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PHYSICO-CHEMICAL CHARACTERIZATION OF ACID-ACTIVATED CLAY: ITS INDUSTRIAL APPLICATION IN THE CLARIFICATION OF VEGETABLE OILS

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Introduction

Clays are natural products which can be used in industry, crude or treated, by physical and chemical methods. The application domains of clay are derived from the nature and the structure of mineral, in addition to its physico-chemical properties. Acid treatments of clay consist to modify its structure by changing the properties of surface, porosity and acidity. The results obtained through acid activation vary according to the type of clay used, its nature, the acid concentration, the temperature and the time of treatment [1]. Acid activated clay is widely used in industry as a bleaching and decontaminating agent, adsorbent, catalyst and catalyst support [2, 3].

Methods

The methods adopted in this study are the following: the chemical analysis of the major elements was carried out by EDTA Complexometric Method [4]; X–ray diffractograms were recorded by a Philips type PW 3710 apparatus; the infrared spectra were recorded by Perkin Elmer 783 Dispersive Spectrometer; the cation exchange capacities (C.E.C.$_{\text{Cu-EDA}}$) were determined by the Copper Ethylene Diamine Method [5] and the total surface was determined by Methylene Blue Adsorption [6]. The acid treatment at reflux temperature is achieved with with 3N hydrochloric acid [7].

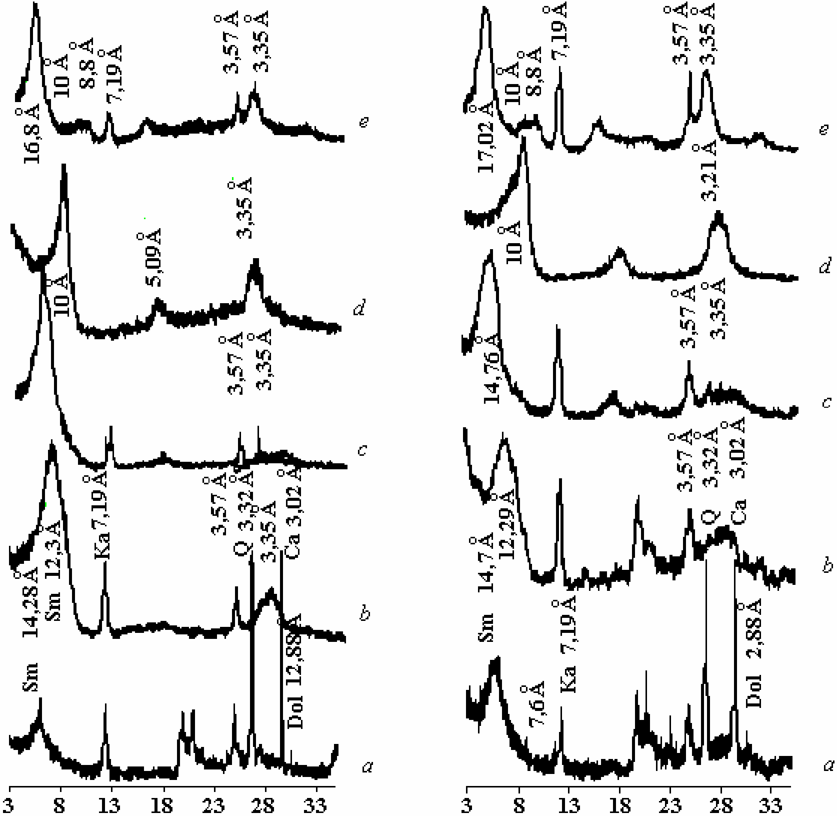

Fig. 1. XRD patterns of some acid activation clays
(a): crude powder; (b): Na exchanged powder (c): oriented Na exchange film;
(d): oriented Na exchange and heated at 500°C film ;(e): oriented Na exchange and glycoleted film

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Results

X–ray diffraction: X–ray diffractograms (fig. 1) show the different positions of 001 reflection of smectite, kaolinite and illite. The 001 reflection of smectite appeared at 14.7 Å of the crude samples. After an exchange with sodium, this reflection appeared at 12.24 Å characteristic of Na smectite. Heating the samples at 500°C for 2 hours reduced interlayer spacing to 10 Å. Treatment with ethylene glycol showed a change of a 001 reflection to 17.4Å. The 001 and 002 reflections of kaolinite appeared respectively at 7.19 and 3.57 Å. These reflections disappeared after heating at 500°C for 2 hours. The reflection at 10Å characterized a small amount of illite. The mineralogical composition estimated by X–ray diffraction is given in table 1. After purification, the smectitic fraction was higher than 70 % of the total clay fraction with small quantities of illite and kaolinite.

Table 1: Mineralogical composition (%) of clay deposit

Samples	Clay mineral (%)			Impurities (%)			
	Sm.	Ill.	Kao.	Q.	Ca.	D.	Gy.
Soht crude	45	3	10	17	23	2	–
Sof crude	42	5	13	16	17.5	3.5	3
Soht Na–purified	78	7	15	–	–	–	–
Sof Na–purified	71	11	18	–	–	–	–

Infrared spectra: The infrared spectra (fig. 2) show the absorbance of purified samples at a frequency range of 4000 to 400 cm^{-1}, [8].

The vibrating bands at 3658 and 920 cm^{-1} (Al-Al-OH group) were observed on the infrared spectra of the different samples, confirming the presence of dioctahedral smectite [9]. The bands at 3435 and 1636 cm^{-1} indicated the adsorption of water molecule on the clay surface [10]. The (Si–O) structural bands of the clay were confirmed by strong absorption bands in the 1100–1000 cm^{-1} region. The bands at 877, 854 and 800 cm^{-1} corresponded respectively to (Fe,Al–OH), (Mg,Al–OH) and (Mg,Fe–OH) in smectitic clay [11]. The band at 3710 and 714 cm^{-1} indicated the presence of kaolinite.

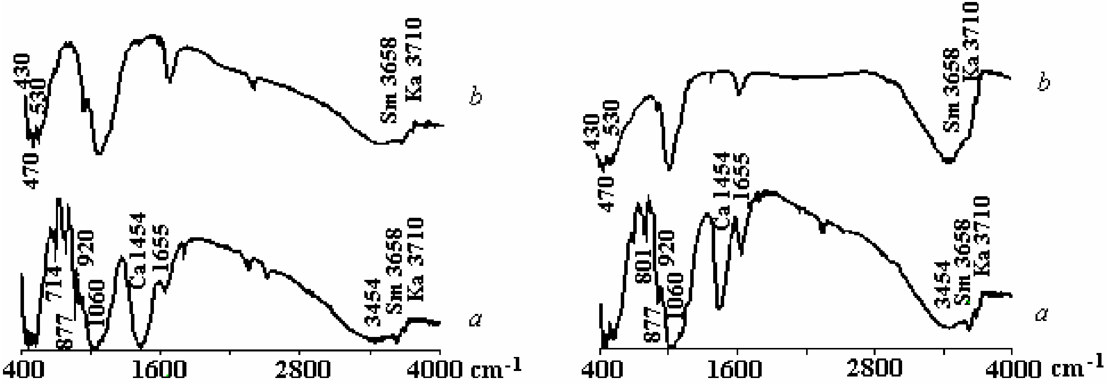

Fig. 2: IR- spectra of Soht and Sof, (a) crude sample and (b) purified sample

Table 2: Chemical analysis of the crude and Na–purified samples
(Dt): deficit tetrahedral, (Do): deficit octahedral.

Samples	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	CaO	H_2O
Na-Soht	43,96	11,98	7,18	5,25	2,46	0,61	7,08	21
Soht crude	53,12	21,92	5,58	2,12	1,76	0,9	–	14
Soht	$Na_{0,48} K_{0,16} (Si_{7,46} Al_{0,54})(Al_{3,08} Fe_{0,59} Mg_{0,44}) O_{22}$							
Na-Sof	46,32	14,57	7,58	5,26	2,73	0,83	5,42	17
Sof crude	55,19	22,02	5,42	2,36	1,59	0,95	–	12
Sof	$Na_{0,42} K_{0,17} (Si_{7,54} Al_{0,46})(Al_{3,08} Fe_{0,56} Mg_{0,48}) O_{22}$							

Chemical analysis: The chemical weight percent composition of the 2 um fraction (crude samples and purified clay fraction) are in table 2. The chemical formula may be calculated for these fractions by using Mauguin Method. The number of cations in the octahedral sheet (Al, Fe end Mg) are closer to 4 than to 6. This result confirms that clays are essentially dioctahedral. The chemical composition data indicated the presence of small amounts of impurities in the solid; the majority of Mg and K must be in the composition of the mica, confirmed by the presence of illite and kaolinite in the XRD diffractograms.

Cation Exchange Capacities and the total surface: the cation exchange capacities ($\text{C.E.C.}_{\text{Cu-EDA}}$) and total surface (Ts) were measured for the crude and purified samples (Soht and Sof). After purification, the cation exchange capacities and total surface increased distinctly. Results are given in table 3.

Table 3: Cation Exchange Capacities (C.E.C. meq/100g of calcined clay) and surface areas (S.A. m^2/g*)*

Samples	Crude		Na–Purified	
	C.E.C.	S.A.	C.E.C.	S.A.
Soht	43	408	80	650
Sof	44	464	75	606

Application in the bleaching of oils

Several methods were adopted for the clarification of vegetable oils, but the most used in industry is clay activated by hydrochloric acid. This method consists in the elimination of the pigments by adsorption from oil. For bleaching test 10g of clay were added to 100 ml of 3N HCl, heated under reflux conditions, for 20 mn. Then, suspensions were centrifuged and solids washed with distilled water until no chloride anions were detected (Ag^+ test) and dried at 75°C. The oil clarification was followed by the measurement of absorbance by oil before and after treatment by clay. The bleaching capacity is given in table 4 and presented in figure 3. The formula used to calculate power decolorisation consists to:

$$\frac{A_{430}\,(\text{C.O.}) - A_{430}\,(\text{T.O.})}{A_{430}\,(\text{C.O.})}$$

A_{430}: absorbance at 430 ŋm of crude oil (C.O.) and after treatment with clay (T.O.)

The spectra of natural oil revealed the carotenoid pigment at 430; 455 and 483 ŋm. Bleaching decrease the intensities of carotenoid pigment until total disappear.

Table 4 : Bleaching capacity and Cation Exchange Capacities of Crude, Purified and Activated clays

		Bleaching capacity		C.E.C.	
Samples		Soht	Sof	Soht	Sof
Purified		12,45	15,24	80	75
Crude		31,29	31,97	43	44
Activated clays	1h	76,56	72,95	39,3	42,2
	2h	87,79	82,12	28,8	32,6
	3h	86,5	80,97	20,9	26,8
	4h	85,27	80,44	17,5	22,1
	5h	80,45	76,44	15,2	17,3
	6h	23,4	22,87	13	13,2

Oils treated with activated clays for 6 hours showed brown coloring of the pigments. In addition, the three maxima at 430, 455 and 483 ŋm were present in the absorption curves. These results showed that activated clays did not absorb large quantities of pigments. This behavior is explained by an intense destruction of the layers and interlayer space of activated clay. Under these new conditions, clay lost absorption and adsorption characteristics. Consequently, clay lost its bleaching capacity. Oils treated with activated clay during 1, 2, 3, 4 and 5 hours became clear, and clay eliminated the pigments. The fall of the bleaching capacity curves indicates that clay absorbed the pigments.

The bleaching capacity curves according to the activation time (Fig. 4) show that the weakest bleaching capacities are given by the crude clays, decarbonated and purified clays; on the other hand, the clays activated with hydrochloric acid present satisfactory values which exceed 85%. These curves make it possible to determine a clarification optimum after 2 hours of activation with 3N hydrochloric acid, which shows the highest values.

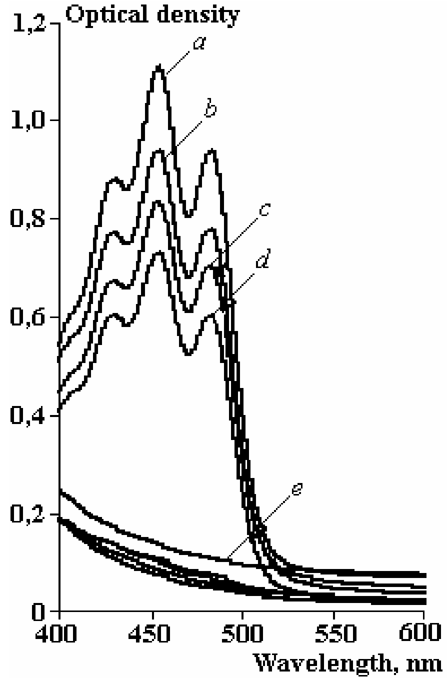

Fig. 3: The absorption spectra of vegetable oil:
a : crude oil ; b : treated oils by purified clay ; c : treated oils by activated clays during 6 hours; d : treated oils by decarbonated clay ; e : treated oils by activated clays during 1, 2, 3, 4 and 5 hours.

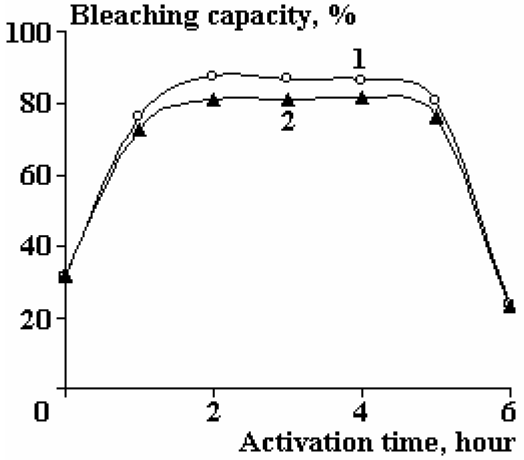

Fig. 4: Bleaching capacity of activated clays at 1; 2 ; 3; 4; 5 and 6 hours

Conclusion

The different analysis of these Tunisian samples shows that the clay fractions are essentially smectitic containing little amounts of illite and kaolinite. The associated minerals are essentially quartz and carbonate. After purification, the smectic fraction is always exceeding 70 %.

The treatment of bentonitic clays with 3N hydrochloric acid shows that once activated, these clays have weak cation exchange capacities. The specific surface which seems the determining factor in the adsorption of the pigments increases and, consequently, the bleaching capacities of these clays become significant. This study makes it possible to determine a clarification optimum of vegetable oils by clay 2 hours after activation by 3N hydrochloric acid.

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Summary

The physico-chemical characterization of Tunisian bentonitic clays is based on the determination of the mineralogical composition (X–ray diffractions and infrared spectroscopy), chemical analysis, cation exchange capacities and the total surface area. The result given by these techniques show that these samples were smectic clay of beidellitic character. In the other hand, the activation of these clays by hydrochloric acid shows an increase of the specific surface area and favorite the clarification of vegetable oils.