



Bleaching Process of Sunflower Oil by Using Bentonite Activated with Different Chemical Substances

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In this research, activation process took place in different times by using different concentration of H₂SO₄, HCl and H₃PO₄ solutions were used to define the proper acid activation circumstances for neutral bentonite clay from Thrace region. Moreover, the acid active clays were used in bleaching of crude sunflower oil. Before and after the bleaching process, absorbance values of sunflower oil had been noted and with the help of the information the bleaching efficiency of the adsorbents was calculated and compared with commercial clay. In the process of bleaching crude sunflower oil with the activated clays and the commercial clay, adsorbent concentration, the heat treatment, the time's effects on bleaching efficiency were analyzed. Optimum adsorbent concentration, temperature and time are found as 1 %, 80 °C, 20 min, respectively. For the bleaching process which contained acid activated clay and commercial bleaching earths, adsorption kinetics, thermodynamics and isotherms were analyzed. To sum up, in the chosen time and the concentration, it has been found out that clay activated with H₂SO₄ and HCl has better values than commercial clay.

Keywords: Acid activated bentonite, Bleaching, Sunflower oil.

INTRODUCTION

Crude oils obtained with pressing, solvent extraction or supercritical fluid extraction, in addition to triglycerides, contain minor components such as diglycerides, monoglycerides, phospholipids, color pigments (chlorophylls, carotenoids, gossypol *etc.*), free fatty acids, odourous substances, natural antioxidants *etc.* Either chemical or physical refining applied to crude oils for purifying and giving consumable properties to oils without any detriment of triglycerides and tocopherols¹. In edible oil refining, the bleaching treatment is a critical step and the conditions for bleaching step depend on the type of crude oil and its quality. The main principle of bleaching is described as; adsorption of the pigments and other unwanted compounds in oils with proper adsorbent and following with the filtration of the adsorbents from vegetable oils. In bleaching process, neutral clays, activated earths, active carbons and synthetic silicates are used as adsorbents². The activated bleaching earths indicate higher activity than natural clays, because their specific surface area increased with acid treatment^{3,4}.

Bleaching is based on physical adsorption, chemical adsorption, ion exchange and chemical decomposition of the pigments and other impurities on the bleaching earth's surface^{3,5}.

Theoretically, Freundlich equation is widely used to describe vegetable oil bleaching by adsorption⁶. Also previous studies show that Freundlich equation is more suitable than

Langmuir equation to clarify bleaching process of vegetable oils⁶⁻⁸. Freundlich equation is described as $x/m = K \cdot c^n$, where x ; adsorbed pigments amount, m ; adsorbant amount (%), c ; not adsorbed pigment amount, K and n ; Freundlich constants^{9,10}. K value shows the bleaching power of the adsorbent, therefore n value gives the adsorption characteristic of the earth².

Despite many studies, no relationship has been defined between the performance of acid activated clay and the composition or other properties of original clay. Therefore, clay has to be specifically activated and tested for its performance depending to the vegetable oil type.

Turkey has rich bentonite reserves in different regions and every bentonite reserves have various properties. The studies about activated bentonite production are not sufficient. With this purpose, the utilization of bentonite obtained from Thrace region was investigated for bleaching of crude sunflower oil and compared with commercial bleaching clay.

EXPERIMENTAL

Crude sunflower oil used for this work was provided by Öztürkler Company (Turkey). Neutral clay and the commercial clays were provided by local producer. Neutral clay was obtained from Malkara town (latitude 40° 50' 30" N, longitude 26° 54' 09" E and altitude 250 m) in the West side of Tekirdag, in Turkey.

All other chemicals used were of Analytical Reagent grade and purchased from Tekkim (Turkey) and Merck (Germany).

Acid activation: 2 N, 4 N and 8 N acidic solutions were prepared with distilled water from H₂SO₄ (d: 1,84 g/mL, 96 g H₂SO₄/100 mL), HCl (d: 1,15 g/mL, 37 g HCl/100 mL) and H₃PO₄ (d: 1,71 g/mL, 85 g H₃PO₄/100 mL). Grinded neutral clays and acid solutions were treated by ratio weight per volume (w/v) 0,1 g/mL in flask under mechanical stirring. Acid activation was carried out according to wet process at boiling point of the slurry for 1, 3 and 5 h¹¹. After activation, the slurries were filtered under vacuum with Whatman No.1 and the solids were washed with distilled water until pH 4,5-5,0. Then solids were dried in oven at 60 °C for 24 h and grounded in porcelain mortar. The obtained acid activated clays were stored in desiccator during the experiments.

Bleaching: Bleaching experiments were carried out with acid activated clays, commercial clay and neutral clay at atmospheric pressure. 100 g of crude sunflower oil was weighed out into a 250 mL conical flask and heated to 70 °C in thermostated water-bath shaker (Nuve ST 402). For each bleaching operation, 1 g clay was added to the crude sunflower oil at desired temperature and then agitated at 150 rpm for 20 min. After bleaching, the solids were filtered from the bleached oils with Whatman No. 1 under vacuum then residual clays were separated by centrifugation (Awel Centrifugation C12) at 3500 rpm for 20 min. The obtained bleached oils were placed in dark colored bottle and stored in dark place.

For determination of bleaching efficiency, the color of crude and bleached sunflower oils were measured by UV-spectrophotometer (Mecasys Optizen POP) at 450 nm. Bleaching efficiencies were calculated by using the following formula^{3,12}.

$$\text{Bleaching efficiency (\%)} = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

A₀ : Absorbance value of the crude sunflower oil

A : Absorbance value of the bleached sunflower oil

RESULTS AND DISCUSSION

Bleaching efficiency: Bleaching efficiency results for acid activated clays were calculated and given in Table-1. The results showed that clays activated with 4 N H₂SO₄ for 5 h give higher bleaching efficiency. The results for H₂SO₄ (concentration: 4 N, contact time: 5 h), HCl (concentration: 4 N, contact time: 3 h) and H₃PO₄ (concentration: 8 N, contact time: 5 h) are 68.65, 62.41 % and 49.35 %, respectively. Generally, when the results were discussed, bleaching efficiencies were decreased in higher concentrations than 4.0 N. In low concentrations of H₂SO₄ (1-2 N) solution dissolves the basic Na⁺ and Ca²⁺ ions occupying the interlayer space as well as extra framework mineral impurities present in the voids between the clay platelets¹³. Treatment with relatively concentrated acid results in the broadening of the slits or voids between the layers because of depleted cation concentration and interlamellar attraction as well as destruction of octahedral layer. There are indications of acid attack on the tetrahedral silica layer at the initial stages, therefore free silica amount increases at higher acid concentrations¹¹. This was attributed to the fact that the increase in the surface area is due to the formation of silica but the surface area of H-clays

remains almost constant over strong acid leaching and silica has very poor bleaching power of vegetable oils¹⁴.

Bleaching efficiency of commercial clay was calculated as 59.51 %. When compared with commercial clay and acid activated clays, bleaching efficiency of clays activated with H₂SO₄ and HCl was higher than commercial clay 9.14 %, 2.90 %, respectively. On the other hand, bleaching efficiency of clay activated with H₃PO₄ was lower than commercial and the other acid activated clays.

TABLE-1
BLEACHING EFFICIENCIES OF DIFFERENT
ACID ACTIVATED CLAYS (%)

Activation parameters	H ₂ SO ₄ (%)	HCl (%)	H ₃ PO ₄ (%)
2 N 1 h	25.83	30.48	18.50
2 N 3 h	33.96	57.33	21.62
2 N 5 h	43.83	54.38	23.95
4 N 1 h	42.45	44.85	24.50
4 N 3 h	57.76	62.41	30.67
4 N 5 h	68.65	61.25	39.19
8 N 1 h	50.75	52.98	28.30
8 N 3 h	56.75	55.73	37.59
8 N 5 h	63.05	55.88	49.35

The effect of adsorbent concentration on bleaching efficiency was studied at 70 °C, 150 rpm stirring rate and 20 min bleaching time. Acid activated clays that reached maximum bleaching efficiencies and the commercial clays were studied for this purpose and the results shown in Fig. 1. Bleaching efficiency increased with the increase in adsorbent concentration. Increase in adsorbent concentration 0.25 to 2 %, bleaching efficiencies for H₃PO₄, commercial clay, HCl and H₂SO₄ were increased from 26.18 to 58.26 %, from 30.19 to 64.40 %, from 30.97 to 73.31 %, from 29.68 to 75.37 %, respectively. This situation is explained by increasing of adsorbent surface area and therefore increasing of the amount of active centers with increasing the adsorbent amount. However, increases of the bleaching efficiencies of each adsorbent were higher on the range 0.25-1.0 % adsorbent concentration than on the range 1.0-2.0 %. Hence 1.0 % adsorbent concentration was determined as optimum for chosen bleaching conditions.

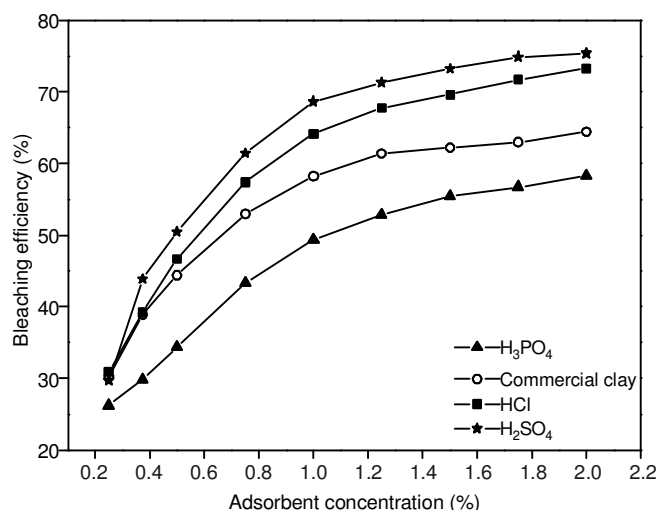


Fig. 1. Effect of adsorbent concentration on bleaching efficiency

The effect of temperature on bleaching efficiency for 4 clays was studied at 1.0 % adsorbent concentration, 150 rpm stirring rate and 20 min bleaching time. It is observed that the bleaching power increases with the increase in temperature from 50 to 80 °C for all the adsorbent used herein but no significant increases on bleaching efficiency were observed with the increase in the temperature from 80 to 90 °C. At 80 °C, bleaching efficiencies for H₂SO₄, HCl, commercial clay and H₃PO₄ were measured 70.63, 67.13, 62.95 and 56 %, respectively (Fig. 2).

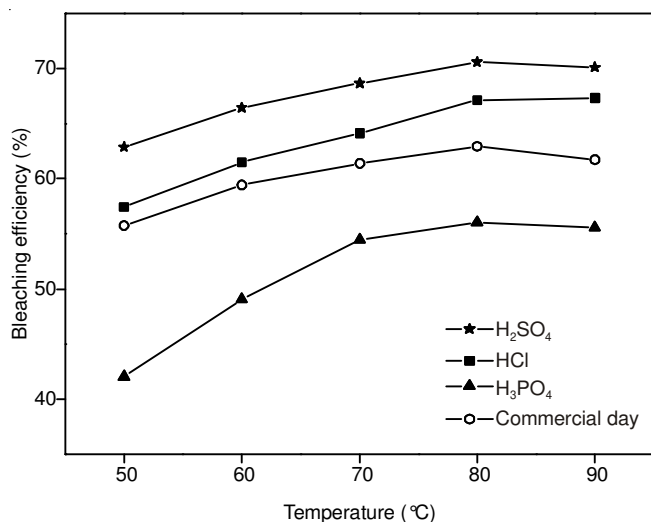


Fig. 2. Effect of temperature on bleaching efficiency

The effect of time on bleaching efficiency for 4 clays was studied at 1 % adsorbent concentration, 150 rpm stirring rate and 70 °C bleaching temperature. The effect of time is shown in Fig. 3. It is observed that the bleaching efficiency increases with the increase in time for all clays used herein. Especially, for H₂SO₄, HCl, commercial clay in first 20 min of bleaching, efficiencies increased significantly, after 20 min these increases in the bleaching efficiencies are very weak. This situation is explained by bounding pigments rapidly to free active centers of the adsorbent surface at the beginning of the bleaching. Afterward, the bleaching efficiencies increased slowly are explained by repulsive force between bounded and free pigments. For 3 clays, the adsorption balance time was determined as 20 min (Fig. 3).

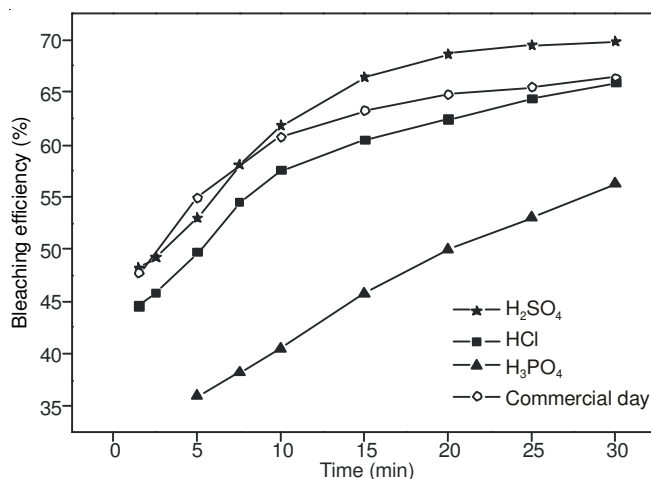


Fig. 3. Effect of time on bleaching efficiency

Adsorption isotherms: Adsorption is a surface phenomenon which depends on the specific affinity between solute and adsorbent. Theoretically, Freundlich equation is widely used to describe vegetable oil bleaching by adsorption⁶. The Freundlich equation is generally expressed with the following formula^{9,10}. For a given temperature, the Freundlich equation relates the specific adsorption (x/m), *i.e.*, the amount of substance adsorbed per unit of adsorbent weight, to residual solute concentration, at equilibrium¹⁵.

$$\frac{x}{m} = Kc^{1/n} \quad (2)$$

where x is the amount of adsorbed material, m the amount of adsorbent (g), c the amount of residual dissolved material (equilibrium concentration) and K and n are constants unrelated to the amounts of solute and adsorbent. The logarithmic form of the eqn. (2) becomes eqn. (3)¹⁶:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \quad (3)$$

Since absorbance results are taken in all experiments for the bleaching process, the amount of pigment adsorbed (X) and the residual amount at equilibrium (X_e) can be obtained from the following equations:

$$X = \frac{A_0 - A_e}{A_0} \quad (4)$$

$$X_e = \frac{A_e}{A_0} \quad (5)$$

where A_0 is the absorbance of the crude sunflower oil at 450 nm and A_e is the absorbance of the oil at equilibrium at 450 nm. Thus, by writing X_e instead of the residual concentrations of substance in the solution at equilibrium, c . Eqn. 3 can be rearranged as follows⁶:

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log X_e \quad (6)$$

A plot of (x/m) versus X_e on log-log scale for various initial concentrations is found to be linear, indicating the applicability of the classical adsorption isotherm to this adsorbate-adsorbent system¹⁶. The values of $\log K$ and $1/n$ can be obtained from the intercept on the y-axis and the slope of the linear line⁶. The typical plots for all bleaching clays are given in Fig. 4.

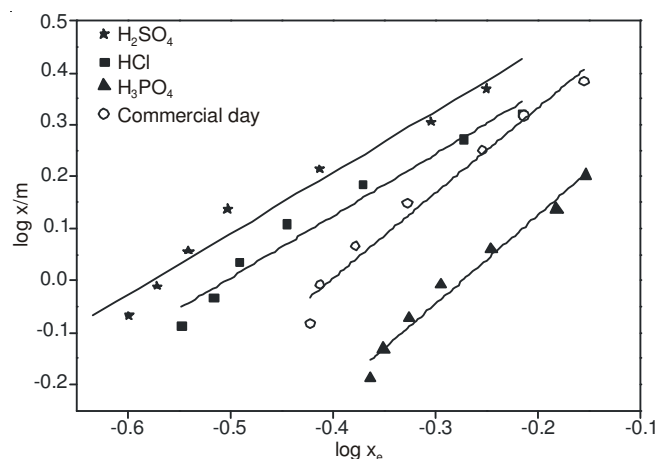


Fig. 4. Isotherm graphics of sunflower oil bleaching with H₂SO₄, HCl, H₃PO₄, commercial clay

The value K is an adsorption capacity coefficient for the system related to bonding energy and describing the amount of substances absorbed onto bentonite for the unit equilibrium concentration. When Freundlich constant K for bleaching earth is high, it means that it absorbs more pigment and that adsorbent would be consumed less in bleaching process¹⁶. The obtained K and n parameters from the Freundlich isotherm equation for all clays are presented in Table-2. From the results examined, clays treated with 4 N H_2SO_4 for 5 h give the high K value as 4.7654 from the other clays. According to K constants for clays, activated clay with H_2SO_4 is expected to be consumed less in bleaching process than the other clays. n value is interested with the adsorption driving force and the adsorbent site energy distribution⁶. And also the adsorbent having higher n value would remove more pigments at the beginning of the bleaching. n values between 1 and 10, represent the adsorption favorable¹⁶. From the results of present study, n values were higher than 1 and related with the information mentioned above, n values show that our adsorption process is favorable.

TABLE-2
FREUNDLICH ISOTHERMS, RATE CONSTANT
AND THERMODYNAMIC PARAMETERS OF
ACID ACTIVATED CLAYS

Bleaching clays	Freundlich isotherm			Rate constants	Thermodynamic parameters	
	K	n	R^2	k (dk ⁻¹)	ΔH_a (kJ/mol)	ΔS (J/mol K)
H_2SO_4	4.7654	1.1738	0.9816	0.02888	10.967	38.40
HCl	3.9781	1.1863	0.9835	0.02196	12.854	42.30
H_3PO_4	2.9319	1.7006	0.9876	0.01575	18.166	56.40
Commercial clay	4.5793	1.6366	0.9877	0.02073	9.329	30.90

Adsorption kinetics: For kinetic studies, adsorption rate constant was calculated by Beer-Lambert's law. For this law as seen at the following, adsorption is proportional to the concentration¹⁵.

$$\ln \frac{A}{A_0} = -kt \quad (7)$$

where A is the absorbance of the pigments at time t and A_0 is the absorbance of the pigments at time $t = 0$. The value of rate constant, k was calculated from the slope of the curves by plotting of $\ln A/A_0$ vs. t . The plotting for all adsorbents given in Fig. 5 and calculated k values were presented in Table-2. As seen from Table-2, the k value of clays activated with H_2SO_4 and HCl is higher than commercial clay's. These results show that these clays can be used as a suitable bleaching earth for bleaching of sunflower oil.

Thermodynamic parameters of adsorption: Thermodynamic parameters for adsorption can be calculated by van't Hoff equilibrium equation as seen at the following:

$$\ln K_e = -\frac{\Delta H_a}{RT} + \frac{\Delta S}{R} \quad (8)$$

$$K_e = \frac{A_0 \times A_e}{A_0} \quad (9)$$

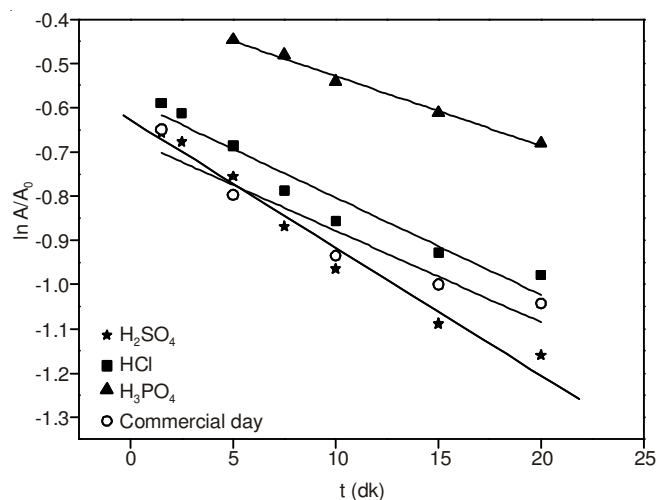


Fig. 5. Kinetic graphics of sunflower oil bleaching with H_2SO_4 , HCl, H_3PO_4 , commercial clay

where T is the temperature, ΔH_a is the enthalpy of adsorption, ΔS is the entropy of adsorption, R and K_e are constants. The equilibrium constant, K_e , was obtained from the eqn. (9). The plot of $\ln K_e$ versus $1/T$ gives thermodynamic parameters (Fig. 6). The values of ΔH_a and ΔS can be obtained from the slope of the curve and the intercept on the y-axis, respectively⁶. The obtained ΔH_a and ΔS parameters for all activated clays are also presented in Table-2. If the parameters in Table-2 are considered, it is seen that the enthalpy parameters are positive. Positive enthalpy parameters indicate that the bleaching process is endothermic. Since the enthalpy value is less than 20 kJ/mol, the forces between adsorbent and the pigments in sunflower oil are weak, like van der Waals forces^{7,17}. And also positive values of entropy show increase randomness at the solid-solution interface during the oil bleaching⁶. From present results, we can say that the bleaching process of sunflower oil with acid activated clays and the commercial clay is endothermic and also entropy is a driving force for this process.

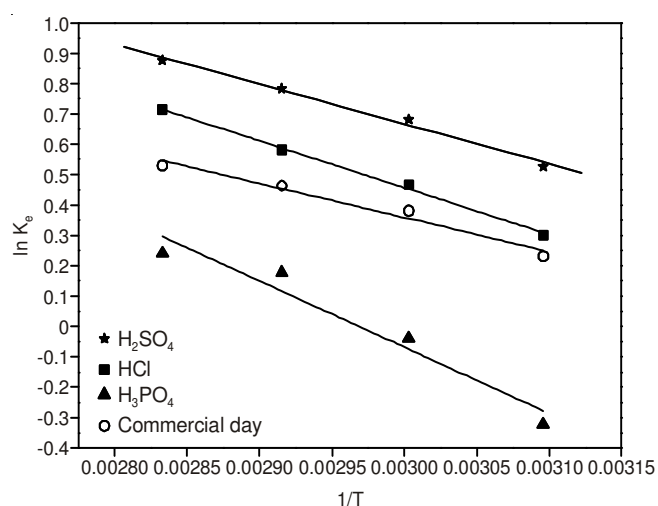


Fig. 6. Thermodynamic graphics of sunflower oil bleaching with H_2SO_4 , HCl, H_3PO_4 , commercial clay

The present study showed that H_2SO_4 (concentration: 4 N, contact time: 5 h), HCl (concentration: 4 N, contact time: 3 h) activated clays have better bleaching efficiencies than commercial

clay. Optimum process conditions of sunflower oil bleaching for acid activated clays and commercial clay were investigated. Optimum adsorbent concentration, temperature and time were found as 1 %, 80 °C, 20 min, respectively. From the thermodynamic, kinetic and isotherm studies, neutral bentonite clay from Thrace region activated with H₂SO₄ and HCl can be used as a suitable bleaching earth in the bleaching process of sunflower oil.

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