

## INVESTIGATION OF ACTIVATED Al - PILLARED CLAY EFFICIENCY IN VEGETABLE OIL PURIFICATION

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*This paper represents a contribution to the applicability of natural clays and their derivatives as adsorbents in the process of purification of vegetable oil. Investigation of textural properties of raw and purified clay samples reveals that during acid activation and Al-pillaring, BET and micropore surface area increases significantly. However, bleaching capacity of clay and its derivatives is not determined by using sample surface area, but rather sample total pore volume. Surface area, especially micropore surface area contributes to removal of smaller molecules. This was confirmed by successful elimination of moisture and volatile materials by samples with an appropriate micropore structure. Used samples of clay and its derivatives do not significantly influence acid and peroxide values of raw sunflower oil during its treatment.*

**KEYWORDS:** Montmorillonite; activated Al-pillared montmorillonite; texture; sunflower oil; purification; bleaching; adsorption

### INTRODUCTION

Natural clays are good adsorbents, but modifications are often necessary to improve their performance in order to obtain highly active and selective materials. Acid activation and pillaring processes are commonly used for improvement of natural clay (filosilicates and especially montmorillonites) adsorption capacity. Today, pillared clays are one of the most widely investigated new microporous materials. Intercalation of metal oxide clusters generates new materials with specific porous structure, different incorporated cations and other active sites, offering thus new possibilities for their applications as adsorbents, catalysts or auxiliary materials in a variety of industrial branches (1).

Our previous results with soybean oil bleaching by Al-pillared montmorillonite suggested that the intercalated aluminum ions improve to some extent the montmorillonite adsorption properties for carotenes and other colored materials (2). In order to improve

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the adsorption capacities of Al-pillared clay samples, montmorillonite type, clays were treated by sulfuric acid, before Al-pillaring. Six different samples were prepared: raw montmorillonite type clay - RM; acid activated raw clay - ARM, acid activated Al-pillared raw clay - AAIRM; purified montmorillonite type clay - PM; acid activated purified clay - APM; and acid activated Al-pillared purified clay - AAIPM. In this paper the influence of the textural properties of raw, purified, acid activated and Al-pillared samples were investigated in correlation with their bleaching capacities.

## EXPERIMENTAL

The investigation was carried out using raw and purified montmorillonite type clay from Šipovo. The raw clay was dried at 105°C, milled and sieved to achieve grain size less than 63 µm. Purified clay with particle size less than 2 µm was prepared by hydro-sedimentation technique (JUS U.BI.018,1980). After hydro-separation the clay was dried at 105°C. Both raw and purified clays were acid activated with 16 mass % sulfuric acid at boiling temperature during 6 hours (3), following Al-pillaring as described elsewhere (4).

The textural properties, specific surface area, average pore diameter, pore volume, micropore surface area and micropore volume measurements were performed using method of static low temperature nitrogen adsorption (LTNA) by Micrometrics ASAP 2000. BET adsorption isotherm was applied in data processing.

Darker raw sunflower oil (RSFO) with higher quantity of oxidation products was stirred with 2 wt% clay samples for 20 minutes at ambient temperature and pressure. After filtration the clay adsorbents were separated from oil. The quality of prepared oil samples was determined according to JUS ISO standard methods. Measurements were carried out by spectrophotometer Hewlett Packard 8452 following bands at 455 nm, 232 and 270 nm for transparency and absorbance, respectively. Also, peroxide and acid values, moisture and volatile materials content in filtered oil samples were determined, as described in (5).

## RESULTS AND DISCUSSION

The textural properties of the samples are given in Table 1. Slight hydro-purification, acid treatment and Al-pillaring strongly enhanced both BET and micropore surface area of the samples. Pillared clay samples have the lowest average pore diameters. The fine pore structure of pillared samples provides well developed BET and micropore surface area.

Bleaching capacity of raw clay and its derivatives was determined by measuring the transparency of raw sunflower treated with clay at 455 nm. Results reveal adsorption capabilities of applied natural and modified clay samples in removal of different pigments from raw sunflower oil (Table 2). Raw sunflower oil has a quite dark color and shows low transparency. The transparency of raw sunflower oil treated with raw and purified unmodified clays does not change significantly, whereas it does change significantly after treating with modified samples. The best results were achieved with acid activated purified clay sample. The transparency of raw sunflower oil sample is enhanced three times after

treatment with acid activated purified clay sample and two times after treatment with acid activated Al-pillared purified clay sample. The obtained results show that BET and micropore surface area are not decisive factors for adsorption capacities of clay and clay derivatives. Samples with higher pore volumes offer the best adsorption capacities in respect of different pigments in raw sunflower oil. These results suggest that pigments with higher molecules can penetrate only into the pores with higher dimensions, so micropores do not take part in pigment adsorption during bleaching processes of raw sunflower oil.

**Table 1.** Textural properties of the applied clay samples

Sample	Surface area (m <sup>2</sup> /g)	Average pore diameter (nm)	Pore volume (cm <sup>3</sup> /g)	Micropore surf. area (m <sup>2</sup> /g)	Micropore vol. (cm <sup>3</sup> /g)
RM	81.51	3.28	0.074	20.12	0.0102
ARM	145.15	4.02	0.125	33.61	0.0148
AAIRM	256.26	1.93	0.092	135.52	0.0632
PM	93.86	4.82	0.098	24.01	0.0108
APM	342.03	3.66	0.292	18.54	0.0051
AAIPM	411.81	2.95	0.241	91.99	0.0405

**Table 2.** Transparency (%) of raw and purified oil samples at 455 nm

RSFO	17.5
RM	21.0
ARM	27.5
AAIRM	27.0
PM	16.5
APM	54.5
AAIPM	41.0

Moisture is undesirable in edible oils, since it contributes to increase of oil acid values and losses during oil refining (5). All samples show good adsorption properties in removal of moisture and volatile materials. The best results were obtained by acid activated and subsequently Al-pillared samples (Table 3).

**Table 3.** Moisture and volatile matter content (%) in raw and purified oil samples

RSFO	0.22
RM	0.12
ARM	0.10
AAIRM	0.08
PM	0.16
APM	0.10
AAIPM	0.09

Considering the textural properties of the samples (Table 1), both BET and micropore surface area significantly influence the adsorption properties of the clay and clay derivatives

in moisture removal. The dimensions of these molecules are significantly smaller than the dimensions of pigment molecules, therefore they can penetrate into the micropores, i.e. the samples with the most developed surface area have the best adsorption capacities.

The applied clay and clay derivatives do not influence significantly the amount of free fatty acids (defined by acid values) during the raw sunflower oil treatment (Table 4).

**Table 4.** Acid values (mg KOH/g) of raw and purified oil samples

RSFO	3.38
RM	3.59
ARM	3.57
AAIRM	3.58
PM	3.19
APM	3.49
AAIPM	3.15

After the treatment, peroxide values show a slight increase (Table 5), although this might be due to direct oxidation with air during mixing of raw sunflower oil with clay samples, rather than a promoted oxidation with the used clay particles. Slight increase of peroxide values in the samples treated by raw clay and its derivatives could be explained by promoting effects of different impurities present in natural clay. However, the majority of these impurities were removed during purification of natural clay using hydro-sedimentation technique. In any case, all the obtained peroxide values are below those allowed for edible nonrefined oils (6).

**Table 5.** Peroxide values (mmol/kg) of raw and purified oil samples

RSFO	1.98
RM	2.10
ARM	3.14
AAIRM	2.86
PM	2.97
APM	2.24
AAIPM	2.47

R-values defined as ratio of absorbance at 232 nm and 270 nm, measure the oxidation changes of unsaturated fatty acids during the treatment. At 232 nm, all treated samples show lower absorbencies than raw sunflower oil (Table 6). The absorbencies of the samples treated with acid activated and acid activated and subsequently Al-pillared raw clay samples are significantly lower than the absorbance of untreated raw sunflower oil. However, these values are higher than the absorbance values of oil samples obtained after treatment of raw sunflower oil with samples of purified clay and its derivatives. Acid treatment and Al-pillaring of purified clay does not significantly influence the absorbance at 232 nm. These values are approximately equal to the value obtained with acid activated Al-pillared raw clay sample.

Clay-treated oil samples, except for those treated with the acid activated Al-pillared purified clay, show lower absorbance values at 270 nm than untreated sunflower oil. However, these reductions are less than the reductions observed at 232 nm.

**Table 6.** Specific absorbance and R-value of raw and purified oil samples

Sample	A <sup>1%</sup> <sub>232 nm</sub>	A <sup>1%</sup> <sub>270nm</sub>	R-value
RSFO	6.25	0.78	7.96
RM	5.26	0.69	7.61
ARM	3.03	0.47	6.45
AAIRM	2.68	0.54	4.93
PM	2.85	0.43	6.60
APM	2.77	1.12	2.42
AAIPM	2.72	0.74	3.70

## CONCLUSION

Acid treatment and especially Al-pillaring causes dramatic increase of both BET and micropore surface area of raw and purified clays. These changes significantly influence the adsorption properties of clay derivatives. The best result during treatment of raw sunflower oil was achieved using acid activated and acid activated and subsequently Al-pillared purified clay samples. However, the crucial influence of clay based adsorbents on oil bleaching efficiency is not in correlation with surface area but with total pore volume values. Micropores do not contribute to oil bleaching because the pigment molecules have bigger dimensions and can not penetrate into the micropores. Micropores can adsorb only moisture and molecules of volatile materials. Increase of both BET and micropore surface area improves the efficiency of adsorption of moisture and volatile matter. The decrease of absorbance values at 232 nm and 270 nm reveals that clay and its derivatives contribute to the removal of secondary oxidation products. The increase of peroxide values during the clay treatment was insignificant, and the acid values remained the same as before the treatment of raw sunflower oil, showing that clay and its derivatives did not produce these undesirable changes.

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## **ИСПИТИВАЊЕ ЕФИКАСНОСТИ АКТИВИРАНИХ Al - ПИЛАРНИХ ГЛИНА У ПРЕЧИШЧАВАЊУ БИЉНИХ УЉА**

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Овај рад представља допринос примени природних глина и њихових деривата као адсорбенса у процесима пречишћавања у индустрији биљних уља. Испитивање текстуре узорака непречишћене и пречишћене глине показује да при киселинском активирању и Al-пиларењу долази до значајног повећања како БЕТ површине тако и површине микропора. Међутим, уочено је да способност бељења уља глином и њеним дериватима није одређена њиховом специфичном површином већ укупном запремином пора, а улога микропора је значајна у одстрањивању мањих молекула, што доказује успешно уклањање влаге и испарљивих материја из уља третираних управо узорцима глина које су имале погодну микропорозну структуру. Позитиван ефекат је и то да добијене глине незнатно утичу на киселински и пероксидни број, што значи да не утичу негативно на оксидативу стабилност уља сунцокрета.

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