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Decolorization of Sunflower Oil by Nanocarbon Obtained from Pyrolysis of Liquid Products

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ABSTRACT

The decolorization process of neutralized sunflower oil using nanocarbon and bleaching earth obtained from pyrolysis of liquid products and activated carbon was comparatively studied and the influence of parameters such as time, temperature and the amount of carbon on the process was investigated. The results of bleaching sunflower oil revealed that the addition of 1% of nanocarbon make better the parameters such as temperature, time and the amount of adsorbents and increases the quality pointers of oil.

INTRODUCTION

More than 90% of oils and fats used for human consumption are obtained from plants. The major vegetable oils present in the market are soybean, cottonseed, canola, sunflower, corn, peanut, palm kernel and coconut oils. Other vegetable oils like olive, rice bran, safflower, sesame and other specialty oils are not extensively used due to their availability and cost. Unrefined oils contain phospholipids, sterols, tocopherols, alcohols, hydrocarbons, and fat-soluble vitamins [1-3].

Crude sunflower oil is a vegetable oil rich in minor components which have nutritional attributes. These components consist of carotenoids, chlorophyll and related compounds. Besides, crude edible oil contains soap residues, phosphatides, pesticides, polycyclic aromatic hydrocarbons and metals at trace concentrations and mentioned substances affect the quality of the end-product by alteration of its taste and color, the process efficiency and also affect its market value. These impurities are removed at various steps in the conventional chemical refining, which includes degumming, neutralization, washing, drying, bleaching, filtration and deodorization[4-5].

The removal of pigment and other trace constituents by adsorption process (bleaching) is one of the most important steps in the vegetable oil refining and this process removes the carotenes, chlorophyll and other pigments as impurities. The process makes the oil more appealing and convenient for use. Originally bleaching was only used to obtain color from oil. Today, however, the bleaching step is used mainly to remove or convert undesired by-products to harmless ones from fats and oils. This will guarantee that such compounds do not interfere with the processing and that the requirements for human food are being met. The usual method of bleaching is adsorption. Refiners have a wide choice of adsorbents to be used and their selections of main criteria are cost and performance of the adsorbent materials. Examples of bleaching agents are natural bleaching earths, acid activated bleaching earths, synthetic silicates, synthetic resins and activated carbons [6-9].

The applications of nanocarbon materials can be related to different disciplines such as medicine, agriculture, biotechnology, drug delivery and bioprocessing (in industry) provide creative solutions and a great potential. Although nanotechnological applications have been less common in Food Science, many investigators are recently interested in the properties of the nanoparticles and nanosensors for the development of different areas such as: food safety, flavor technology and food analysis [10-12].

The main task of the presented research was to investigate bleaching process with nanocarbons obtained from pyrolysis of liquid products and as well as to investigate the possibilities of production and main technological properties of sunflower oil.

MATERIALS AND METHODS

2.1. Materials

Nanocarbon sample A1 obtained from C_5 fraction pyrolysis in the presence of a ferrocene catalyst and on the surface of MgO in 920^0C, during 20 minute and Argon atmosphere in CVD unit. Afterwards sample washed sulfuric acid for purifying Mg and other ions and then dried under vacuum. A commercial black colored activated carbon sample A2 and bleaching earth sample A3 were supplied from different companies. Sunflower oil (SF) that had been degummed and neutralized was obtained from Baku Oil Factory in Azerbaijan Republic. All chemicals and solvents were of analytical or HPLC grade and obtained from commercial source (Merck, Germany).

2.2. Methods

The bleaching experiments were conducted with different mass of bleaching materials (0, 0.5, 1, 2, 3, 4, and 5 %) at different contact time (15, 20, 25, 30, 35 and 40 minutes) and different temperatures (60-120 ^{0}C). Bleaching level was measured in the visible region (400-750nm) and the maximum absorbance was observed at 455nm and bleaching performance calculated. The microphotography of nanocarbon materials was taken with "JSM7401F" (Japan), and determination of the elements "Bruker-AXS XFlash^R 4030" detector was used.

2.3. Analysis of Oil Quality

The bleaching performance of the nanocarbon was determined on the basis of the amounts of pigments that could be removed from sunflower oil. The bleaching performance (BP) was calculated using the following formula:

$$BP = (A_0 - A_b) / A_0 \times 100\ \%$$

Where A_o and A_b are respectively the absorbance at 455nm of the sunflower oil before and after bleaching.

The color of the sunflower oil was measured by a Lovibond Tintometer Model F (Wilts, England). The melted oil sample was poured into a $5^{1/4}$ cell and the color was measured as described by AOCS Official Method Cc 13e-92. FFA content was determined by titration according to AOCS Official method Ca 5a-40. Anisidine value of the oil was determined by Bruker MPA according to AOCS Official method Cd 1e-01.The determination of chlorophyll in the bleached oil is mostly done by spectroscopy, as these compounds have characteristic absorption peaks in the red range of visible light. There are standardized methods for the determination of chlorophyll. In this study, chlorophyll content of sunflower oil was measured by a Lovibond Model PFX-I 995 as described by AOCS Cc 13d-55 [13].

RESULTS AND DISCUSSION

Synthesized nanocarbon was analysed with the scanning electron microscopy and it was determined that, in 100 times enlarged description (Fig 1.a.) carbon materials visible in the form of lent or lamella are organized tubes. These tubes are clearly visible in 10000 times magnified microphotography (Fig 1.b). The length of tubes is 100-300nm, diameter is 3-10nm. Protrusions on tubes clearly visible in 100000 times enlarged description (Fig 1.c), it may be due to defect elements in the structure of nanocarbon.

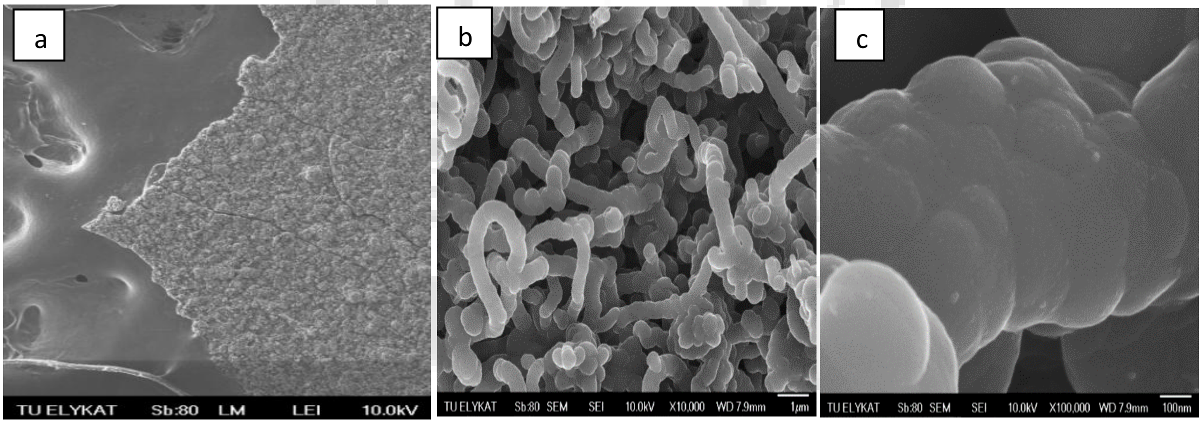

Fig 1: (a, b, c). The microphotography of nanocarbon samples obtained pyrolysis of C_5 fraction

According to element analysis, nanocarbon obtained from C_5 fraction consists of 99,16% C, 0,11% Fe, 0,31% O, 0.03% Mg and 0,26% H elements. The synthesized carbon nanotubes were compared with activated carbon and conventional bleaching earth in the bleaching process of sunflower oil. The effect of different parameters such as time, temperature and dosage were investigated.

There are numerous interactions between the process variables that influence the removal of oil contaminants and the efficiency of the bleaching process. A single change of a given operational parameter can cause many changes in the oil properties at the same time - some good and some bad. The table 1 shows the effect of the most common processing variables on the most common quality parameters. The effect of dosage and type on the removal of color, chlorophyll, anisidine value (AV) and FFA is given in table. The reason for remaining stable AV in bleaching process with nano carbon and activated carbon due to low temperature and short time. Also, The FFA of sunflower oil is minimized when nano carbon using bleaching process.

Table 1. The analysis results of sunflower oil in different refining stages

Oil sample	FFA, %	Anisidine value	Color, red	Chlorophyll, mq/l
Crude oil	2.2 ± 0.1	2.26 ± 0.5	6.2 ± 0.2	0.32 ± 0.05
Neutralized oil	0.6 ± 0.1	3.56 ± 0.5	4.4 ± 0.2	0.26 ± 0.05
A1 (nano carbon), 1 % dosage	0.4 ± 0.1	3.62 ± 0.5	0.9 ± 0.2	0.02 ± 0.05
A2 (activated carbon), 4 % dosage	0.5 ± 0.1	3.61 ± 0.5	1.0 ± 0.2	0.06 ± 0.05
A3 (bleaching earth), 5 % dosage	0.7 ± 0.1	3.74 ± 0.5	1.4 ± 0.2	0.16 ± 0.05

Effect of temperature

As it is obvious, the temperature for the bleaching process of oil typically ranges in 90–125^{0}C. Temperature effects oil viscosity and adsorption kinetics. Oil viscosity decreases with increasing temperature resulting in better dispersion of particles, improved adsorbent oil interactions, and flowability. A higher temperature may be beneficial with removing chlorophyll, producing color, and filtration rates, however it deteriorates deodorized color and increases the speed of oxidation reactions [14, 15]. As it is shown in Fig. 2, the bleaching performance (BP) were increased with respect to increased temperature from 60 to 120^{0}C and the highest bleaching performance was obtained at 110 ^{0}C with 1% dosage of sample A1, 4% dosage of sample A2 and 5 % dosage of sample A3 during the contact time of 35 minutes. Sample A1 (nanocarbon) and A2 (commercial activated carbon) reached a maximum bleaching performance 86 % at 110 ^{0}C, thus performing better than A3 (commercial bleaching earth), 77%. After 110 ^{0}C, the bleaching performance remained constant [16, 17].

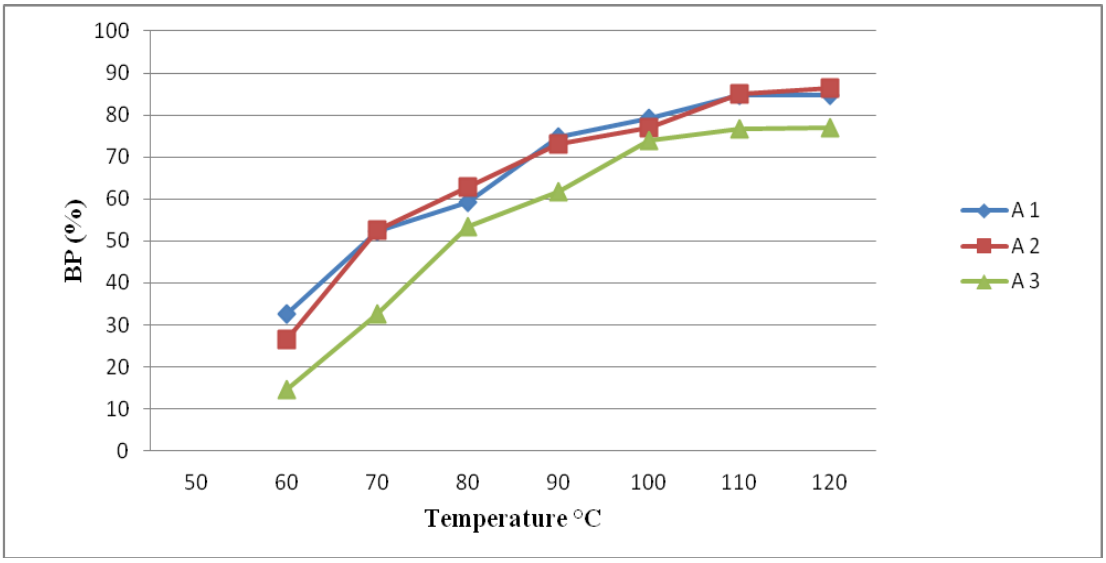

Fig 2: Effect of temperature on bleaching performance (BP) (35 minutes, 1 % dosage of samle A1, 4% dosage of sample A2 and 5% dosage of sample A3).

Effect of Contact Time

Contact time refers to the total time that the adsorbent is in contact with the sunflower oil. Time typically ranges between 15 and 45 minutes, with 20 to 30 minutes being the most common. The positive effect of increased contact time is that it may improve bleached color and chlorophyll removal. Due to the danger of color reversion, the contact time between oil and the adsorbent should not be too long. The recommended contact time is no longer than 40 min [18].

The effect of contact time on bleaching of sunflower oil with commercial bleaching earth and activated carbon was studied for comparison with the nanocarbon. It was observed that the adsorption of pigments increased with increasing contact time. As it is obvious from Fig. 3, although the bleaching curve for sample A2 is similar to sample A1 the latter performed slightly better. The removal of pigments by adsorption process on all samples started 15 minutes; sample A1 and A2 showed maximum adsorption after 30 minutes with 1% dosage of samples A1, 4% dosage of sample A2 and 5% dosage of sample A3 and at 110 ^{0}C. However, sample A3 reached maxima after 40 minutes. With increasing contact time, no dramatical enhancement was observed for these samples.

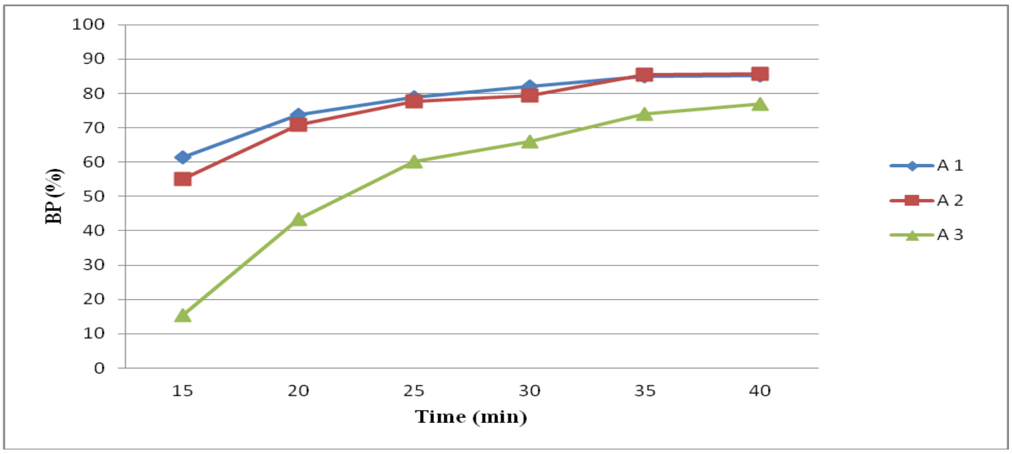

Fig 3: Effect of bleaching time on bleaching performance (BP) (110 ºC, 1% dosage of samples A1, 4% dosage of sample A2 and 5% dosage of sample A3).

Effect of dosage

The amount of adsorbents in bleaching process is an important factor. Bleaching adsorbent dosage requirements vary depending on the type and quality of the oils. The variance covers a range of typically 0.1 to 2.0%, but can increase up to 5.0% in some special cases. In this study, the bleaching experiments were conducted with different mass of adsorbent (0.5, 1, 2, 3, 4 and 5 %) [19, 20]. Fig. 4 shows that, the bleaching performance is directly proportional with increasing mass of adsorbents. The best result for bleaching process of neutralized sunflower oil by 86% was observed with 1% of sample A1 within the contact time of 35 minutes and temperature of 110°C. Compared with A1, approximately 4% of sample A2 gave the same result of the bleaching performance by 86% within the contact time of 35 minutes. Sample A3 reached to an optimum value with 5% dosage and further increase in dosage had only a little effect on performance.

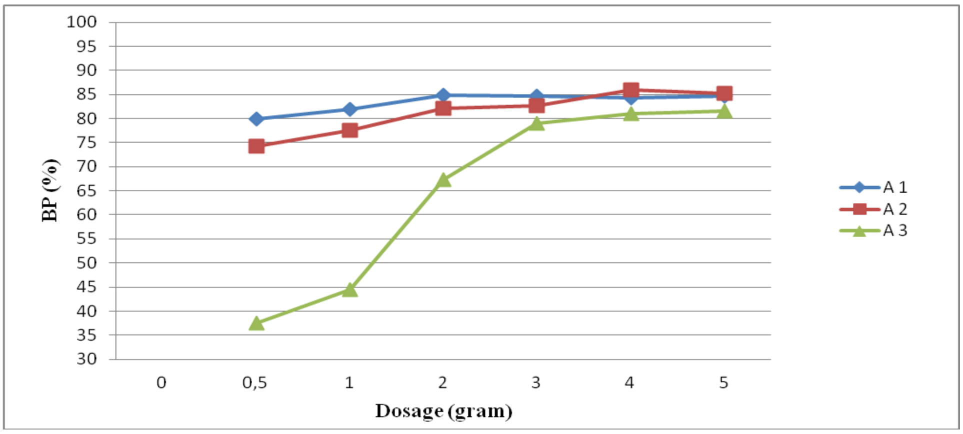

Fig 4: Effect of dosage on bleaching performance (BP) (110 ºC, 35 minutes).

CONCLUSIONS

In this study, the importance of nanocarbon in bleaching process of sunflower oil was assessed. The result of the bleaching process of neutralized sunflower oil by using nanocarbon indicates that the bleaching performance increases with respect to contact time, temperature and dosage. Absorbance and color results directly prove that nanocarbon removes the unwanted pigments from oil. Therefore, this nanocarbon sample can be used to bleach sunflower oil instead of activated carbon and bleaching earth.

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