



Investigation of using bleaching earth and activated carbon mixture in sunflower oil refining

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Abstract: Adsorption is one commonly used technique for treatment of sunflower oil. In this study, activated carbon and bleaching earth as a bleaching agent mixed with certain proportions and 1% of the mixture added to sunflower oil in the bleaching process. The combination of bleaching earth and activated carbon produced higher adsorption capacity than the single bleaching earth. This article focuses more particularly on heavy metals and polycyclic aromatic hydrocarbons (PAHs) removal. It was detected that, the mixture is an excellent adsorbent in the adsorption of PAHs and metals from sunflower oil with the highest adsorption capacity. The results showed that, the adsorption of metals and PAHs depend strongly on activated carbon and decreased with increasing activated carbon mixture and the maximum adsorption was reached after using B5 (95 % bleaching earth and 5 % activated carbon combination).

Keywords: *sunflower oil, bleaching, bleaching earth, activated carbon, polycyclic aromatic hydrocarbons (PAHs)*

1. INTRODUCTION

Most vegetable oils are obtained from the seeds and fruits of plants. Vegetable oils are eaten directly and also used in the production of margarines, frying oils and other edible products in food industry. Besides the food industry, they also have applications in leather, paint, rubber, oleo-chemical, textile and pharmaceutical industries. Sunflower oil is composed mainly of triacylglycerol and a small amount of monoacylglycerols, diacylglycerols, phospholipids, tocopherols, sterols, peroxides, metals, free fatty acids, carotenoids, chlorophylls and waxes and so on. Carotenoids and chlorophylls give sunflower oil light-amber color, turning to pale yellow upon the bleaching process [1].

It is important to have proper refining process in order to produce high quality finished product with specified quality range that meet user's requirements. The aim of refining process is to remove colored particles, phosphatides, trace metals, and free fatty acids which may produce oxidation products leading to decomposition [2]. There are basically two types of refining processes available in the vegetable oils industries, namely, chemical and physical refining [3, 4]. Chemical refining involves degumming, neutralization, bleaching, dewaxing, and deodorization process. Among these stages, bleaching is the most critical process; it helps to improve the flavor, taste, appearance and stability of the vegetable oil [5]. Bleaching stage is designed to remove not only pigments, but also other impurities such as soaps, phosphatides and free fatty acids. The main method of bleaching is adsorption of the coloring substances on adsorbents. In vegetable oil industry, factories usually use acid activated bleaching earth (bentonite), natural bleaching earth, activated carbon and synthetic silicates [6, 7].

During the bleaching process, the oil is brought into contact with bleaching substances that adsorb undesired particles. Then, the adsorbent and the adsorbate are filtered off, and the oil leaves the process with the desired color. However, bleaching agents may play as a catalyst for oxidation in the participation of oxygen at high temperatures. These oxidation products lead to degradation of triacylglycerol and final product shelf life is reduced. Therefore the bleaching process is carried out under vacuum. Oxidation products should also be removed during bleaching to provide suitable shelf life oil. Lastly, some heavy metals should also be removed in this stage [8, 9]. Color is an important indicator of bleaching effectiveness, soaps, phosphorus, peroxide, and anisidine values are also some key quality indicators associated with the bleaching process. Furthermore, for an efficient bleaching process you must remove some contaminants before bleaching in the refining process. For example, phosphorus (P) after degumming and neutralization processes should be reduced to 10 mg/kg, free fatty acids (FFA) to 0.1 % and soaps to 50 mg/kg [10, 11].

Adsorption is the separation process with the help of special adsorbents. There is a variety of adsorbents. The most well-known are bleaching earth (BE), activated carbon (AC), synthetic silicates, and synthetic resins in vegetable oil industry. AC is an efficient adsorbent, which has a large internal surface area and large pore volume. Good porous texture gives activated carbon very high adsorption capacity in the removal of organic compounds such as PAHs, chlorophyll from vegetable oil. It is known that the treatment of oils and fats with certain activated carbons leads to an effective removal especially of the 'heavy' PAHs. The activated carbons can be used alone or together with the bleaching earth to adsorb PAHs. Activated carbons available commercially are produced from various base materials and have consequently different adsorption capacity for PAHs. Some manufacturers offer activated carbons with a standardized efficiency. The removal of the heavy PAHs is done by means of activated carbons. But light PAHs removed from oil in deodorization. Therefore activated carbon treatment and deodorization complement each other ideally to obtain fats and oils free of PAH [12-14].

Heavy metals such as cadmium, arsenic and mercury enter to vegetable oil from environment. Copper and iron are found in the vegetable oil naturally; they can also enter the oil from iron and copper-containing equipment during processing. Codex Alimentarius and the European Commission have been determined limit values of these metals in vegetable oil [15-16].



Removal of metals and PAHs using of AC and bleaching earth combination was investigated in this work, and it was found that the ratio of 5 : 95 activated carbon and bleaching earth combinations are more effective in the treatment of sunflower oil than single bleaching earth.

2. MATERIALS AND METHODS

2.1. Materials

Activated carbon sample A1 obtained from C₅ fraction pyrolysis in the presence of a ferrocene catalyst and on the surface of Al₂O₃ in 920°C, during 20 minute and Argon atmosphere in CVD unit. Then chemical agents (Mg, Al and other ions) are removed by washing with sulfuric acid, which leaves a highly porous structure and then dried under vacuum. A bleaching earth sample A2 was supplied from a commercial company. After that, bleaching earth and activated carbon are mixed certain proportions and then 1 % mix is added to sunflower oil bleaching process. The crude and neutralized sunflower oil (SF) was obtained from Baku Oil Factory in Azerbaijan Republic. All reagents, solvents and standard stock solutions used were from Merck.

2.2. Methods

The bleaching of sunflower oil was carried out according to AOCS Cc 8f-91. Initially, 100 gram of sunflower oil was poured into a 500 ml Erlenmeyer flask. Bleaching earth and activated carbon are mixed certain proportions which shown below: B1 - 1 % activated carbon and 99 % bleaching earth mixture; B2 - 2 % activated carbon and 98 % bleaching earth mixture; B3 - 3 % activated carbon and 97 % bleaching earth mixture; B4 - 4 % activated carbon and 96 % bleaching earth mixture; B5 - 5 % activated carbon and 95 % bleaching earth mixture. Then 1 gram of sample B1 was added to the 100 gram sunflower oil and mixed. The temperature was maintained at 40°C for 30 minutes. Then, the mixture was filtered through Whatman No 4 filter paper. This process was repeated with B2, B3, B4 and B5 samples in order to determine the effect of increase in activated carbon proportion. The effect of temperature was studied at 60, 70, 80, 90 and 100 °C[17].

2.3. Analysis of oil

Trace metals

The metal analysis was made on Perkin Elmer Nexion 300 ICP-MS. Approximately 1 gram samples were weighed and digested with 9 mL HNO₃ and 1 ml H₂O₂ in microwave digestion system. After complete digestion and removal of acid, the samples were adjusted to 5 mL with ultrapure water, and ready for measurement. Also, one blank sample was subjected to same procedure. Appropriate quality assurance and quality control procedures were followed to ensure the reliability of obtained data[18]. The experiments were performed in duplicate.

Polycyclic aromatic hydrocarbons (PAHs)

The removal processes of PAHs from sunflower oil with activated carbon have been revised in this article. The PAHs were analyzed by on-line coupling of donor-acceptor complex chromatography (DACC) and HPLC with fluorescence detection according to ISO 22959 in vegetable oils. PAHs which can be determined by this method are: anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[e]pyrene, benzo[a]pyrene, perylene, benzo[ghi]perylene, anthanthrene, dibenzo[a,h]anthracene, coronene, indeno[1,2,3-cd]pyrene, benzo[a]fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene [19, 20]. Calibration was performed using standard PAH mixtures at seven different concentrations: 0.5, 1, 2, 5, 10, 20, and 50 µg/L (conversion to the samples of 2, 4, 8, 20, 40 and 200 µg/kg) for all 17 PAHs. The linearity of the calibration curves was assessed by the peak area. Good linearity was observed in the concentration range studied with correlation coefficients >0.999.

3. RESULTS AND DISCUSSION

Adsorption has been widely studied as an effective technique for removing organic contaminants and metals from vegetable oil. The removal efficiency is influenced by various factors such as adsorbent types, bleaching time, adsorbent dosage and temperature and so on. In this study, metal and PAH content were determined to see oil quality before and after bleaching process.

3.1 Adsorption of PAHs

PAHs contaminated vegetable oils pose a threat to human health and ecology. During the refining process all PAHs should be eliminated. Heavy PAHs are eliminated by the deodorization step, whereas light ones are eliminated when treated with activated carbon during the bleaching step. The one of main proposes of this work was to adsorb this pollutants from sunflower oil using activated carbon mixed samples[21].

In order to establish the concentration for maximum adsorption of PAHs from sunflower oil, bleaching earth and activated carbon mixed. The study was carried out with 1 gram adsorbent in 100 ml sunflower oil. The changes in the amount of PAHs depending on the adsorbents are reported in the Table 1. The bleaching using bleaching earth sample (A2) shows that there was no significant change in the removal of PAHs. However, the maximum PAH removal was achieved at using activated carbon (A1). When comparing B1 and B5 mixtures, PAH removal increased with increasing activated carbon in the mixture. The lowest adsorption capacity was achieved at using B1 and it slightly increase with increasing the activated carbon in mixture. Both B4 and B5 showed similar behavior at PAH removal, although benzo (b) fluoranthene removal with

B5 is considerably higher than B4. It is clear that, activated carbon adsorbed especially heavy PAHs. The heavy PAHs removal was significantly higher than light PAHs removal using B5.

The chromatograms of a standart PAH mixture (1) and crude sunflower oil (2) are shown in Figure 1. It is clear that, 15 PAHs found in crude sunflower oil and their quantity are 11.05 µg/kg and benzo(b) fluoranthene is the highest PAH (1.18 µg/kg) in the sunflower oil.

Moreover, temperature impact on PAHs removal was investigated and it was determined that increase of temperature does not impact to removal PAHs. Bleaching in 100 °C temperature is not differ compared to 40 °C in PAH removal, but color removal in 100 °C is more than 40 °C due to bleaching earth comparing B1 and B5.

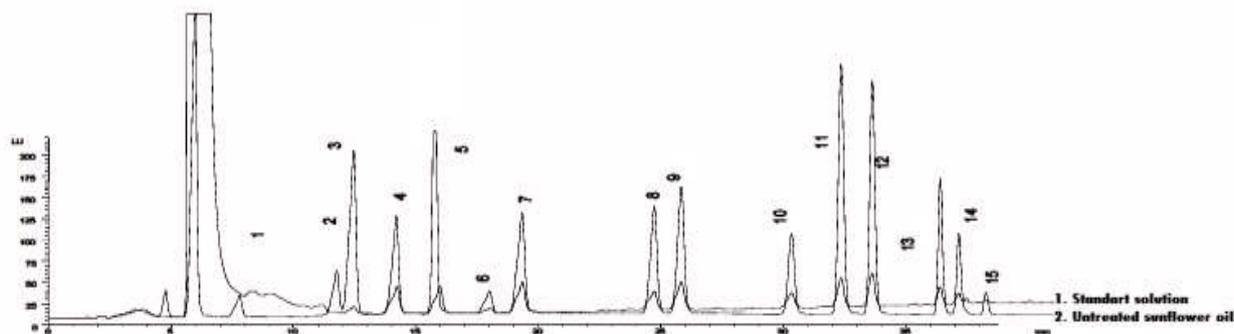


Figure 1. Chromatograms of standard solution (1) and crude sunflower oil (2).

Table 1. The analysis results of the polyaromatic hydrocarbon contamination (PAH) of sunflower oil samples before and after bleaching.

| Adsorbents PAHs | Sunflower oil | Expanded uncertainty | A1 | A2 | B1 | B2 | B3 | B4 | B5 |
|------------------------------------|---------------|-------------------------|-----------------|--------------|-------------|-------------|-------------|-------------|-----------------|
| Naphtalene | 0.62 | 0.082 | 0.63 | 0.61 | 0.61 | 0.62 | 0.63 | 0.61 | 0.61 |
| Acenaphthylene | 0.55 | 0.059 | 0.56 | 0.55 | 0.54 | 0.57 | 0.56 | 0.54 | 0.56 |
| Acenaphthene | 0.72 | 0.073 | 0.71 | 0.72 | 0.72 | 0.73 | 0.71 | 0.72 | 0.71 |
| Fluorene | 0.79 | 0.077 | 0.78 | 0.79 | 0.79 | 0.8 | 0.78 | 0.79 | 0.78 |
| Phenanthrene | 0.72 | 0.106 | 0.71 | 0.72 | 0.72 | 0.71 | 0.73 | 0.71 | 0.72 |
| Anthracene | 0.56 | 0.054 | 0.56 | 0.57 | 0.57 | 0.56 | 0.55 | 0.57 | 0.56 |
| Fluoranthene | 0.79 | 0.039 | 0.8 | 0.79 | 0.8 | 0.78 | 0.79 | 0.79 | 0.8 |
| Pyrene | 0.84 | 0.068 | 0.83 | 0.83 | 0.84 | 0.82 | 0.83 | 0.84 | 0.83 |
| Benzo (a) anthracene | 0.78 | 0.079 | 0.78 | 0.79 | 0.78 | 0.79 | 0.77 | 0.78 | 0.78 |
| Chrysene | 0.83 | 0.09 | 0.82 | 0.82 | 0.82 | 0.83 | 0.81 | 0.82 | 0.81 |
| Total light PAHs(µg/kg) | 7.2 | | 7.18 | 7.19 | 7.19 | 7.21 | 7.16 | 7.17 | 7.16 |
| Benzo(b) fluoranthene | 1.18 | 0.048 | < 0.5 | 1.18 | 0.97 | 0.89 | 0.76 | 0.55 | < 0.5 |
| Benzo(k) fluoranthene | 1.1 | 0.061 | < 0.5 | 1.11 | 0.93 | 0.67 | 0.52 | < 0.5 | < 0.5 |
| Benzo(a) pyrene | 0.58 | 0.043 | < 0.5 | 0.59 | 0.51 | < 0.5 | < 0.5 | < 0.5 | < 0.5 |
| Dibenzo (ah) anthracene | 0.53 | 0.057 | < 0.5 | 0.51 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 |
| Benzo(ghi) perylene | 0.64 | 0.118 | < 0.5 | 0.63 | 0.6 | 0.51 | < 0.5 | < 0.5 | < 0.5 |
| Total heavy PAHs(µg/kg) | 4.03 | | < 0.5 | 4.02 | 3.01 | 2.07 | 1.28 | 0.55 | < 0.5 |
| TOTAL PAHs (µg/kg) | 11.05 | | 7.18 | 11.21 | 10.2 | 9.28 | 8.44 | 7.72 | 7.16 |

Value showed in the Table 1 should be multiplied by the expanded uncertainty for corresponding concentration in order to receive the result with uncertainty. Results are given in the following form:

Results = Value obtained ± Expanded uncertainty x Value obtained



3.2 Adsorption of trace metals

The determination of trace metals in vegetable oils is an important criterion for the assessment of oil quality. The adsorption of some metals from sunflower oil onto activated carbon and bleaching earth mixture was investigated under bleaching conditions, 100 °C temperature and 30 minutes contact time. The results were obtained as the average of two replicates of each sample and are shown in Table 2. The results showed that the untreated sunflower oil contained many elements (Fe, Pb, As, Hg, Ni, Cd, Cu, Sn and Zn) which are useful or harmful to human health, and the concentrations ranged from 1.4 to 38.1 µg/kg [21, 22].

The adsorption effect of metals for both bleaching earth and activated carbon, and their mixtures were illustrated in Table 2. As shown, the metals adsorption capacity using activated carbon (A1) is higher than bleaching earth (A2). The highest metal adsorption capacity was achieved at using B5 and the lowest adsorption capacity was achieved at using B1. B5 remove metals more than B1 due to the amount of activated carbon. Generally, the highest result is shown B4 and B5, the result of 7 metals are negative bleaching with B5. It can be concluded that activated carbon (A1) is more appropriate adsorbents for the removal of metals from sunflower oil. Moreover, the results showed that the concentrations of heavy metals in bleached sunflower oil sample was low, all of which met the national hygiene standards and the dietary intakes of the selected heavy metals pose no significant health risk to population.

Table 2. The analysis results of the metals of the crude and bleached sunflower oil samples.

| Metals, µg/kg | Crude sunflower oil | A1 | A2 | B1 | B2 | B3 | B4 | B5 |
|---------------|---------------------|-----------|------------|------------|------------|-----------|-----------|-----------|
| Pb | 13.5±0.96 | < 0.5 | 6.21±0.44 | 5.4±0.38 | 4.11±0.29 | 2.84±0.2 | 1.52±0.11 | < 0.5 |
| As | 11.2±0.61 | < 0.5 | 11.1±0.61 | 9.94±0.54 | 6.54±0.36 | 3.49±0.19 | 1.07±0.06 | < 0.5 |
| Hg | 5.4±0.34 | < 0.5 | 3.63±0.23 | 1.87±0.12 | 0.66±0.04 | < 0.5 | < 0.5 | < 0.5 |
| Ni | 16.8±1.38 | 0.62±0.05 | 15.44±1.27 | 12.62±1.04 | 9.07±0.75 | 4.2±0.35 | 2.17±0.18 | 1.74±0.14 |
| Cd | 8.3±0.48 | < 0.5 | 3.7±0.22 | 2.8±0.18 | 1.05±0.06 | 0.62±0.04 | < 0.5 | < 0.5 |
| Cu | 38.1±1.17 | 1.48±0.04 | 24.96±0.77 | 20.81±0.64 | 14.94±0.46 | 8.85±0.27 | 3.12±0.1 | < 0.5 |
| Fe | 26.4±1.61 | < 0.5 | 19.75±1.21 | 17.15±1.05 | 11.6±0.71 | 7.1±0.43 | 4.23±0.26 | 0.97±0.06 |
| Sn | 1.4±0.11 | < 0.5 | 0.92±0.07 | 0.8±0.06 | 0.64±0.05 | < 0.5 | < 0.5 | < 0.5 |
| Zn | 51.1±3.28 | < 0.5 | 51.11±3.28 | 30.95±2 | 18.84±1.21 | 6.62±0.42 | 1.54±0.1 | < 0.5 |

4. CONCLUSION

The analysis results show that the studied adsorbents can effectively adsorb PAHs and heavy metals from sunflower oil. The lowest adsorption capacity was found using B1 (1 % activated carbon and 99 % bleaching earth mixture) and the highest adsorption capacity was found using B5 (5 % activated carbon and 95 % bleaching earth mixture). Both B4 (4 % activated carbon and 96 % bleaching earth mixture) and B5 showed very familiar behavior at PAH removal, but B5 results are higher than B4. Moreover, B5 metal adsorption capacity was very high than B4. Also, it was determined that, temperature does not impact on PAH removal. It can be concluded that, the combination of activated carbon and bleaching earth is a good method to enhance the capacity of bleaching earth to adsorb contaminants, and 5 % activated carbon and 95% bleaching earth combination (B5) exhibited a highest adsorption capacity and can be considered as the best adsorbent for the removal of PAHs and metals from vegetable oil.

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