Using natural zeolites to improve the quality of unrefined vegetable oils

L V Tereshchuk¹, K V Starovoytova¹* and A N Crol¹

¹Kemerovo State University, 6 Krasnaya str., Kemerovo 650043 Russia

E-mail: centol@mail.ru

Abstract. The article is devoted to the study of the possibility of using natural zeolites as adsorbents for the purification of unrefined vegetable oils, intended for direct consumption in food, from undesirable concomitant substances. To increase their sorption capacity, various activation methods were used, such as physical and chemical. The best sorption properties were found in zeolites, activated by the complex method (heat and acid treatment). Conducted refining of unrefined sunflower oil allowed to increase its quality to meet the requirements of the state standard for the highest grade oil.

1. Introduction

The beneficial properties of sunflower oil are determined mainly by its fatty acid composition, which to a very large extent depends on the climatic conditions of the area, cultivation methods, and varietal characteristics of sunflower. Among the many cultivated varieties on the basis of the predominant fatty acid in the composition, there are traditional low-oleic acids, as well as later derived medium and high-oleic acids. The sunflower seed oil of traditional varieties contains linoleic acid most (up to 75%). In the oil of high-oleic varieties, the predominant acid is oleic, its content reaches 70%, which makes this oil closer in properties to olive. High oleic oil has a greater, compared to linoleic varieties, oxidation resistance and can be successfully used for direct consumption, for example, as a salad dressing. It should also be noted that oleic acid, which does not possess the physiological activity of essential fatty acids, enhances the action of linoleic acid, being its synergist. The nutritional value of high oleic sunflower oil, especially unrefined, is determined not only by the high content of unsaturated oleic and linoleic acids, but also by the fact that it contains the highest amount of tocopherols (738 ± 82 mg / kg) and tocotrienols (270 ± 61 mg / kg), with E-vitamin activity. Refining according to the classical scheme leads to almost complete loss of these substances, which significantly reduces the nutritional value.

Sunflower oil, intended for direct consumption in unrefined form, is obtained only by pressing from the collapsed sunflower seeds. After pressing in unrefined vegetable oils, along with the presence of free fatty acids, there are about 2% non-fatty substances belonging to the unsaponifiable fraction. They consist of phospholipids, sterols, waxes, hydrocarbons, pesticides, proteins, trace amounts of metals and pigments [1]. Most of the unsaponifiable substances are undesirable in oil, and their removal is an urgent task in the problem of improving the quality of unrefined vegetable oils. At the same time, the cleaning of oils should be strictly directed and not accompanied by the removal of useful components, which is observed during classical refining [1]. In addition to physico-chemical and organoleptic indicators, safety indicators, including the content of toxic elements such as iron,
lead and arsenic, as well as indicators of oxidative damage (acid and peroxide number [2]) are important in assessing the quality of oils. Metals are usually found in oilseeds in trace amounts, the highest concentration in plants is reached during the growing season. For removal of vegetable oils of compounds like chlorophyll, carotene, phospholipids, peroxides, soaps in the oil and fat industry use highly active polar sorbents supplied by foreign companies, mainly natural active or chemically activated aluminosilicate bentonite bleaching clays. At present, chemisorption and acid catalysis are mainly used for these purposes [3], [4].

Recently, interest in natural zeolites has increased, and their multifaceted useful properties have been identified. Zeolite is an aluminosilicate with a skeletal structure containing voids occupied by large ions and water molecules that have significant freedom of movement, which leads to ion exchange and reversible dehydration. The zeolite lattice is constructed from silicon and aluminum-oxygen tetrahedra SiO₄ and AlO₄, which are the primary structural units and are designated TO₄, where T is a silicon or aluminum atom. The main structural element of zeolites is a tetrahedral orthogroup SiO₄ of the metal type with a cation in the center surrounded by four oxygen atoms located at the vertices of the tetrahedron, where part of the Si⁴⁺ ions are replaced with Al³⁺ ions in order for the crystal to maintain stability, it is necessary to maintain its electrical neutrality. The negative charge of the alumina-oxygen tetrahedron is compensated by cations of alkali, alkaline-earth and other metals [5].

Despite the virtually absent literature data on the use of zeolites in the oil and fat industry, it can be assumed that zeolites can be used as adsorbents for the extraction of related substances from vegetable oils. Research on zeolites as a new sorbent in the oil and fat industry is an urgent task that requires its solution.

The aim of the work was to study the possibility of using zeolites in the oil and fat industry as adsorbents for the purification of unrefined vegetable oils (intended for direct consumption) from unwanted concomitant substances.

2. Materials and Methods

We selected the samples of high oleic sunflower oil, obtained by hot pressing, as well as natural zeolites of the Pegasus field in the Kemerovo region. To study the phase composition of zeolite rocks, an X-ray phase analysis was used. To determine the chemical composition of the zeolite tuff, an X-ray fluorescence analysis was used. The fatty acid composition of vegetable oils was determined on an Agilent 7890A gas chromatograph [5]. Determination of the color of vegetable oils was also carried out [6]. The content of free fatty acids in the oil before and after filtration through a layer of zeolites was determined by the level of acid number [7]. The content of toxic elements in oils was determined by the atomic absorption method [8].

3. Results

We were faced with the task of obtaining unrefined sunflower oil, intended for direct consumption, which meets the requirements of the standard for unrefined oil of the highest grade [1]. To solve this problem, the possibility of using natural zeolites for cleaning press oil from free fatty acids and related non-fatty substances was investigated.

The X-ray fluorescence analysis showed that the zeolite tuffs of the Pegasus field in the Kemerovo region are characterized by the following chemical composition: Na – 0.92%, SiO₂ – 66.8%, TiO₂ – 0.4%, Al₂O₃ – 13.92%, Fe₂O₃ – 3.60%, FeO – 0.05%, MgO – 1.66%, CaO – 4.92%, K₂O – 0.88%, SiO₂ – traces, P₂O₅ – 0.06%, Pb – 0.002%, Cu – 0.0044%, Co – 0.00055%, Mo – 0.00036%, Zn – 0.0069%. Along with zeolites, volcanic glass, quartz, feldspar, mica, and clay minerals are present in the tuff. It is characterized by the following unit cell parameters: a = 17.73 Å, b = 17.82 Å, c = 7.43 Å, β = 116 Å, density 2.198 g/cm³, a unit cell volume = 210 Å³.

Before carrying out a trial purification of vegetable oil, the zeolites were dried. The dried zeolite has a free-flowing structure, which facilitates its grinding. Next, the zeolites were crushed and sieved to different fractions, with a particle size of up to 0.25 mm, 0.25–0.4 mm, 0.4–0.65 mm, 0.8–1 mm. In the course of the
study, it was found out that the fraction with a particle size of up to 0.25 mm has the best adsorption properties.

The sorption capacity of zeolites is determined by the size of the free surface. Natural zeolites contain a lot of water, which covers the entire active surface and reduces its sorption capacity [9]. The zeolite fraction was heat treated at different calcination temperatures. During heat treatment, part of the adsorption water leaves, which leads to the release of the surface of the sorbent. Found that both excessive moisture content in the sorbents, and excessive dehydration greatly reduces their activity. Adsorption water is retained by the zeolite mainly by forces of a physical nature and therefore a significant part is removed at temperatures up to 350–380 °C. Chemically bound water is removed at sufficiently high temperatures. In this regard, we carried out the activation of zeolites at a temperature range from 200 °C to 700 °C.

Cleaning of sunflower oil from related substances was carried out by thermally activated zeolites by contact method with the following process parameters: the amount of adsorbent is 2.5% by weight of the oil, mixing with a paddle stirrer at a speed of 60 min⁻¹, at a temperature of 80 °C, for 30 minutes. Data on changes in color and acid numbers of sunflower oil are presented in Table 1.

| Activation temperature, °C | Values of indicators | Before cleaning | After cleaning | Before cleaning | After cleaning |
|---------------------------|----------------------|----------------|----------------|----------------|----------------|
|                           | Color number (mg I₂) | Acid number (mg KOH / g) |                |                |                |
| 200                       | 35                   | 4.67           | 1.34           |
| 300                       | 35                   | 4.67           | 1.38           |
| 400                       | 35                   | 4.67           | 1.50           |
| 500                       | 35                   | 4.67           | 1.35           |
| 600                       | 35                   | 4.67           | 1.35           |
| 700                       | 35                   | 4.67           | 1.35           |

However, our research also shows that the use of thermal activation only does not lead to the removal of the entire complex of related substances. The number of pigments, determined by the indicator “color number” decreases slightly (from 35 mg iodine to 30 mg iodine). The decrease in the content of free fatty acids is noticeable, since acid number significantly decreased to 1.34 - 1.38 mg KON / g. This is probably due to the fact that these free fatty acids are more easily adsorbed on thermally activated zeolites than chlorophylls and carotenoids. Thus, it can be concluded that heat treatment is an insufficient measure of the activation of the sorption capacity of zeolites. At the next stage, chemical modification of zeolites was performed.

The activations were carried out as follows: 50 g of dry ground zeolites and 250 ml of hydrochloric acid solution, taken at the rate of 50% acid by weight of dry zeolites, were placed in a 500 ml round flask equipped with reflux condenser and stirrer. The treatment was carried out at different temperatures, with stirring for different periods of time, from 30 minutes to 6 hours. The activated zeolite was filtered on a Buchner funnel, washed with distilled water heated to (40–50) °C to neutrality by methyl orange, then dried in a thermostat at (105–110) °C. After this, the sorption properties of the modified zeolite were studied. The results of the research indicators of quality and safety of the sample, purified by chemically activated zeolites are presented in Table 2.

Thus, our research clearly shows that the maximum increase in adsorption activity with respect to pigments takes place when zeolite is treated with a solution of 10% hydrochloric acid at a temperature of 80 °C for (4.5–5.0) hours, with a quantitative ratio of solid and liquid phases of 1: 4. We found that the zeolite in the activation process responds well to processing. Suspension is well transported when being settled, it quickly separates and is freely filtered.
References

Acknowledgments

Table 2. The results of raw sunflower oil filtration by thermally treated and chemically activated natural zeolites.

| Indicators                          | Value before filtering | Value after filtering | Требования НД [1,11]. |
|------------------------------------|------------------------|-----------------------|-----------------------|
| Transparency                       | Turbid, there is sediment | Transparent with a slight turbidity | Light turbidity or “mesh” is allowed. |
| Smell and taste                    | Peculiar to sunflower oil, without foreign smell and taste | Peculiar to sunflower oil, without foreign smell and taste | Peculiar to sunflower oil, without foreign smell and taste |
| Color number, mg iodine            | 35                     | 13                    | No more 15            |
| Acid number (mg KON / g)           | 4.67                   | 1.1                   | No more 1.5           |
| Tocopherol content, mg / 100 ml    | 74                     | 71                    | -                     |
| Plumbum, mg / kg                   | Less 0.01              | Less 0.01             | No more 0.1           |
| Arsenicum                          | Less 0.03              | Less 0.03             | No more 0.1           |
| Ferrum                             | 0.79                   | 0.41                  | No more 1.5           |
| Caesium-137, Bq / kg               | 2.67                   | 1.15                  | No more 40 Bq / kg    |
| Strontium-90, Bq / kg              | 2.55                   | 1.11                  | No more 80 Bq / kg    |

4. Discussion

Processing of unrefined sunflower oil with zeolites that have undergone double activation allowed reducing the color number to 13 mg of iodine, which corresponds to the requirements of the state standard for unrefined highest quality vegetable oil; in addition, the content of tocopherols in the oil remained almost unchanged. It should be noted a significant decrease in the content of free fatty acids in the oil, as well as a decrease in the amount of iron and radionuclides 137Cs и 85Sr. Apparently, this is due to the specific ion-exchange properties of zeolites, and the presence of a large amount of silicon dioxide (66.8% of SiO2 in a content), the main component of quartz sand, a known agent used for wastewater treatment [11], [12].

5. Conclusion

Natural zeolites of the Pegassky deposit of the Kemerovo region can be successfully used in the oil and fat industry to obtain high-quality sunflower oil, suitable for both direct consumption and for food production, including baby food.

6. Acknowledgments

The authors are grateful to the staff of the laboratory of the department “Technology of food from vegetable raw materials” (KemSU), who took part in practical research.

References

[1] State Standards 2013 Sunflower oil: Technical conditions (with amendment) – GOST 1129-2013 (Moscow, Russia)
[2] Anirudhan T S, and Suchithra P S 2010 Heavy metals uptake from aqueous solutions and industrial wastewaters by humic acid-immobilized polymer/bentonite composite: kinetics and equilibrium modeling. Chem Eng J 156 pp146-56
[3] Anirudhan T S, Divya L, Bringle C D, and Suchithra P S 2010 Removal of copper(II) and zinc(II) from aqueous solutions using a lignocellulosic-based polymeric adsorbent containing amidoxime chelating functional groups. Sep Sci Technol. 45 pp 2383-93
[4] Batistela V R, Fogaca L Z, Favaro S L, Caetano W Fernandes-Machado NRC, and Hioka N 2017 ZnO supported on zeolites: photocatalyst design, microporosity and properties. Colloid Surface A. 513 20-7
[5] Anirudhan T S, Suchithra P S, and Radhakrishnan P G 2009 Synthesis and characterization of humic acid immobilized-polymer/bentonite composites and their ability to adsorb basic dyes from aqueous solutions. Appl Clay Sci. 43 336-42
[6] Cobzaru C 2012 Modified zeolites: modification of natural zeolites for catalytic applications In Handbook of Natural Zeolites (pp 185-213) (Sharjah, U.A.E: Bentham Science Publishers)
[7] Vegetable oils: Method for determination of fatty acid composition (GOST 30418-96) 1996 (Moscow, Russia)
[8] Vegetable oils: Methods for determining chromaticity (GOST 5477-2015) 2015 (Moscow, Russia)
[9] Vegetable oils: Methods for determining the acid number (GOST 31933-2012) 2012 (Moscow, Russia)
[10] Raw materials and food products: Atomic absorption method for the determination of toxic elements: GOST 30178-96 1996 (Moscow, Russia)
[11] Technical Regulations of the Customs Union 2011 Technical Regulations on oil and fat products (TR TS 024/2011) (Minsk, Belarus: Customs Union)
[12] Suchithra Padmajan Sasikala, T A Nibila, Kunnathuparambil Babu Babitha, Abdul Azeez Peer Mohamed, and Ananthakumar Solaiappan 2019 Competitive photo-degradation performance of ZnO modified bentonite clay in water containing both organic and inorganic contaminants Sustainable Environment Research 29(1)