Al-Pillared Clay for Cottonseed Oil Bleaching: An Optimization Study

Mustafa Oguzhan Caglayan*, Suleyman Kafa, and Nevzat Yigit
Cumhuriyet University, Chemical Engineering Department, 58140, Sivas, Turkey

ABSTRACT: In this study, Al-pillared white bentonite (Ordu-Unye, Turkey) was used for cottonseed oil bleaching. Pillaring process parameters were optimized in terms of bleaching efficiency as the bleaching capacity of cottonseed oil. The initial cation concentration, hydrolyzing agent ratio, and thermal treatment temperature were chosen as major process parameters. Pillared clays were characterized by FTIR and differential thermal analysis. The bleaching efficiency of bentonite increased from 11.8 to 17.5% by acid activation and to 33.5% by further Al pillaring. The optimal pillaring process conditions for cottonseed bleaching were an initial concentration of $AlCl_3$ of 0.5 M, a OH^-/Al^{3+} molar ratio of 0.3, and a thermal treatment temperature of 700°C.

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KEY WORDS: Al-pillared clay, bleaching, cottonseed oil.

Acid-activated clays [i.e., activated bleaching earths (ABE)], which are traditionally activated by an inorganic acid, are widely used to bleach edible oils. Montmorillonitic clays naturally have the crystal lattice distortion to contain active sites and have a high cation-exchange capacity (CEC). Such clays are generally modified by applying a known type of activation (i.e., acidic, cationic, anionic, organo-cationic, or thermal) to form new active sites and/or to reinforce existing ones. In the acid-activation mechanism (e.g., dry or wet process), the free protons formed attack the –OH groups that exist in tetrahedral and octahedral layers to increase the number of Lewis and Brønsted acid sites over the lattice (1).

β-Carotene, a red pigment, is the major colorizing agent in cottonseed oil. It has a slightly alkaline character and a relatively high aspect ratio (i.e., rodlike). Based on the size and acidity of β-carotene, acidic adsorbents having mezopores are needed to remove this species from cottonseed oil by the bleaching process (2). However, the adsorption capacities of naturally occurring low-grade bentonites cannot be increased to levels as high as those of commercial products by acid activation alone (e.g., Tonsil; Südchemie, Hilden, Germany). For these types of clay minerals, combined activation methods (i.e., a combination of acid and organo-cationic activation with further thermal treatment) may result in better oil bleaching capacities compared with the traditional activated clays.

A number of studies appear in the literature about applying almost all types of activated clays to cottonseed oil bleaching (3). Characteristic differences between β-carotene and α-chlorophyll (the major colorants in cottonseed and olive oil, respectively) have motivated the development of cheaper and more active adsorbents for bleaching. Silicon-based adsorbents, hectorite-based activated clays, and organo-cationic clays are the groups of adsorbents most often studied for removing colorants from oils (4). In the last decades, catalyst researchers have investigated new approaches for developing heterogeneous (clay-based) catalysts by using clay minerals as a substrate. Pillaring clay (bentonite, hectorite, etc.) by altering the basal spacing with polycations of group IVB (Ti, Zr), group VB (V), group VIIB (Fe, Ni, Pd), groups I and IIB (Cu, Zn), or group IIIA (Al) cations have been examined the most. The pillared clays have been shown to have higher surface areas with selective activity. The mechanism of the pillaring process involves two subprocesses: cation exchange and further stabilization. The process can be performed either by inserting initially formed polycations into the basal space by a cation-exchange mechanism or by forming polycations *in situ* at CEC sites of the layered clay structure. These hydrated polycation pillars can be stabilized by severe heat treatment (e.g., at over 400°C) (5). These types of structures, called pillared clays (PILC), and Keggin-type polycations are the inorganic pillaring components most widely studied in the literature (6–9). Al_{13}-polycations can be formed by forced hydroxylation of either $AlCl_3$ (with or without crystalline H_2O) or $Al(NO_3)$ salts by reacting them with a hydrolyzing agent (i.e., NaOH) in aqueous solution with or without a buffer (8,10,11). Although the components vary widely in their clay-pillaring properties, they are generally inorganic cations. A few studies can be found in the literature concerning organic pillars (12).

Al-pillared clays having large surface areas with high catalytic activity have been reported previously (13). These higher surface area (>200 m^2/g) clays could be intended for use in bleaching vegetable oils.

In this study, preactivated (i.e., acidic and thermal) clay was pillared with Al-polycations by investigating the effect of major parameters assumed in the pillaring process (i.e., hydrolyzing agent ratio, initial cation concentration, and thermal treatment temperature). Al-pillaring conditions and the effects of major parameters on the bleaching process were optimized by comparing the bleaching efficiencies of each adsorbent type as a measure of the activity of the clay.

EXPERIMENTAL PROCEDURES

Preactivation of bentonite. Original white bentonite (Ordu-Unye, Turkey) having a CEC of 103 mequiv/100 g clay (denoted as "O"), which was dried and crushed to less than 63 μm, was activated without purification (i.e., organic compounds and

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*To whom correspondence should be addressed at Hacettepe University, Chemical Engineering Department, Beytepe, Ankara, 06800, Turkey. E-mail: oguzhanc@hacettepe.edu.tr soluble salts removed) by 2 M H_2SO_4 at a 0.10 clay/solution (g/mL) ratio for 1.0 h at the boiling temperature of the slurry. The original chemical content of sample O is shown in Table 1. The ABE samples were washed with distilled water to remove excess ions until no change in conductivity was observed in the remaining washing water. All clay samples were stored at 105°C.

Pillaring process. This process involves forming polycations *in situ* at the CEC sites of a layered clay structure by hydrolyzing a cation source by NaOH. In this process, a hydrolyzing agent is slowly poured into the cation source–clay slurry without buffer, with continuous stirring to prevent local pH changes (the preferred pH is between 4 and 6). By this route, the cations/polycations will migrate to the basal space by means of cation exchange and the clay slurry with $AlCl_3$ solution (pH between 3 and 5) will maintain the pH of the slurry by buffering so that relatively more hydrolyzing agent can be added to the solution. This pillaring route is finalized by stabilizing the hydrated pillars *via* severe heat treatment (e.g., over 400°C).

In this study, the pillaring process was examined by optimizing the initial $AlCl_3$ concentration (cation source concentration), OH^-/Al^{3+} molar ratio (hydrolyzing agent ratio), and further heat treatment temperature (oxide pillar-forming temperature). The minor parameters assumed in the pillaring process [forced hydroxylation (i.e., ion exchange) temperature (25°C), NaOH flow rate (20 mL/min), agitation speed (1,000 rpm), and duration of the hydrolyzing reaction (1 h)] were fixed during the overall optimization processes.

Optimizing the OH^-/Al^{3+} ratio. The hydrolyzing agent/cation source molar ratio (i.e., OH^-/Al^{3+} molar ratio) was assumed to be a major factor directly affected by the system pH, which in turn was affected by the solubility of the polycations. Hence, the initial $AlCl_3$ concentration was maintained at 0.5 M (equivalent to 5 mequiv Al^{3+}/g clay, approximately five times the CEC) during optimization. A 25-mL solution of NaOH (at 25°C) was slowly poured into the slurry (at 25°C) of 2.5 g clay and 25 mL $AlCl_3$ solution (i.e., a ratio of 0.1 g clay/mL solution) by means of a peristaltic pump. To prevent the local precipitation of Al^{3+} as a hydroxide salt, the slurry was stirred continuously during the time course of the addition of the hydrolyzing agent. Stirring was maintained for another hour to allow for complete ion exchange. The OH^-/Al^{3+} molar ratio was brought to the specified value at a total solution volume of 50 mL (final solution volume). Any excess ions were removed by washing and subsequently centrifuging the clay samples. The polycation-pillared clays were oxidized in an atmospheric furnace at 500°C for 12 h. The oxidized PILC were stored at 105°C.

TABLE 1
X-Ray Fluorescence Analysis (dried material) of White Bentonite[a]

Element	%	Element	%
SiO_2	71.5	SO_3	0.06
Al_2O_3	15.1	K_2O	1.10
MgO	2.66	TiO_2	0.13
CaO	1.45	Fe_2O_3	0.87
Na_2O	0.52	Ignition loss	6.63

[a]The X-ray fluorescence analysis was conducted using a Philips PW2400 X-ray spectrometer (Philips, Almelo, The Netherlands). The white bentonite was obtained from Ordu-Unye, Turkey.

Optimizing the initial concentration of $AlCl_3$. Initial $AlCl_3$ concentration optimization studies were performed at a range of 0–2.0 M $AlCl_3$. In this part of the study, the OH^-/Al^{3+} molar ratio was fixed at the optimal value that had been determined from the OH^-/Al^{3+} molar ratio optimization study. Other fixed variables were chosen as the first part of the optimization study: The clay/$AlCl_3$ ratio was 0.1 g clay/mL $AlCl_3$ solution in a 25-mL $AlCl_3$ solution; the volume of NaOH added was 25 mL (the overall volume after addition was 50 mL); and the system temperature was 25°C. Following the cation-exchange and excess ion removal processes, the PILC samples were oxidized at 500°C and stored at 105°C for bleaching experiments.

Optimizing the oxidation temperature. The effect of oxidation temperature on the pillaring process was studied between 100 and 800°C in an atmospheric furnace for 12 h. The minor variables were fixed as had been applied previously except for the OH^-/Al^{3+} ratio and the initial $AlCl_3$ concentration. The latter two major factors were fixed at their determined optimal values.

Determination of the optimal conditions for cottonseed oil bleaching. The effect of the selected parameters on the pillaring process for adsorbents in the bleaching process was determined by using prepared adsorbents for alkali-refined cottonseed oil bleaching. The bleaching process was conducted at a ratio of 0.5% clay/oil (mass/vol), under 0.8 mbar vacuum, at 110°C for 0.5 h. The bleaching capacity was determined by colorimetric analysis at 420 nm with a spectrophotometer (UV1601; Shimadzu, Kyoto, Japan) using 1-cm pathlength disposable polymethylmethacrylate cuvettes, and the bleaching ratio and bleaching efficiency were calculated as differences in terms of absorbance at 420 nm by the following relation:

$$\text{BE\%} = \frac{(A_{\text{unbleached oil}} - A_{\text{bleached oil}})}{A_{\text{unbleached oil}}} \times 100 \qquad [1]$$

Bleaching efficiency was reported as a percentage (BE%), with the SD obtained from four discrete replications (clay sample preparation and bleaching).

Determination of structural changes. Structural changes in the clay samples that arose during the pillaring process were determined by FTIR (FTIR-8000; Shimadzu) and differential thermal analysis (DTA) (TG50; Shimadzu). FTIR samples were prepared as KBr pellets, and IR spectra were then recorded between the wavenumbers of 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}. The DTA analyses, against α-Al_2O_3 as a reference, were carried out to determine the temperature range of dehydroxylation and crystal structure change reactions in the clay samples at a 10°C/min heating rate.

RESULTS AND DISCUSSION

The optimal process parameters of pillared clay intended for use as an adsorbent in bleaching alkali-refined cottonseed oil were determined by examining the major parameters.

Effect of the OH^-/Al^{3+} molar ratio. OH^-/Al^{3+} molar ratios between 0 and 2.0 were selected to achieve the optimal bleaching efficiency ratio at an initial Al^{3+} concentration of five times the $CEC_{original}$ (i.e., 0.5 M Al^{3+}). The bleaching efficiency value of the original clay, 11.8 ± 0.7%, was increased to 17.5 ± 0.7% by acid activation with 2 M H_2SO_4. As shown in Figure 1, the bleaching efficiency increased to 18.6 ± 0.7% at 0.5 M $AlCl_3$ without the NaOH solution (i.e., the OH^-/Al^{3+} ratio was 0). Only by inserting Al^{3+} cations was the observed bleaching efficiency increased to 6.3%. By increasing the OH^-/Al^{3+} ratio, the BE% increased to a maximum at a OH^-/Al^{3+} ratio of 0.3, after which the BE% value decreased. Over the 2.0 OH^-/Al^{3+} ratio, again a small local maximum was observed (at 2.5), likely formed because of the second type of polycations (Al_7) at pH over 5 (not shown in Fig. 1). Although the Al_{13} and Al_7 hydroxy aluminum polycations could be formed between pH 4 and 6, at pH between 4 and 5 the solubility of the Al_{13} polycation was higher than that of the Al_7 polycation; over pH 5 (up to 8), the Al_7 polycations were likely formed while at pH between 4 and 6; these polycations were at equilibrium with each other (14). At a OH^-/Al^{3+} ratio of 0.3, this equilibrium resulted in the best BE% value. Above a OH^-/Al^{3+} ratio of 3.0 (up to 4.0), the BE% value tended to decrease quickly owing to $Al_2(OH)_3$ salt formation (i.e., pH over 7; data not shown). The achieved maximum BE% value in this set was 25.3 ± 0.7%.

Effect of the initial concentration of $AlCl_3$. The second major parameter investigated was the initial concentration of the cation source. Although the major parameter affecting the solubility of Al-polycations was pH, the initial cation concentration affected both the solution pH and the yield of the hydrolyzing reaction. The preferred initial $AlCl_3$ concentration was in the range of 0.2 M (2.0 × $CEC_{original}$) to 2.0 M (20.0 × $CEC_{oirignal}$) at a OH^-/Al^{3+} ratio of 0.3. As shown in Figure 2, we observed the maximum BE% value at a 0.5 M (5 × $CEC_{original}$) initial $AlCl_3$ concentration. After a plateau was reached between 0.3 and 0.6 M $AlCl_3$, the BE% value began to decrease slowly. Furthermore, the experimental results showed that the higher $AlCl_3$ concentrations were not suitable for bleaching because of the unfeasibility of the required amount of NaOH for high $AlCl_3$ concentrations (at a OH^-/Al^{3+} ratio of 0.3).

Salerno *et al.* (15) reported the conventional $AlCl_3$ concentration for pillaring processes as being less than 0.5 M, in general agreement with the observed maximum at a 0.5 M initial $AlCl_3$ concentration. The achieved maximum BE% value in this set was 25.3 ± 0.7%.

Effect of oxidation temperature. Hydroxide pillars have been stabilized by oxidizing the Al-pillars to form rigid oxide bridges between the clay layers (16). The oxidation of pillars was performed in an atmospheric furnace at a temperature range between 105 and 800°C for 12 h. During the heat treatment experiments, the OH^-/Al^{3+} molar ratio was set at 0.3 and the initial $AlCl_3$ concentration was 0.5 M.

The DTA analysis of activated and nonactivated clay samples showed a dehydroxylation peak in the temperature range between 400 and 600°C. By acid activation, the initial temperature of this dehydroxylation reaction was decreased to approximately 350°C. Thus, according to the DTA results, to achieve better bleaching capacities, the clay samples (ABE and PILC) must be heat-treated to at least 400°C to remove the bound water. As shown in Figure 3, BE% values of PILC began to rise above 400°C as expected and reached a maximum at 700ºC. Above this temperature, the BE% values slowly decreased to the previous value at 600°C. The BE% values further decreased slowly at extreme temperatures such as 1000°C (data not shown). In the DTA analysis, crystal lattice changes were observed in the clay samples at a temperature range between 800 and 1100°C. The temperatures at which crystal lattice changes were observed in PILC samples were higher than those of the ABE and original clay, according to the DTA analysis. These results were interpreted as showing increased structural stability of the clay lattice after pillaring. The maximum BE% value in this set was 33.5% ± 0.7 at

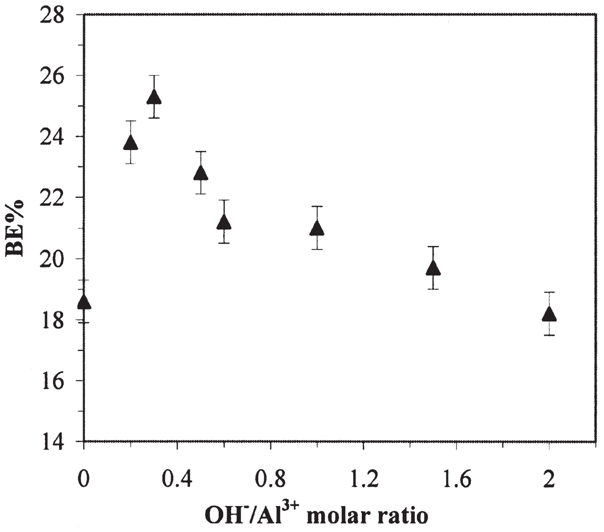

FIG. 1. Effect of OH^-/Al^{3+} ratio on the bleaching efficiency (BE%) of pillared clay (0.5 M Al^{3+}concentration, heat treatment at 500°C). The SD for four discrete runs (sample preparation and bleaching) was ± 0.7.

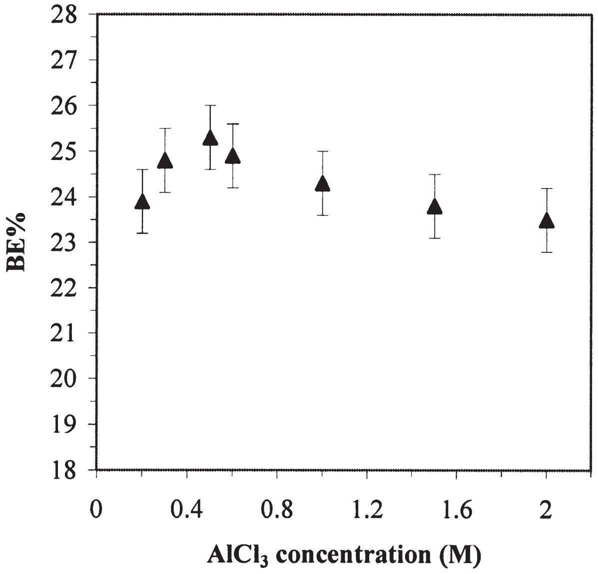

FIG. 2. Effect of the initial concentration of $AlCl_3$ on the BE% of pillared clay (OH^-/Al^{3+} molar ratio of 0.3, heat treatment at 500°C). For abbreviation see Figure 1. The SD for four discrete runs (sample preparation and bleaching) was ± 0.7.

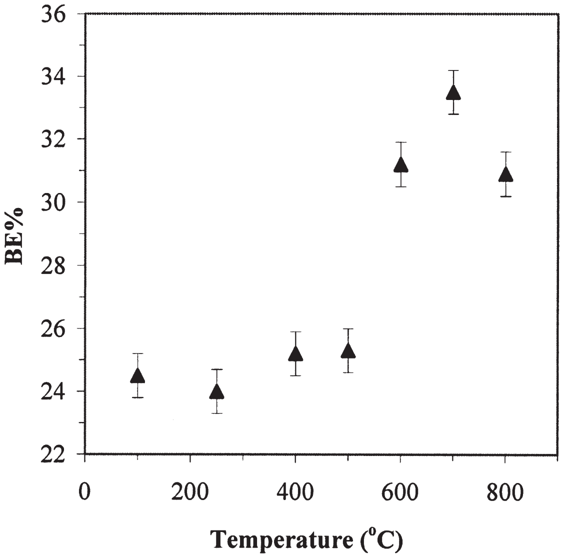

FIG. 3. Effect of oxidation temperature on the BE% of pillared clay (OH^-/Al^{3+} molar ratio of 0.3, initial $AlCl_3$ concentration of 0.5 M). For abbreviation see Figure 1. The SD for four discrete runs (sample preparation and bleaching) was ± 0.7.

700°C (at a OH^-/Al^{3+} molar ratio of 0.3 and an initial $AlCl_3$ concentration of 0.5 M).

Structural differences in the clay samples after the pillaring processes were determined by FTIR analysis. The polycation pillared samples showed –OH stretching modes for Al-OH and Al-H_2O at 3160 and 3245 cm^{-1}. Although the intensity of these modes decreased after severe heat treatment, the –OH modes of Al did not disappear completely until the relatively high temperature of 900°C was reached. However, the peak observed at 3245 cm^{-1} shifted to 3230 cm^{-1} with increasing temperature. Another –OH mode of H_2O at 1620 and 1070 cm^{-1} decreased quickly owing to either heat treatment over 400°C or acid activation without heat treatment. The oxide pillars that were likely formed after heat treatment were determined to be AlO_4 because of an increased absorbance of the symmetric stretching mode at 621 cm^{-1}. The asymmetric stretching mode of AlO_4 was not observed because of the intensity of the free silica absorption peak that existed at 720 cm^{-1}. This free silica IR absorption peak arose from the acid-activation process as a result of the attack of protons on the tetrahedral layer, and this peak covered the peak of the asymmetric stretching mode of AlO_4.

A comparison of the BE% of the clay samples is shown in Table 2. The PILC sample (at optimal conditions) showed an 80.1% increase in BE% compared with ABE and a 183.9% increase compared with original clay. The maximum BE% achieved was 33.5%. The PILC samples also had good thermal stability for bleaching applications (over 800ºC), a property that can possibly be used in the reactivation process of spent bleaching earths.

TABLE 2
Comparison of Adsorbents

Clay sample	BE%[a]	Efficiency change[b] (%)
Ca-bentonite	11.8	0.0
ABE (2 M H_2SO_4)	17.5	48.3
Al^{3+}-exchanged ABE (0.5 M Al^{3+})	18.6	57.6
Al-PILC (at optimum)	33.5	183.9

[a] The SD of bleaching efficiency (BE%) for four discrete runs (sample preparation and bleaching) was ±0.7.
[b] Compared with the original clay. ABE, activated bleaching earth; PILC, pillared clay.

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