Technology of regeneration and recycling of frying fats by using a new microgranulated nanosorbent in the catering

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Abstract. The article considers the technological capabilities and prospects for regeneration of frying fats in the catering enterprises using active filtration by a micro-granulated nanosorbent with subsequent recycling. The offered recycling technology involves the restoration of the quality of degraded frying fat with the purpose of its reuse and/or subsequent utilization. It is known that degraded frying fats contain products of oxidative and hydrolytic decomposition which vary according to their composition and structure. Actually, there is no universal technology that would provide the quality and safety indicators of frying fat for its further usage both in catering or for recycling in the market of secondary raw materials. Development of new microgranulated nanosorbent is based on fundamentally new technologies for modifying the surface of highly dispersed clay minerals of the Russian raw materials market using carbon nanomaterials. The granular sorbent is more preferable for use in catering, it allows easy separation of oil from the adsorbent without significant effort spent on filtration. The granular sorbent is lighter, more voluminous, and it significantly increases the adsorption efficiency even by contact method. The authors propose the technology of regeneration and recycling of frying fats with using new microgranulated nanosorbent in the catering enterprises.

1. Introduction

Despite the relevance of a wholesome diet, due to the tendency of modern man to lead a healthy lifestyle, there exists an obvious popularity of fast food, especially among young people, for which the food fries is dominated [1 - 4]. However, the systematic consumption of deep fried foods causes many alimentary diseases [5 - 8]. In addition, growth in production of fried potatoes is accompanied by an increase of waste of the fourth class danger to the environment which is degraded frying fats. The problem of its utilization and recycling has not yet been solved in Russia.

Nowadays there arises an issue concerning extension the shelf life of the used fried fats. For this purpose many fast food companies practice its daily passive filtering in order to remove charred particles of fried foods that accelerate the thermal oxidation of the used fat. However, the only filtration cannot remove fat-soluble polar compounds that accumulate during the frying process. One of the rational ways of saving food resources is periodic adsorption cleaning, as a stage of the process of deep frying, during the whole cycle of frying and at its final stage [9 - 17].

Regeneration of used fat is also a solution to the problem of their disposal. As a result, the regenerated fat is sold in the secondary market, where the demand for it is large enough, since the cost
of the processed fat is 60% lower than the cost of it while it is fresh. The regeneration and cleaning of waste fat are the only correct and legitimate alternative for recycling of solid wastes of food industry and catering [18].

Currently, despite a large variety of sorbents for water purification [19-29], there is no industrial production of special sorbents in Russia, which would provide effective purification of the used fat from oxidation products. The existing technology is difficult to implement in the conditions of work of public catering enterprises. Also it do not meet all the requirements of quality, allowing one to reduce to the maximum permissible values only certain indicators of safety of used fats. So, there is a problem of development new "green technologies" aimed at ensuring the safety of fast foods fried in deep frying and solving the problem of utilization of used fat as solid waste in the food industry.

The solution proposed by the authors, involves using of simple technology, applicable to the catering enterprises and is based on the removal of products of oxidation of frying fats by adsorption purification method with the use of a high dosage nanosorbent. It is a special effective and relatively cheap product, made on the basis of mineral raw materials, which are mined in Russia.

The aim of this work was to develop a prototype of microgranulated nanosorbent and technology of regeneration and recycling of deep used fat for using in the food industry and catering.

The technical task of the work was to develop a prototype of microgranulated nanosorbent based on Russian natural materials. The efficiency of the sorbent was evaluated by a number of toxic secondary oxidation products removed from the purified fat, the speed of the purification process, organoleptic indicators of the quality of the purified fat, the possibility of using the purified fat in the process immediately after purification without additional operations or compliance with the quality indicators of the purified fat indicators acceptable for processing and disposal.

2. Objects and methods of research
The objects of this research were: nanosorbent based on natural materials; samples of deep fat (palm oil) initial and after heat treatment; the frying fats (palm oil), regenerated after treatment with a nanosorbent.

In order to develop and study the nanosorbent, we used laser diffraction analyzer of particle size SALD-2201 from SHIMADZU (Japan). Study of the porous structure of the nanosorbent samples was carried out by low-temperature nitrogen adsorption using the high-speed gas sorption analyzer Quantachrome NOVA (USA). Determination of structural characteristics was performed using the Brunauer-Emmett-Taylor technique. The desorption or adsorption branch of the isotherm in the pressure range 0.967 - 0.4 p/p0 was used as the initial data for calculations by the BJH method.

The granulated material was produced on the basis of the natural mineral raw components: flask, dolomite, magnesium silicate and montmorillonite. Usage of montmorillonite (Al₂O₃•4SiO₂•H₂O) is governed by the presence of all properties which are characteristic for natural nanoscale particles with a layered expanding cell.

Preparation of natural raw components for nanosorbent production included the stages of washing and drying. After bringing the particles of the composition of the natural materials to an equal size (from 0.5 to 10 µm) in a ball planetary mill, a pilot batch of adsorbents was produced by vortex rolling.

The composition of the modified natural mineral raw materials (flask, dolomite, magnesium silicate and montmorillonite) in certain ratios was gradually added into the container of the device intended for mixing bulk materials with water. In the rotating drum, the complex of adsorption materials was wetted with an aqueous solution, which was fed at a given speed. As a result of uniform mixing, a ductile mass with a moisture content of 15-30% and a density of 1 to 2 g/cm³ was obtained. To impart strength or obtain sorbents with improved properties at the time of mixing there were added carbon nanomaterials.

In the special cylinder, absorbing the liquid phase, the sorbent particles fall on the inner surface of the cylinder due to centrifugal forces and are rolled into regular spherical granules. At the end of the granulation process heat treatment is carried out.
The optimum heat treatment temperature is defined as the minimum of the temperature range for the granulate 2 hour-holding time (with rotation) with the condition of compliance with the requirements for chemical and mechanical resistance of the granules. The experimentally determined optimum annealing temperature was 550°C.

The obtained granules are sent to a conveyor moving at a low speed from 0.01 to 0.05 m/s, which is blown with hot air from a heat gun at a temperature from 50 to 90°C. The granules of the adsorbent composition are dried to a humidity of 5-8% in a muffle furnace at a temperature of 450-700°C for 50 - 60 minutes or in a microwave oven for 5-8 minutes. The radiation frequency of the microwave device is 2450 MHz, its power is from 1 to 10 kW. The remaining in the granules moisture evaporates, forming a porous structure of the granules, which contributes to an increase in its specific surface area, and hence the sorption capacity. At the end of heat treatment, the granules are cooled to ambient temperature by blowing in a directed air flow. After cooling, the granules are sieved by fractions.

The quantitative analysis of the elemental composition of the nanosorbent was carried out using the energy dispersive x-ray fluorescence spectrometer Rayny EDX-720 SHIMADZU by calibration curves of fundamental parameters.

The acid number (Q.p.), the peroxide number (P.P.) and the total content of copolymers insoluble in petroleum ether (CIPE, %) were determined in all samples of used fats.

3. Results and discussion

The indicators of the elemental composition of the nanosorbent in mass fractions (%) are shown in Figure 1.

![Figure 1. Indicators of the elemental composition of the nanosorbent, mass fractions (%).](image)

In accordance with the required indicators of appearance and technical characteristics, the complex granulated nanosorbents should comply with the requirements specified in Table 1.

| Table 1. Technical characteristics of the nanosorbent. |
|-------------------------------------------------------|
| Indicators | Units | Characteristics |
| Appearance | Irregular gray granules |
| Particle size | mm | 0.25-0.5 |
Humidity % 3.0
The sieve residue:
Sieve 60 % 17.0
Sieve 50 %
Sieve 36
Sieve 10
Abrasion resistance % 0.2 ± 0.2
Bulk density g/dm³ 1.2

The data on specific surface, total pore volume and distribution of the pores of the nanosorbents by its diameter are shown in Table 2

| Nanosorbent | Specific surface, m²/g | Total pore volume, cm³/g | Average radius of micropores, Å | Distribution of pore diameters (nm), % |
|-------------|------------------------|--------------------------|-----------------|--------------------------------------|
|             |                        |                          |                 | 1.5-2.0 | 2.0-5.5 | 5.0-11.0 | More than 11 |
| 510         | 0.27                   | 16.097                   | 2.80            | 32.39   | 26.79   | 38.47    |

The main tasks of this method were to simplify the technology of cleaning and separating the nanosorbent from fat, increase the amount of toxic products removed (CIPE), improve organoleptic characteristics of cleaned fat, and consider the possibility of introducing this technology into the production process in food industry and catering.

Regeneration of degraded fat was carried out on a laboratory setup in the Department of "Food Technology" of Vavilov Saratov State Agricultural University.

The oxidized fat, depending on the stage of the technological process, is heated or cooled to 70°C, nanosorbent is introduced in the amount of 5-10% from weight of fat, all the components are stirred for 15-30 minutes at 50-70°C, and then filtered.

According to this study, the content of CIPE in the purified palm oil when using the microgranulated nanosorbent is reduced by more than 70%, which significantly exceeds the degree of purification of used fats achieved by imported synthetic adsorbents based on magnesium silicate - Magnesol XL and Dalsorb.

In order to study the efficiency of the developed technology, we performed the quality assessment of products fried in the refined fat using safety and organoleptic indicators (Figures 2-4).

Under the conditions of a real technological process, the product from flour (Chak-Chak) was fried at 150°C. The palm oil was used for 10 hours, during the entire heating time, the samples were taken to study the safety performance and sensory properties of the product. The kinetics of peroxide accumulation during the operation of purified fat is presented in Figure 2.

![Figure 2. The accumulation of peroxides in purified palm oil used for 10 hours in the actual production process.](image-url)
When using the palm oil as frying fat, cleaned with a nanosorbent, the kinetics of changes of the peroxide number both in the purified or fresh fat are identical, that characterizes its sufficient thermal stability. After 10 hours of continuous heating of the palm oil, its peroxide number approaches a limit value of 10 mEq of active oxygen/kg.

The peroxide number of the palm oil extracted from the product is close to the peroxide number of the oil in which the product was fried, Figure 3.

![Figure 3](image)

**Figure 3.** Comparative evaluation of the content of peroxides in palm oil extracted from the product and palm oil, in which the product was fried.

Figure 4 shows a behavior graph for content of toxic oxidation products of CIPE in palm oil without and with usage the purification technology.

![Figure 4](image)

**Figure 4.** Changes in the content of CIPE, % in palm oil without cleaning and using cleaning with a nanosorbent.

As we can see from Figure 4, the application of the proposed cleaning technology allows one to increase the life of using of the palm oil to 10 hours, taking into account its indicators of safety.

Thus, the offered technology allows one to improve the indicators of safety of thermally oxidized frying fat in order to prolong its time-of-use up to 10 hours and to reuse it in the technological cycle after cleaning, as well as for subsequent disposal of used frying fat in terms of oxidative damage.

The organoleptic indicators of quality in purified oil corresponded to the norm.

4. **Conclusion**

As a result of the work, we developed the prototype microgranulated nanosorbent and the technology of regeneration and recycling of frying fat for applying in the food industry and catering enterprises. The advantages of the microgranulated nanosorbent consist in: a significant decrease in the concentration of CIPE in the cleaned fat by 70%; ease of applying in the practical process; simplicity of separation of the adsorbent from the fat; use of domestic raw materials for the production of sorbent.

The developed method of regeneration of frying fats allows use of purified fat immediately after cleaning, without subsequent deodorization, since the listed adsorbents have got a neutral or basic reaction without any acid.
The technology of purification of frying fats by nanosorbent developed by the authors is universal and the areas of its application are extensive. The authors have considered the possibility of using this technology on the example of the production of fast food products, but there is a huge potential for using nanosorbent in the technology of purifying vegetable oils from oxidation products during storage or preparation for recycling.

References
[1] Sahin S, Gulsum Sumnu S 2009 Advances in deep-fat frying of foods (Boca Raton: CRC Press, Taylor & Francis Group)
[2] Billek G 2000 Eur. J. Lipid Sci. Technol 102 pp 587-93
[3] Simakova I V, Perkel R L, Volovey A G, Kutkina M N 2013 Bulletin of the Vavilov Saratov State Agrarian University 10 pp 47-50
[4] Simakova I V, Nosov A S, Makarova A N 2013 Bulletin of the Vavilov Saratov State Agrarian University 8 pp 59-62
[5] Blumenthal M M 1991 Food Technology 45 (2) pp 68–74
[6] Cohn J 2002 Curr. Opin. Lipidol. 13 pp 19-24
[7] Simakova I V, Makarova A N, Perkel R L 2011 Sci. and Tech. J "Technology and Commodity Innovative Food Products" 3 (8) pp 67-74
[8] Simakova I V, Nosov A S, Kotukova N A 2012 Storage and processing of agricultural products 5 pp 42-44
[9] Boki K, Wada T, Ohno S 1991 J. Amer. Oil Chem. Soc 68 (8) pp 561-5
[10] Bouchon P, Pyle D L 2005 Food and Bioproducts Processing 83 pp 253–60
[11] Brian S 2006 Adsorbent Treatment of Frying Oil: Commercial Frying Case Study. Abstracts of World Conference and Exhibition on Oilseed and Vegetable Oil Utilization, 14–16 August 2006, Istanbul, Turkey p 14
[12] Buckley H A, Eatson A J, Johnson L R 1984 Miner. Mag 48 (346) pp 119-26
[13] Yates R A, Caldwell J D 1992 JAOSCS 69 Sep
[14] Yates R A, Caldwell J D 1993 JAOSCS 70 May
[15] Proctor A 2006 Vishal Jain. Production of CLA Rich Soy Oil. Abstracts of World Conference and Exhibition on Oilseed and Vegetable Oil Utilization, 14–16 August 2006, Istanbul, Turkey p 9
[16] Christie W W, Dobson G 2000 Eur. J. of Lipid Sci. and Tech. 102 pp 515–20
[17] Claxson A W D, G E Hawkes, D P Richardson, D P Naughton 1994 FEBS Lett 335 pp 81–90
[18] Kutlu B, Atac O, Turkar S 2006 Pretreatment of Used Frying Oil for Biodiesel Production Abstracts of World Conference and Exhibition on Oilseed and Vegetable Oil Utilization, 14-16 August 2006, Istanbul, Turkey p 12
[19] Leshchinskaya A P, Ezhova N M, Pisarev O A 2016 Synthesis and characterization of 2-hydroxyethyl methacrylate-ethylene glycol dimethacrylate polymeric granules intended for selective removal of uric acid Reactive and Functional Polymers 102 pp. 101-9
[20] Chechevichkin A V, Vatin N I, Samonin V V, Grekov M A 2017 Purification of hot water by zeolite modified with manganese dioxide Magazine of Civil Engineering 76(8) pp. 201-213
[21] Politaeva N A, Slugin V V, Taranovskaya E A, Alferov I N, Soloviev M A, Zakharevich A M 2017 Granulated sorption materials for waste waters purufucation from zink ions (Zn2+) Izvestiya Vysshikh Uchebnykh Zavedenii, Seriya Khimiya i Khimicheskaya Tekhnologiya 60(7) pp. 85-90
[22] Smyatskaya Y, Kosheleva A, Taranovskaya E 2018 Sorption properties of materials based on residual biomass MATEC Web of Conferences 245 18005
[23] Kosheleva A, Atamaniuk I, Politaeva N, Kuchta K 2018 Adsorption of rare earth elements using bio-based sorbents MATEC Web of Conferences 245 18001
[24] Garkushina I S, Polyakova I V, Pisarev O A 2017 Frontal dynamics of erythromycin sorption on monolithic molecularly imprinted polymer sorbents Russian Journal of Physical Chemistry
[25] Groshikova A R, Medvedev R Y, Panarin E F 2017 Synthesis of organic–inorganic sorbent containing phenylboronic acid as glucose-binding ligand Russian Journal of General Chemistry 87(10) pp. 2376-79

[26] Zhenisbekovna U S, Satayev M I, Viktorovich S V 2016 Production of active carbons from apricot pit shells by thermal activation in the mixture of carbon dioxide and water vapors Biosciences Biotechnology Research Asia 13(3) pp. 1319-25

[27] Taranovskaya E A, Sobgayda N A, Markina D V 2016 Absorbent materials based on chitosan for sewage treatment from heavy metal ions Ecology and Industry of Russia 20(5) pp. 34-39

[28] Marchenko G N, Akhmetova I G, Mindubaeva L M and Moiseeva M A 2006 Efficiency of use of granulated chitosan in the complex process of water conditioning at thermal power plants Power Technol. Eng. 40 185–9

[29] Sobgaida N A, O"lshanskaya L N, Makarova Y A 2009 Removing heavy-metal ions from effluents by means of sorbent formed from wood-working and agribusiness wastes Chemical and Petroleum Engineering 45(9-10) pp. 580-584