFA value (0.80%) was measured in Dowex treated sample, followed by Magnesol XL (0.86%), respectively. A similar trend was evident for PV data. The lowest PV (8.47 meqO<sub>2</sub>/kg) was measured in the Dowex treated sample, and the highest (26.30 meqO<sub>2</sub>/kg) for molecular sieve Å treated sample compared with control (17.73 meqO<sub>2</sub>/kg). There was no similar study in literature for Dowex, and these findings could be important for further evaluations. Similar to the natural and

acid-modified natural clays groups, secondary peroxides adsorption patterns were not similar, and almost all treatment resulted higher specific extinction values than control sample.

Two mixed bed ion-exchange resins (Dowex Monosphere MR-450 UPW and Amberlite MB-150) were used to remove oleic acid from a laboratory-prepared 5% (w/w) oleic acid/soybean oil mixture (Jamal and Boulanger, 2010). Results indicated over 93% of free oleate

removal. Although there was no bleaching study, FFA removal ability of Dowex and amberlite resin was confirmed. Possibility of using chitin as ion exchange resin was discussed (Samonin et al., 2021), but application of chitin in oil bleaching has not been investigated. Silica gel 60 and activated carbon among some other adsorbents were studied to bleach soybean oil. Adsorption of FFA and lutein was highest with silica gel 60 (Gil et al., 2014). After evaluating the data presented in Table 3, the Dowex was selected as the most promising synthetic adsorbent for oil bleaching activity, and further analyses were completed.

### The Oil Bleaching Ability of the Metal-Organic Frameworks

Eight different metal-organic frameworks (MOF) were investigated for oil bleaching capacity evaluation in this study, and the analytical results of the treated oil samples against control are shown in Table 4, and the oils are presented in Figure 5. The highest L values were detected in Al-MOF (33.56), MIL-53-MOF (33.42) and Mg-

MOF (33.28) treated samples. These MOFs enhanced oil brightness, while only Ti-MOF treated sample a little decreased (29.59) it. Considering the  $a^*$  values, all treatment enhanced the level of greenness, or in other word they all reduced the amount of some red pigments. The yellow color reduction capacity of Al-MOF (5.20) and Ti-MOF (5.79) samples were higher than the rest. As color change respect, it seems that Al-MOF and Ti-MOF yielded the better results. On the other hand, Al-MOF yielded a very significantly higher (32.10%) oil loss value compared to the lower values of Cr-MOF (12.05%) and  $\gamma$ -CD-MOF (12.98%), respectively. The FFA reduction was highest in Al-MOF (0.64%),  $\gamma$ -CD-MOF (0.67%), and Ti-MOF (0.68%), respectively. The PV values from lower to higher were ordered as  $\gamma$ -CD-MOF < Ti-MOF < Cr-MOF, as could be observed from Table 4. There was no clear trend for secondary oxidation compounds, but the specific extinction of  $K_{232}$  showed an increase in all treated samples, and  $K_{270}$  values also indicated some enhancements.

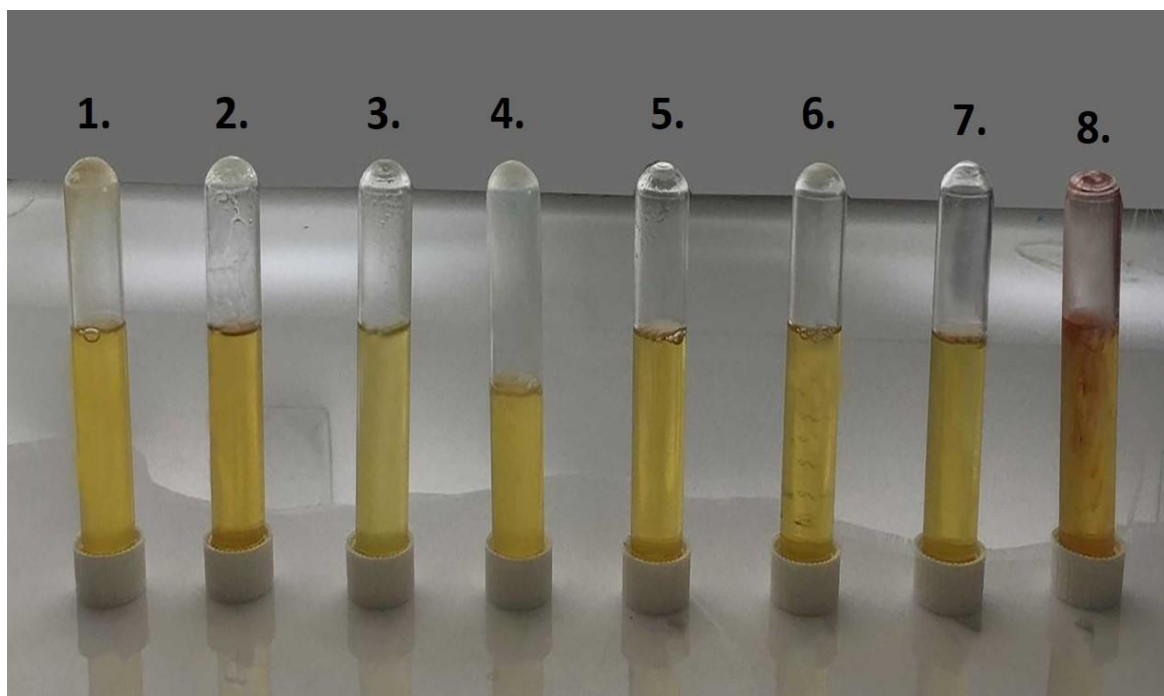


Figure 5. The oil samples treated with metal-organic frameworks (1. Ti-MOF, 2.  $\gamma$ -CD-MOF, 3. Cr-MOF, 4. Al-MOF, 5. Zn-MOF, 6. Mg-MOF, 7. HKUST-MOF, 8. MIL-53-MOF).

Table 4. The color and weight loss values, and chemical parameters measured for the oil samples treated with the metal-organic frameworks.

	L Value	a* Value	b* Value	Weight Loss (%)
Control	30.28±0.44 <sup>ce</sup>	-1.35± 0.07 <sup>d</sup>	6.23± 0.27 <sup>d</sup>	–
Ti-MOF	29.59±0.67 <sup>d</sup>	-1.35±0.04 <sup>d</sup>	5.79±0.38 <sup>e</sup>	16.08±0.80 <sup>c</sup>
γ-CD-MOF	32.66±1.08 <sup>b</sup>	-1.55±0.15 <sup>b</sup>	8.15±0.16 <sup>b</sup>	12.98±0.45 <sup>f</sup>
Cr-MOF	30.91±0.19 <sup>c</sup>	-1.52±0.02 <sup>b</sup>	6.41±0.40 <sup>d</sup>	12.05 ±0.13 <sup>f</sup>
Al-MOF	33.56±0.80 <sup>a</sup>	-1.46±0.05 <sup>c</sup>	5.20±0.34 <sup>e</sup>	32.10±1.82 <sup>a</sup>
Zn-MOF	32.72±0.62 <sup>b</sup>	-1.90±0.04 <sup>a</sup>	8.83±0.65 <sup>a</sup>	14.59±0.42 <sup>e</sup>
Mg-MOF	33.28±2.03 <sup>a</sup>	-1.36±0.16 <sup>d</sup>	7.11±0.21 <sup>c</sup>	15.12±0.46 <sup>d</sup>
HKUST-MOF	32.38±0.81 <sup>b</sup>	-1.90±0.06 <sup>a</sup>	7.80±0.55 <sup>b</sup>	17.01±0.91 <sup>b</sup>
MIL-53-MOF	33.42±0.72 <sup>a</sup>	-1.51±0.11 <sup>b</sup>	8.12±0.22 <sup>b</sup>	16.21±0.25 <sup>c</sup>
	Free Fatty Acidity (% Linoleic)	Peroxide Value (meqO <sub>2</sub> /kg)	Specific Extinction (K <sub>232</sub> )	Specific Extinction (K <sub>270</sub> )
Control	1.01±0.00 <sup>a</sup>	17.73±0.20 <sup>b</sup>	2.49±0.00 <sup>g</sup>	0.41±0.00 <sup>e</sup>
Ti-MOF	0.68±0.01 <sup>d</sup>	12.50±0.16 <sup>g</sup>	3.28±0.02 <sup>f</sup>	0.55±0.00 <sup>c</sup>
γ-CD-MOF	0.67±0.00 <sup>d</sup>	9.31 ±0.25 <sup>h</sup>	3.83±0.10 <sup>b</sup>	2.26±0.00 <sup>a</sup>
Cr-MOF	0.85±0.05 <sup>c</sup>	12.62 ±0.31 <sup>g</sup>	3.25±0.04 <sup>f</sup>	0.41±0.00 <sup>e</sup>
Al-MOF	0.64 ±0.02 <sup>d</sup>	13.84 ±1.24 <sup>e</sup>	3.56±0.07 <sup>d</sup>	0.58±0.00 <sup>c</sup>
Zn-MOF	0.90±0.00 <sup>b</sup>	14.41 ±0.25 <sup>d</sup>	3.48±0.08 <sup>e</sup>	0.57±0.00 <sup>c</sup>
Mg-MOF	0.97±0.05 <sup>a</sup>	13.10 ±0.14 <sup>f</sup>	3.62±0.10 <sup>c</sup>	0.50±0.00 <sup>d</sup>
HKUST-MOF	0.90±0.00 <sup>b</sup>	26.31 ±0.45 <sup>a</sup>	3.91±0.05 <sup>a</sup>	0.66±0.00 <sup>b</sup>
MIL-53-MOF	1.05±0.05 <sup>a</sup>	16.28 ±0.58 <sup>c</sup>	3.92±0.07 <sup>a</sup>	0.55±0.00 <sup>c</sup>

\*Small uppercase letters indicate the statistically significant differences within each column for the mean±SD values calculated from four determinations by one-way ANOVA and Tukey's test ( $p \leq 0.05$ ).

In literature, there are some studies with selected MOFs to purify crude vegetable oils. In an early one (Li et al., 2014), some herbicides from soy, sunflower, corn and peanut oils were adsorbed by MIL-101 MOF, and successfully removed. In another one (Vlasova et al., 2016), MIL-53 (Al), Zn-MOF and MIL-125 (Ti) MOFs were used to remove FFA, peroxides, and color pigments from crude vegetable oils, and some success were achieved. In one of our study (Yılmaz et al., 2019), seven different MOFs were used to purify crude sunflower oil, and Ti-MOF and γ-CD-MOF have shown to be quite effective. The difference of this study from our previous study is that we included the HKUST-MOF, and MIL-53-MOF first time for this purpose in addition to the potentially good MOFs studied before to get a comparison. Theoretically there are many types of MOFs could be synthesized, but we select non-toxic and potentially safe candidates applicable in food processing. After evaluating all data in the MOF group, we selected the Ti-MOF to be included in further comparisons.

#### Comparison of the Selected Adsorbents with Commercial Bleaching Earths

Montmorillonite from the natural clays group, Halloysite-AA from the acid-activated natural clays group, Dowex from the synthetic adsorbents group, and Ti-MOF from the metal-organic frameworks group were selected based on their bleaching performance, and they were compared with two different commercial bleaching earths (C.B.E.-I and C.B.E.-II) in another set of experiment. The findings of this comparison study were presented in Table 5. Halloysite-AA brightened the oil most with 34.76 L value compared to 30.28 L value of the control. It was even higher than the C.B.E.-I which had a 33.35 L value. This indicates a certain potential of Halloysite-AA. Similarly, the lowest – b\* value (-1.13) was measured for Halloysite-AA treated sample, indicating that some green pigments were removed. Contrarily, Dowex treated sample had the highest –a\* value (-2.03) showing that the level of greenness enhanced or the level of red color reduced significantly to get green pigment

more measurable. Yellow color decreased most with C.B.E.-II treated sample (3.20), followed by Halloysite-AA treated (3.88) sample. Clearly Halloysite-AA had certain potential to remove yellow pigments as well. Oil weight loss values

were varied, and the lowest (11.88%) was with Dowex treatment followed by Halloysite-AA (12.08%) treated sample. Both were lower than the commercial bleaching earths to again indicate certain potentials.

Table 5. The color and weight loss values, and chemical parameters measured for the oil samples treated with the commercial bleaching earths and the selected adsorbents.

	L Value	a* Value	b* Value	Weight Loss (%)
Control	30.28±0.44 <sup>c*</sup>	-1.35±0.07 <sup>c</sup>	6.23±0.27 <sup>b</sup>	—
C.B.E.-I	33.35±0.55 <sup>b</sup>	-1.26±0.02 <sup>d</sup>	4.16±0.36 <sup>c</sup>	14.24±0.16 <sup>c</sup>
C.B.E.-II	32.79±0.37 <sup>b</sup>	-1.09±0.11 <sup>e</sup>	3.20±0.27 <sup>d</sup>	14.95±0.10 <sup>c</sup>
Montmorillonite	28.30±1.11 <sup>d</sup>	-1.76±0.15 <sup>b</sup>	7.97±0.76 <sup>a</sup>	18.19±0.15 <sup>a</sup>
Halloysite-AA	34.76±1.44 <sup>a</sup>	-1.13 ±0.07 <sup>e</sup>	3.88±0.18 <sup>c</sup>	12.08±0.21 <sup>d</sup>
Dowex	32.28±0.20 <sup>b</sup>	-2.03±0.07 <sup>a</sup>	8.44±0.38 <sup>a</sup>	11.88±0.19 <sup>e</sup>
Ti-MOF	29.59±0.67 <sup>d</sup>	-1.35±0.04 <sup>c</sup>	5.79±0.38 <sup>b</sup>	16.08±0.80 <sup>b</sup>
	Free Fatty Acidity (% Linoleic)	Peroxide Value (meq O <sub>2</sub> /kg)	Specific Extinction (K <sub>232</sub> )	Specific Extinction (K <sub>270</sub> )
Control	1.01±0.00 <sup>at</sup>	17.73±0.20 <sup>b</sup>	2.49±0.00 <sup>g</sup>	0.41±0.00 <sup>f</sup>
C.B.E.-I	0.76±0.03 <sup>d</sup>	7.94±0.52 <sup>f</sup>	3.76±0.05 <sup>c</sup>	2.68±0.00 <sup>a</sup>
C.B.E.-II	0.85±0.04 <sup>b</sup>	10.19±0.37 <sup>d</sup>	3.56±0.00 <sup>d</sup>	2.27±0.00 <sup>b</sup>
Montmorillonite	0.44±0.01 <sup>e</sup>	19.38±0.35 <sup>a</sup>	3.02±0.02 <sup>f</sup>	0.31±0.00 <sup>g</sup>
Halloysite-AA	0.92±0.00 <sup>b</sup>	7.83±0.35 <sup>e</sup>	3.99±0.00 <sup>a</sup>	1.68±0.00 <sup>c</sup>
Dowex	0.80±0.00 <sup>c</sup>	8.47±0.33 <sup>e</sup>	3.98±0.00 <sup>b</sup>	0.49±0.00 <sup>e</sup>
Ti-MOF	0.68±0.01 <sup>d</sup>	12.50±0.16 <sup>c</sup>	3.28±0.02 <sup>e</sup>	0.55±0.00 <sup>d</sup>

\*Small uppercase letters indicate the statistically significant differences within each column for the mean±SD values calculated from four determinations by one-way ANOVA and Tukey's test ( $p \leq 0.05$ ). C.B.E.: commercial bleaching earth

FFA reduction capacity of montmorillonite treated sample (0.44%) was the best among all, and followed by Ti-MOF treated (0.68%) sample. Halloysite-AA treated sample had higher FFA (0.92%) among all samples. The lowest PV was with halloysite-AA treated sample (7.83 meq O<sub>2</sub>/kg), followed by C.B.E.-I (7.94 meq O<sub>2</sub>/kg), and Dowex (8.47 meq O<sub>2</sub>/kg), respectively. The specific extinction values indicated some enhancement to prove that some secondary oxidation took place during the treatments, and precautions suggested as previously.

Comparison of the 4 selected adsorbents with the commercial bleaching earth under the same conditions proved that Halloysite-AA and Dowex had certain potentials to be improved for oil bleaching applications.

### Comparison of the Adsorbent Mixture with Commercial Bleaching Earths

To compare the commercial bleaching earths (C.B.E.s) with the adsorbent mixture we prepared by mixing equal proportions of natural montmorillonite, halloysite-AA, Dowex, and Ti-MOF, the same experiments were completed and the results are collected in Table 6. The purpose was to include individual beneficial effects of the 4 selected adsorbents together, and to compare it with the C.B.E.s. The L value of adsorbent mixture was the lowest (27.99), unfortunately. Clearly this mixture enhanced some turbidity components (Figure 6). This might also be due to inefficient filtering of the small particles present in the mixture. Obviously C.B.E.-I yielded the most bright sample. While C.B.E.s reduced  $-a^*$  value compared to control (-1.35), the adsorbent mixture enhanced it to -1.41 value. Clearly after adsorbent mixture treatment, level of greenness

enhanced. This could be due to some removal of red pigments, since  $a^*$  value indicates the proportional changes of redness and greenness. Similar trend was evident with the  $b^*$  values, and adsorbent mixture treatment resulted significantly higher (6.04)  $b^*$  value than others (3.75 and 3.03). Since  $+b^*$  value indicate level of yellowness, clearly adsorbent mixture was ineffective in removing yellow pigments. Overall, adsorbent mixture was not as good as the C.B.E.s in correcting oil color values. The oil loss value of

the adsorbent mixture was also the highest among all, showing another negative aspect of it. The FFA value and PV of the adsorbent mixture were lower than the C.B.E.s, indicating that the mixture was more effective in removing free fatty acids and peroxides from the oil. Specific extinction values were also proved this finding (Table 6). Obviously, the adsorbent mixture was not worked as expected to be better an adsorbent for bleaching than the commercial earths.

Table 6. The color and weight loss values, and chemical parameters measured for the oil samples treated with the prepared adsorbent mixture and commercial bleaching earths.

	L Value	$a^*$ Value	$b^*$ Value	Weight Loss (%)
Control	$30.28 \pm 0.44^{b*}$	$-1.35 \pm 0.07^a$	$6.23 \pm 0.27^a$	—
Adsorbent				$18.49 \pm 0.12^a$
Mixture	$27.99 \pm 0.05^d$	$-1.41 \pm 0.03^a$	$6.04 \pm 0.09^a$	
C.B.E.-I	$33.07 \pm 0.11^a$	$-1.22 \pm 0.00^b$	$3.75 \pm 0.03^b$	$14.29 \pm 0.13^c$
C.B.E.-II	$30.11 \pm 0.02^c$	$-1.02 \pm 0.00^c$	$3.03 \pm 0.01^c$	$15.74 \pm 0.03^b$
	Free Fatty Acidity (% Linoleic)	Peroxide Value ( $\text{meqO}_2/\text{kg}$ )	Specific Extinction ( $K_{232}$ )	Specific Extinction ( $K_{270}$ )
Control	$1.01 \pm 0.00^{a*}$	$17.73 \pm 0.20^d$	$2.49 \pm 0.00^d$	$0.41 \pm 0.00^d$
Adsorbent			$3.36 \pm 0.01^c$	
Mixture	$0.92 \pm 0.00^c$	$18.33 \pm 0.17^c$		$0.57 \pm 0.02^c$
C.B.E.-I	$0.94 \pm 0.03^b$	$20.1 \pm 0.18^b$	$3.88 \pm 0.02^a$	$2.56 \pm 0.02^a$
C.B.E.-II	$1.02 \pm 0.01^a$	$23.43 \pm 0.17^a$	$3.67 \pm 0.02^b$	$2.26 \pm 0.01^b$

\*Small uppercase letters indicate the statistically significant differences within each column for the mean  $\pm$  SD values calculated from four determinations by one-way ANOVA and Tukey's test ( $p \leq 0.05$ ). C.B.E.: commercial bleaching earth

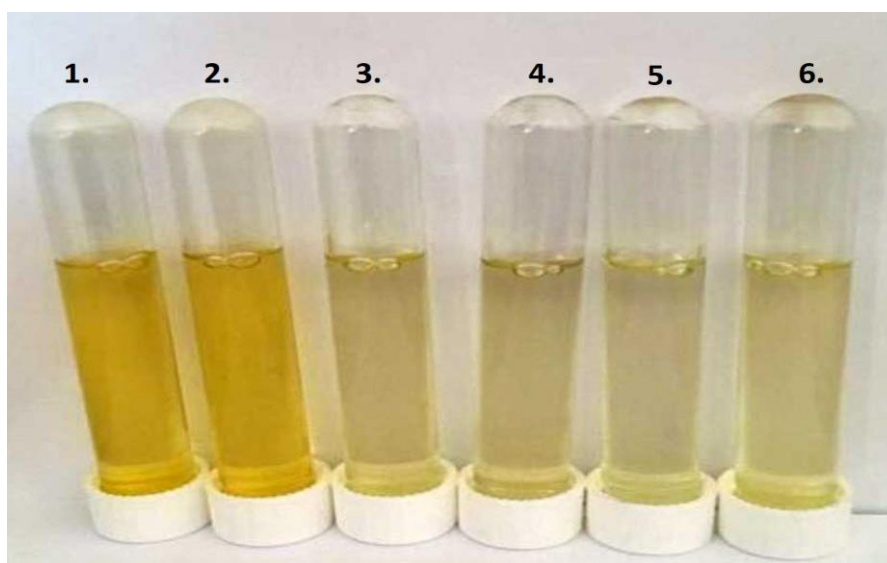


Figure 6. The oil samples treated with adsorbent mixture and commercial bleaching earths (1. Adsorbent mixture-I, 2. Adsorbent mixture -II, 3. C.B.E.-I-1, 4. C.B.E.-I-2, 5. C.B.E.-II-1, 6. C.B.E.-II-2).



## CONCLUSIONS

The aims of this study were to screen and select some potential adsorbent materials for oil bleaching activity. There were four main groups tested. In the first group, 6 different natural clays were screened after adsorbent treatment and oil color, weight loss, FFA, PV, and specific extinctions measurements. Natural montmorillonite was elected the best one among the six clays. In the second group, the same six natural clays were acid-activated and tested in the same way. From this group, acid-activated halloysite yielded the most promising results. In the third group, 10 synthetic adsorbent materials were tested, and Dowex was selected based on its performance. Lastly, 8 different metal-organic frameworks (MOF) were screened and Ti-MOF was chosen. Then, the selected 4 potential adsorbents (natural montmorillonite, halloysite-AA, Dowex, and Ti-MOF) were tested against two commercial bleaching earths (C.B.E.) under the same condition to possibly observe their potential oil bleaching ability. Acid-activated halloysite and Dowex had certain potential to be enhanced with further studies. In the last part of this study, an adsorbent mixture of the selected 4 adsorbents with equal proportions were prepared and tested against the C.B.E.s. Unfortunately, this mixture was not yielded better results. Consequently, mixing selected adsorbents could not produced a better new adsorbents. The literature is lack for halloysite for oil bleaching studies, and this study firstly put this potential to be further studied. Different modification techniques, or acid-activations with different acids at various concentrations and durations must be searched to improve oil bleaching capacity of halloysite. Further, Dowex could be studied for the same purpose in upcoming studies. Although Ti-MOF was selected among the 8 materials, more new MOFs could be synthesized and tested for this purpose, as an open research challenge. More researches are expected to find out or to create new adsorbent materials for optimum crude vegetable oil bleaching.

**CONFLICT OF INTERESTS:** The author declares that for this article they have no actual, potential, or perceived conflict of interests.

## AUTHOR CONTRIBUTIONS

Manuscript writing: Emin Yılmaz, planning the experiments: Emin Yılmaz and Elif Yücepete, laboratory experiments: Elif Yücepete, the idea of the study: Emin Yılmaz, designing the study: Emin Yılmaz, editing original draft: Emin Yılmaz. All authors have read and approved the final manuscript.

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