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Using Nanotechnology in Bleaching Vegetable Oils

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THE present study aimed to investigate the efficiency of nanotechnology in bleaching three important Egyptian oils (soybean, corn and sunflower). The raw bleaching earth powder was milled for 10 h in a planetary ball mill. X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM) were used to investigate morphology, crystallite size, lattice strain and particle size of as-received and milled powders. The mechanical alloying process succeeded to obtain nano-sized bleaching earth powders after 10 h of milling and the morphology appeared rod with 46.6 nm in length and 4.46 nm in diameter. The milled nano-sized bleaching powder was used in bleaching of oils under study. Comparing color indices, peroxide values and spectral absorbencies at 232, 270 nm for the resulted bleached oils with the unbleached and control ones bleached with raw bleaching earth, it was concluded the high bleaching efficiency of nano-sized bleaching earth in reducing color indices, peroxide values and spectral absorbencies at 232, 270 nm.

Keywords: Nanotechnology, Bleaching earth, Vegetable oils, Bleaching efficiency.

Introduction

Vegetable oil is one of the basic food items which are consumed by almost every human being. Therefore quality of vegetable oil should be good enough so that it accounts for healthy life. In vegetable oil manufacturing there are four major steps involved which are neutralization, degumming, bleaching and deodorization. Among these steps bleaching is the very important and critical step because it ensures the good color and odor of vegetable oil [1].

Bleaching of edible oils is a part of the refining process of crude oils, which removes contaminants that adversely impact their appearance and performance. Typically, edible oils are extracted together with impurities in various quantities. Many of these impurities have to be removed from the oil to achieve the high quality oil standards necessary for edible applications. Preceded generally by degumming and refining (neutralization) processes, bleaching is required to remove specific detrimental contaminants that are not effectively removed by these processes before the oil progresses through deodorization [2]. Unbleached oils contain pesticide residues, oxidation products and heavy metals which can become harmful when consumed. So it is essential to bleach the oils. Oxidation products in the crude vegetable oils are removed by adsorption on the active surface of the bleaching earth to improve color and stability of the final oil [3].

The bleaching of edible vegetable oils involves the removal of a variety of impurities, which include phosphatides, fatty acids, gums, trace metals, etc., followed by decolorization [4]. Bleaching requires the use of adsorbents singly or in combination for the removal of colored pigments and impurities or contaminants from oil

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to give it a desirable quality [5]. Bleaching earth refers to natural or activated clay which has the capacity to adsorb colored materials and other impurities during oil purification processes in their natural or activated status [6].

Bleaching or adsorption criteria are quantity of activated earth, dosage, time, mixing, temperature, and atmospheric pressure and vacuum. The primary function of the bleaching process is to remove peroxides and secondary oxidation products, pigments and any trace of gums and soaps [7]. Diatomaceous earth, clay, peroxide or carbon may be used to bleach and adsorb the dark colored impurities in the oil by adsorptive purification [8]. Spent bleaching earth is used to remove metals gums, oxidized products residual gum and color from the oil. It engrosses about 0.5 % by weight of oil in the process [9]. Bleaching efficiency was monitored by measuring the reduction in color bodies, metal contaminants and oil retention by the bleaching clay [10].

Mathematically, the bleaching process is based on adsorption isotherms, where the differences between bleached and unbleached oils are clearly seen by adsorption isotherms. Adsorption isotherms are based on the equilibrium relationship between the concentration of adsorbent particles and the concentration in liquid phase at certain temperatures. The most commonly used isotherms are Langmuir and Freundlich isotherms. Freundlich isotherm is more suitable for adsorption liquid contaminant. This type of isotherm is also used for bleaching oils [11]. The process is physical adsorption by weak bonds between the dark colored compounds in oil and the clay adsorbent [12].

Nanotechnology is defined as the creation, utilization, and manipulation of materials, devices, or systems at the nanometer scale. Nanomaterials are usually defined as materials smaller than 100 nm and have unique properties due to the high surface to volume ratio and novel physicochemical properties such as color, solubility, and thermodynamics. These novel properties provide opportunities to improve the sensory qualities of food such as taste, texture, and color [13].

The advent of nanotechnology has allowed the synthesis of nanomaterial in various fields, including optic and optoelectronics, photocatalysis, electrical and sensor devices, biomedical applications, and so on due to their excellent chemical, thermal and mechanical properties [14].

The aim of this study was to evaluate the efficiency of nanoparticles bleaching earth of different mesh size used in bleaching three important oils in Egypt (sunflower, corn and soybean).

Materials and Methods

Materials and Experimental Procedures

Soybean, corn and sunflower oils were obtained from Arma Company for Edible Oils, Egypt after degumming process and before bleaching. Engelhard F160 bleaching earth (USA). All solvents and chemicals used in all studies were obtained from Sigma Chemical Co. and were of analytical and HPLC grades.

The bleaching earth powder was milled for 10 h in a planetary ball mill. The milling conditions were; (a) ball to powder weight ratio equal to 15:1, (b) 12 mm balls in diameter, and (c) 350 rpm rotating speed. X-ray diffraction (XRD; Philips PW) technique was employed to detect the phases of the milled powders. The crystalline size (D) and lattice strain (ε) were determined from the X-ray line broadening using the equations mentioned in References [15-17] as following:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad \text{............ (1)}$$

$$\varepsilon = \frac{B}{4\tan\theta} \quad \text{.......... (2)}$$

Where λ=1.540591°A (Cu–Ni radiation), B is the full width at half maximum (FWHM) and θ is the angle in radians.

Both morphology and particles sizes of the powders were characterized using transmission electron microscopy (TEM type JEOL JEM-1230).

$$\text{Bleaching Efficiency \%} = \frac{\text{Color of crude oil - Color of bleached oil}}{\text{Color of crude oil}} \times 100$$

Analytical Determinations

20 g of each crude vegetable oil (soybean, corn and sunflower), after degumming process and before bleaching was stirred and heated together with 0.4 g of the bleaching earth (2% wt. of oil), in a rotary evaporator (BUCHI Labortechnik AG) at 100 ºC in a hot water bath under reduced pressure for 20 min. The oil was then filtered through a Whatman No. 1 filter paper. The color of each oil was measured using a Lovibond tintometer according to the method (Cc 13e-92) described in the AOCS [18]. The peroxide value (mequivalent of O_2/kg oil) was determined according to the procedure described in AOAC [19]. Natural conjugated constituents were determined by measuring UV absorption at specific wavelengths in purified solvent as described by Kates [20].

Results and Discussion

Characterization of the prepared powders

Fig. 1 shows XRD patterns of bleaching earth as-received as well as milled bleaching earth powders for 10 h. It is clearly appear that the XRD peaks of the un-milled bleaching earth are intense and sharp due to higher crystallinity. After 10 h of milling, the diffraction peaks become broader and less intense because of distortion effect caused by dislocation in the lattice which consequently, produces refinement for the crystallite size and enhancement for the lattice strain [21, 22]. The crystal size and lattice strain of the un-milled bleaching earth were 66.41 nm and 0.2085 %, while after 10 h milled their values were 28.94 nm and 0.4785 %. The crystalline size (D), reduced with increasing milling time (t) according to the equation [23] as following:

$$D = kt^{-2/3}$$ Where; K is constant.

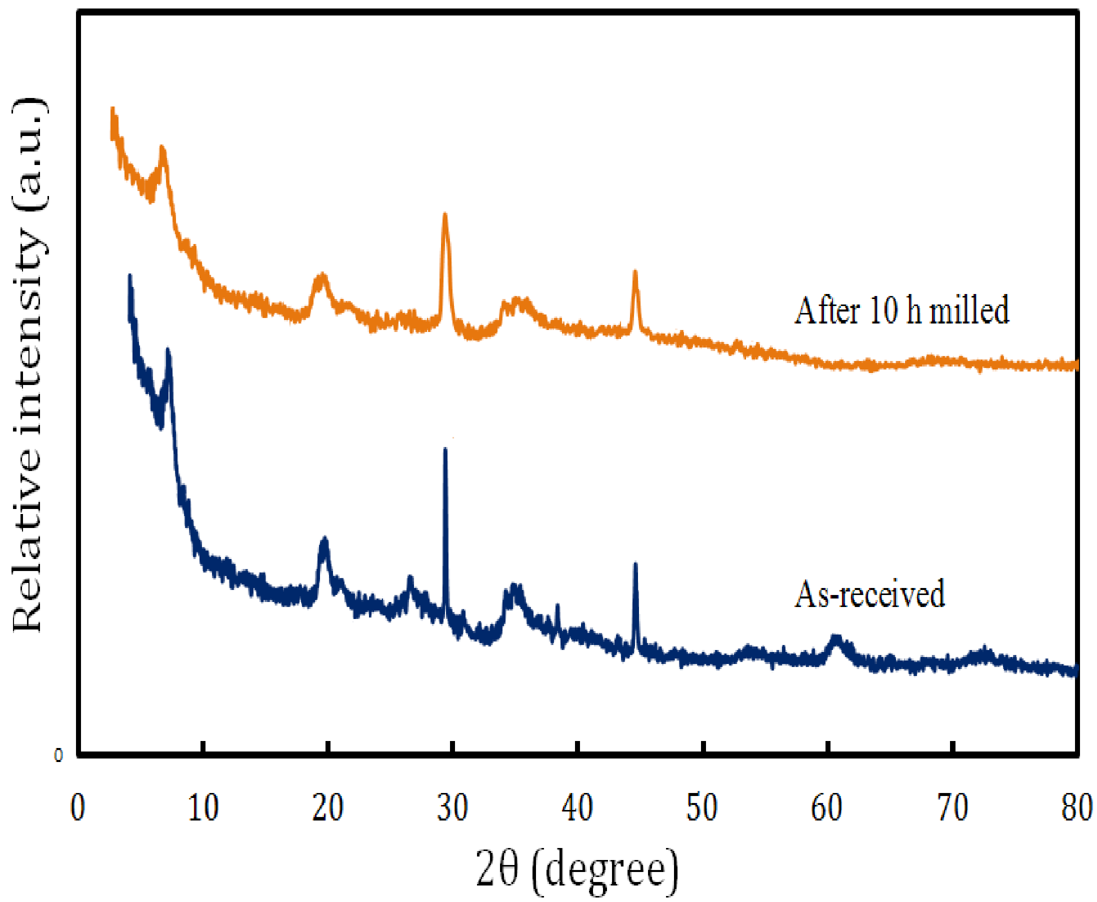

Fig. 1. XRD patterns of bleaching earth as-received powder and after milled for a 10 h.

The size and morphology of the as-received and after 10 h milled bleaching earth were further examined by TEM as shown in **Fig. 2** (a&b). It is obvious to notice from the figure that the bleaching earth powders before and after milling have mostly rod-like structure. During milling, the particles change in size as a consequence of repeated deformation, fracturing and welding processes [24]. The length and diameter of as-received powders were about 341.8 and 24.7 nm, respectively. However, after 10 h of milling, the length and diameter of rods decreased to 46.6 and 4.45 nm, respectively.

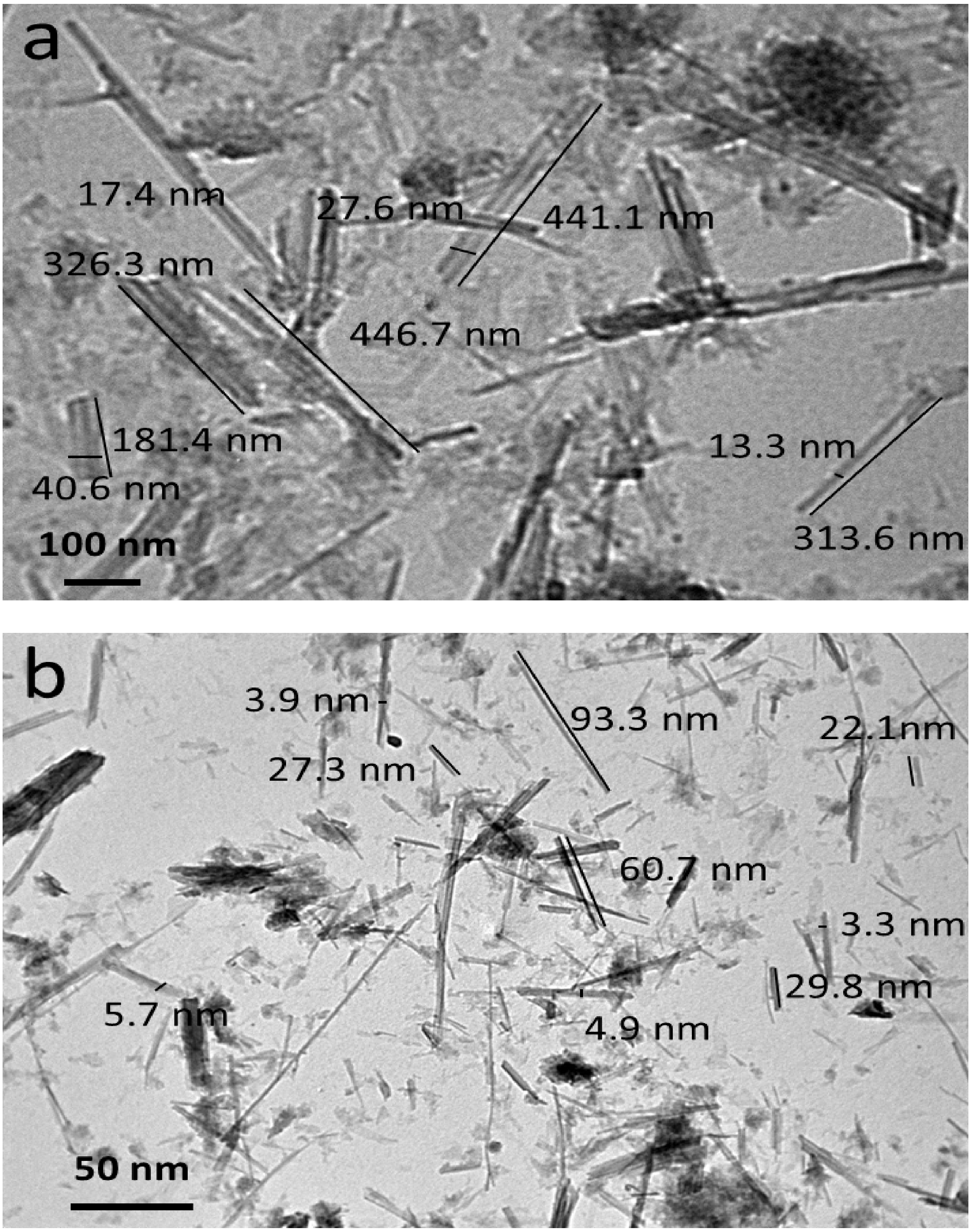

Fig. 2. TEM micrographs of bleaching earth: a) as-received powder and b) after milled for a 10 h.

Characterization of the Bleaching Process

Color Index

In this research the evaluation of bleaching efficiency was based on the Lovibond color indices [25]. Bleaching efficiency was monitored by measuring the reduction in color bodies, metal contaminants and oil retention by the bleaching clay [10].

Table (1) represents the reduction in red color indices during bleaching processes of soybean, corn and sunflower oils with three treatments; before bleaching, after bleaching with raw bleaching earth and after bleaching with nano bleaching earth.

It is obvious the apparent decrease in color indices for the red color before bleaching which were 8.0, 7.0, 2.7 for soybean, corn and sunflower oils, respectively, that changed into to 6.0, 5.0 and 2.0 after bleaching with raw bleaching earth. Whereas, the color indices were 3.0, 2.0 and 1.0 for the studied oils after bleaching with nano bleaching earth, which indicates the high efficiency of nano size bleaching earth. Also, regarding to the bleaching efficiencies percents for oils bleached with raw bleaching earth; their values were 25.0, 28.6 and 25.9 for soybean, corn and sunflower oils, respectively. Whereas, their values increased to 62.5, 71.0 and 63.0 after bleaching with nano bleaching earth.

Differences in bleaching power might be depended on the adsorbents particle size and their compositions that is the result of increase in active sites available for adsorption. From the view point of diffusion, small particles may shorten the diffusion path to the pore surface for adsorption, thus enhancing adsorption as a result of increase in surface area, pore volume of the particles [25].

Peroxide Value

Presence of peroxides and other oxidation products in vegetable oils imparts unpleasant odors and shorten the shelf life of the oil. The bleaching process combines catalytic action such as peroxide decomposition and equilibrium adsorption of pigments from oil. Bleaching earths eliminate oxidation products and other impurities from oils and in this way improve the quality shelf life of the oils. It is therefore necessary to determine the quantities of peroxides that may be still present to find out if bleaching effectively eliminated oxidation products [3].

Table (2) represents the reduction in peroxide values during bleaching processes of soybean, corn and sunflower oils with three treatments; before bleaching, after bleaching with raw bleaching earth and after bleaching with nano bleaching earth.

It is obvious the apparent decrease in peroxide values before bleaching which were 4.21, 3.80, 3.40 for soybean, corn and sunflower oils, respectively, that changed into to 3.08, 1.90 and 1.80 after bleaching with raw bleaching earth. Whereas, the peroxide values were 1.43, 0.50 and 0.30 for the studied oils after bleaching with nano bleaching earth, which indicates the high efficiency of nano size bleaching earth.

Ultraviolet (UV) Spectral Analysis

Decomposition of hydroperoxides and isomerization of unsaturated fatty acids lead to the formation of conjugated dienes and trienes, which show absorption maxima at 232 and 270 nm, respectively. These compounds are very unstable to oxidation and are much more sensitive, so bleaching parameters should be chosen to avoid formation of these compounds [10].

Table (3) represents the reduction in spectral absorbencies at 232, 270 nm during bleaching processes of soybean, corn and sunflower oils with three treatments; before bleaching, after bleaching with raw bleaching earth and after bleaching with nano bleaching earth.

It is obvious the apparent decrease in spectral absorbencies at 232 nm before bleaching which were 1.910, 1.842, 1.487 for soybean, corn and sunflower oils, respectively, that changed into to 1.789, 1.741 and 1.295 after bleaching with raw bleaching earth. Whereas, the spectral absorbencies at 232 nm were 1.415, 1.650 and 1.147 for the studied oils after bleaching with nano bleaching earth.

Whereas, the apparent decrease in spectral absorbencies at 270 nm before bleaching which were 0.537, 0.393, 0.232 for soybean, corn and sunflower oils, respectively, that changed into to 0.415, 0.374 and 0.199 after bleaching with raw bleaching earth. Whereas, the spectral absorbencies at 270 nm were 0.399, 0.343 and 0.190 for the studied oils after bleaching with nano bleaching earth, which indicates the high efficiency of nano size bleaching earth.

TABLE 1. Color Indices of the studied oils.

Oil	Before bleaching		After bleaching with raw bleaching earth		After bleaching with nano bleaching earth		Bleaching efficiency %	
	Yellow	Red	Yellow	Red	Yellow	Red	with raw bleaching earth	with nano bleaching earth
Soybean	30	8.0	30	6.0	30	3.0	25.0	62.5
Corn	30	7.0	30	5.0	30	2.0	28.6	71.0
Sunflower	30	2.7	30	2.0	30	1.0	25.9	63.0

TABLE 2. Peroxide Values (mequivalent of O_2/kg oil) of the studied oils.

Oil	Before bleaching	After bleaching with raw bleaching earth	After bleaching with nano bleaching earth
Soybean	4.21	3.08	1.43
Corn	3.80	1.90	0.50
Sunflower	3.40	1.80	0.30

TABLE 3. Spectral absorbencies at 232, 270 nm of the studied oils.

Oil	Before bleaching		After bleaching with raw bleaching earth		After bleaching with nano bleaching earth	
	Abs_{232} (Diene)	Abs_{270} (Triene)	Abs_{232} (Diene)	Abs_{270} (Triene)	Abs_{232} (Diene)	Abs_{270} (Triene)
Soybean	1.910	0.537	1.789	0.415	1.415	0.399
Corn	1.842	0.393	1.741	0.374	1.650	0.343
Sunflower	1.487	0.232	1.295	0.199	1.147	0.190

Conclusions

It can be concluded the high efficiency of nanotechnology in bleaching of Egyptian oils (soybean, corn and sunflower). The mechanical alloying process succeeded to obtain nano-sized bleaching earth powders after 10 h of milling and the morphology appeared rod with 46.6 nm in length and 4.46 nm in diameter. The milled nano-sized bleaching powder was used in bleaching of oils under study. Comparing color indices, peroxide values and spectral absorbencies at 232, 270 nm for the resulted bleached oils with the unbleached and control ones bleached with raw bleaching earth, it was concluded that using nano-particles bleaching earth had high bleaching efficiency % in reducing color indices (25.0%, 28.6%, 25.9%) for oils bleached with raw bleaching earth to (62.5%, 71.0%, 63.0%) for oils bleached with nano bleaching earth. Peroxide values (3.08, 1.90, 1.8) for oils bleached with raw bleaching earth were reduced to (1.43, 0.50, 0.30) for oils bleached with nano bleaching earth. Spectral absorbencies (second oxidation products) at 232 nm were (1.789, 1.741, 1.295) for oils bleached with raw bleaching earth were reduced to (1.415, 1.650, 1.147) for oils bleached with nano bleaching earth, whereas at 270 nm, the values were (0.415, 0.374, 0.199) for oils bleached with raw bleaching earth that were reduced to (0.399, 0.343, 0.190) for oils bleached with nano bleaching earth.

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