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TECHNOLOGICAL ASPECTS OF APPLICATION OF THE PHYTOSORBENT WITH NANOTUBES IN THE PROCESS OF ADSORPTIVE OIL PURIFICATION

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Keywords: adsorptive purification, sunflower and soybean oil, free fatty acids, peroxide compounds, metals.

Introduction

Refined vegetable oils after technological operations of hydration and alkaline neutralization contain some groups of chemical compounds in dissolved state: pigments, primary and secondary oxidation by-products, toxic elements (heavy metals), residual soap, phospholipids, moisture and other impurities. Being presenting in oils they worsen their salable condition and quality, also for various reasons they complicates heat exchange and hydrodynamic regimens in further processing of vegetable oils [1]. Adsorptive purification provides first (and in certain cases the only one) possibility to considerably reduce presence of contaminating materials in oils. For this reason adsorptive purification makes the greatest influence on product quality among all other purification stages.

Analysis of scientific-technical data and problem statement.

According to traditional purification scheme oils are exposed to adsorptive purification after passing the processes of hydration, neutralization, rinsing and drying [2]. To reduce oxidation of oils during adsorptive purification it's recommended to vacuumize adsorbents before their adding into oils and to provide the whole process under vacuum. In periodic schemes of fat purification an adsorbent is fed into the apparatus under vacuum at temperature of 90-95^{0}C, and after agitating and exposition it is separated on frame filter-presses. In world practice devices for continuous purification are widely applied which composition includes tight filters of various design with mechanized removing of a deposit. For all technological flowcharts the following processing stages are common: preparation of concentrated oil suspension of an adsorbent; deaeration, preliminary and final refining; separation of an adsorbent on cyclically working filters [3].

Theoretical laws of the adsorptive purification process, in particular, chemosorption of contaminating materials containing in vegetable oils are described thoroughly enough in scientific and technical literature [3,4,5].

The key question of effective adsorptive purification is an applied adsorbent. Adsorbents existing today can be divided conventionally into several groups.

The first one includes high-effective adsorbents of imported origin (mainly of German (Sud-Chemieag firm) and american (Endelguard company) manufacture), which are peculiar in their high service of suppliers and quality at relatively low costs.

The second group are presented by adsorbents of Russian production having 1,5–2 times lower average coefficient of purification and oil-absorption power that consequently leads to their increased consumption and losses of oil with waste materials [6].

Unfortunately, in Ukraine activated bleaching clays are not manufactured. Among the ones used in fat-and-oil industry the most known are [7]:

– polish bleaching soil of the trademark Ieltar–100 produced by chemical industrial complex Siarkopol (Tornobzheg, Poland) of precipitate raw bentonites from Zakarpatye and Cherkassy regions;

– bleaching soil of the trademark «Ag-Optimum-210FF» produced by chemical industrial complex Sued–Chemie (Germany);

– «Engelguard – F» bleaching soil of the USA production.

Testing of these clays in Ukrainian fat-and-oil enterprises have shown that all indexes (oil-absorption power, acidity, powder formation, filtration index) of the above-stated clays are approximately the same. Purification factor of the American soil «Engelguard–F» is by 10% more than of the Polish one «Ieltar–100», but cost of the first one is twice more. Besides, raw materials for the Polish bleaching soil are supplied from Ukraine. Therefore, most of the enterprises of fat-and-oil and even petrochemical branches in the western regions of Ukraine (in particular, close corporation «Lvov complex», public corporation «Nezhinsky complex», public corporation «Lvov Petro-oil plant») work with Polish bleaching soil already more than 5 years.

The adsorptive purification is a complex process engaging many chemical reactions both desired and undesired ones. For example, bleaching soil schematically looks like [8]:

$$\text{– NHP – } Ca^{2+}H^{+} \text{ (bleaching soil) – phosphatidic acid + } Ca^{2+}$$
$$\text{–+R – COO – Na + } H^{+}\text{(bleaching soil) - R–COOH}$$
$$\text{– Chlorophyll + } H^{+}\text{(bleaching soil) - pheophytin}$$
$$\text{Hydroperoxides + } H^{+}\text{(bleaching soil) – Ketones + Aldehydes}$$

As a result of this process some impurities are adsorbed within pores of a bleaching soil and some of them transform into secondary impurities which negatively influence not only organoleptic properties, shelf-life of oils and fats, subsequent manufacturing processes (hydrogenation or re-etherification), final costs of industrial expenses, but also on the most important – consumer health.

That's why it's very important to choose correctly grade of a bleaching soil with properties and characteristics providing obtaining of a high-quality product with minimum quantity of primary and secondary impurities, basing on the following parameters:

– type of processed raw materials;

– features of an equipment;

– aims of bleaching or sorption;

– quality of oil or fat.

For adsorptive purification of plant oils adsorbents traditionally used can be divided into two groups: mineral and carbon-containing ones. Mineral native, naturally activated bentonites and synthetic amorphous compounds of silicon dioxide are attributed to the first group. The most widespread reagents are activated bleaching clays. The second group is presented by carbon-containing substances obtained from organic raw materials by pyrolysis with the subsequent activating in a flow of water steam or carbon dioxide [9].

Analysis of current state in scientific research concerning adsorptive purification shows that in Ukraine only 2 dissertation papers are devoted to this problem. The first one [10] is about a choice for the most effective sorbents from proven territories of minerals in Ukraine and development of advanced technology for adsorptive purification of sunflower oil. Author of this work has shown that non-activated palygorskite of the Cherkassy proven terri-

tory can be used as effective and inexpensive adsorbent allowing to substantially reduce content of peroxide compounds, phospholipids and colorants in sunflower oil.

Another work is devoted to elaboration of new adsorbent from sunflower peel obtained by acid hydrolysis with rinsing and leaching [11].

The obtained sorbent had the following composition: carbon – 54,62–55,63 %; hydrogen – 5,26–5,36 %; nitrogen – 0,82–1,48 %; oxygen – 37,23–39,0 %; sulphur – not more than 0,3 %. Use of this adsorbent has appeared effective in technology of alkaline neutralization that minimized losses of neutral fat.

Proceeding from the above-stated, we have developed new composition and improved technology for the adsorbent from peel with nanotubes using method of pyrolysis.

The purpose and tasks of the research

The purpose of this research is scientific substantiation for the technology of adsorptive purification of vegetable oils using phytosorbent from sunflower peel with nanotubes.

Research tasks:

– to carry out experimental research of adsorptive activity of a new adsorbent towards free fatty acids, phospholipids, colorants and metals containing in non-refined sunflower and soybean oils;

– to develop practical recommendations concerning further research.

Objects and methods of the research

As research objects the samples of non-refined sunflower and soybean oils, bleaching clay of «Ieltar–100» trademark and adsorbent from sunflower peel with nanotubes have been chosen.

Determination of acid and peroxide values, mass fraction of phospholipids and colour indexes was carried out by standard methods used in oil-and-fat industry, metal content (Fe,Na,K) – by method of X-ray-fluorescent spectroscopy using Elvatech firm device.

Research results for adsorptive activity of the adsorbent from sunflower peel with nanotubes.

For last years an increasing attention was paid to safety of foodstuff including vegetable oils and fats. Safety is evaluated by impurity limit level of technogenic and natural origin – dioxines and polycyclic aromatic hydrocarbons [10].

On the first stage adsorptive activity of a new adsorbent with nanotubes against free fatty acids, phospholipids, colorants and some metals presenting in non-refined sunflower and soybean oils has been researched.

Processing conditions for vegetable oils within a laboratory reactor were the following: temperature +45–72 °C, duration of agitating – 25–60 mines; agitating intensity – 120–400 rpm; residual pressure in a reactor – 1,2 mm Hg.

The table 1 presents experimental data concerning change of some organoleptic, physico-chemical and structure parameters and also content of Fe,Na,K in samples of sunflower and soybean oils prior to and after processing with commercial bleaching clay of the «Ieltar–100» trademark and the adsorbent developed from sunflower peel with nanotubes.

The data shown in the table 1 prove that adsorbent with nanotubes from sunflower peel efficiently eliminates free fatty acids, peroxide compounds, phospholipids, colorants and some metals from non-refined vegetable oils, and in more extent than it's provided with application of commercial bleaching clay of the «Ieltar– 100» trademark [10–12].

Thus, high adsorptive activity of the new phytosorbent with nanotubes from sunflower peel is confirmed.

Conclusions

1. Basing on analysis of scientific advances in the field of adsorptive purification the especial importance of the latter in technology of vegetable oil purification from contaminating materials and impurities and also insufficiency of scientific researches in development of domestic sorbents have been pointed out.

Table 1 – Influence of adsorbents on quality parameters of oils

The parameters evaluated	Sunflower oil	Soybean oil
Initial sample		
Acid value, mg KOH/g	3,02± 0,3	4,1± 0,36
Peroxide value, ½ mMol O / kg	0,101± 0,01	1,79 ±0,20
Phospholipids, %	0,45± 0,39	2,1± 0,19
Colour index, iodine units	30,0± 0,28	57± 4,9
Metals, mg/kg	Na 115,0 ± 10,7 K 120,0 ± 11,0 Fe 49,0 ± 4,8	Na 35,0 ± 3,9 K 96,3 ± 9,2 Fe 7,0 ± 0,8
Adsorption with clay «Ieltar– 100»		
Acid value, mg KOH/g	0,5 ± 0,04	0,8 ± 0,06
Peroxide value, ½ mMol O / kg	0,036 ± 0,004	0,85 ± 0,07
Phospholipids, %	0,25 ± 0,03	0,9 ± 0,08
Colour index, iodine units	8,0 ± 0,7	10,0 ± 1,2
Metals, mg/kg	Na 2,81 ± 0,3 K 20,52 ± 2,1 Fe 0,23 ± 0,02	Na 2,72 ± 0,3 K 10,4 ± 1,2 Fe 2,3 ± 0,2
Adsorption with adsorbent from peel with nanotubes		
Acid value, mg KOH/g	0,25 ± 0,02	0,20 ± 0,18
Peroxide value, ½ mMol O / kg	0,015 ± 0, 002	0,56 ± 0,06
Phospholipids, %	0,2 ± 0,02	0,15 ± 0,02
Colour index, iodine units	5,0 ± 0,4	6,0 ± 0,07
Metals, mg/kg	Na No K No F No	Na No K No Fe No

Taking into account the above information, the main directions of research were identified, which are to develop a technology for the synthesis of carbon adsorbents based on

carbon-containing sorbents and to establish the relationship between the characteristics of the obtained carbon adsorbents and the conditions of their formation.

Conclusions

1. Thus, by modification it is possible to vary the properties of the obtained carbon products in the desired direction. Modification of VU will make it possible to obtain a viscoadsorption carbon material on its basis.

2. High adsorptive activity of the developed phytosorbent with nanotubes towards free fatty acids, peroxide compounds, phospholipids, colorants and some metals (Fe,Na,K) has been found.

3. The results obtained point on necessity of further continuation of scientific research concerning influence of the phytosorbent with nanotubes on qualitative characteristics of vegetable oils including safety parameters.

4. The research provided by us testifies that raw materials for production of the sorbent is wastes of oil-and-fat manufacture. It allows to carry out strategy for complex processing of raw materials which is one of the main trends in modern technology.

Литература

1. Артемов А.В., Пинкин А.В. Сорбционные технологии очистки воды от нефтяных загрязнений //Вода: химия и экология. – 2008, №1.–С.19–25.

2. Guo X., Zhang S., Shan X. Adsorption of metal ions on lignin // J. Hazard. Matter.– 2008.–V. 151.–P. 134–142.

3. Wan Ngah W.S., Hanafiah M.A. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A Review // Bioresource. Technol. 2008. –V. 99. – P. 3935–3948.

4. Тарнопольская М.Г. Фильтрующие материалы для очистки воды от нефтепродуктов и критерии их выбора //Вода и экология: проблемы и решения. –2005. №3. – С.74–79.

5. Передерий М.А., Сиротин П.А., Казаков В.А. Хотуляева В.Н. Безотходная переработка бурых углей в пористые углеродные материалы различного назначения // Химия твердого топлива. 2002. №6. – С.19–27.

6. Еремина А.О., Головина В.В., Угай М.Ю., Степанов С.Г., Морозов А.Б. Адсорбция фенолов и нефтепродуктов на сорбционных материалах из бурого угля //Химия твердого топлива. 2004. №4. – С.32–39.

7. Еремина А.О., Головина В.В., Угай М.Ю., Рудковский А.В. Углеродные адсорбенты из древесных отходов в процессе очистки фенолсодержащих вод //Химия растительного сырья. 2004. №2. – С. 67–71.

8. Багровская Н.А., Никифорова Т.Е., Козлов В.А., Лилин С.А. Сорбционные свойства древесных опилок. //Химия в интересах устойчивого развития. 2006. Т.14., №1. –С. 1–7.

9. Кнатько В.М., Кнатько М.В., Юлин В.А. Сорбент для очистки объектов окружающей среды. //Экологические системы и приборы. 2004. №12. – С. 38.

10. Андриевский Г.В., Клочков В.К. Гидратированные фуллерены как универсальные биоантиоксиданты и роль в этом особых упорядоченных структур воды. //Сб. Тезисов УП Междун. Симп. «Биологические механизмы старения». Харьков. – 2006. – С.91–92.

11. Buseck P.R. Geological fullerenes: review and analysis. (англ.)// Earth and Planetary Science Letters. (2002) 203(I 3–4): 781–792.

12. Скороходов В.Ф., Месяц С.П., Остапенко С.П. Решение проблемы очистки сточных вод промышленных предприятий от многокомпонентных загрязнений // Горный журнал. 2010. – № 9. – С. 106–108.

Bibliography (transliterated)

1. Artemov A.V., Pinkin A.V. Sorbtsionnyie tehnologii ochistki vodyi ot neftyanyih zagryazneniy //Voda: himiya i ekologiya. – 2008, #1.–P. 19–25.

2. Guo X., Zhang S., Shan X. Adsorption of metal ions on lignin // J. Hazard. Matter.– 2008.– V. 151.–P. 134–142.

3. Wan Ngah W.S., Hanafiah M.A. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A Review // Bioresource. Technol. 2008. –V. 99. – P. 3935–3948.

4. Tarnopolskaya M.G. Filtruyuschie materialyi dlya ochistki vodyi ot nefteproduktov i kriterii ih vyibora //Voda i ekologiya: problemyi i resheniya. –2005. #3. – P.74–79.

5. Perederiy M.A., Sirotin P.A., Kazakov V.A. Hotulyaeva V.N. Bezothodnaya pererabotka buryih ugley v poristyie uglerodnyie materialyi razlichnogo naznacheniya //Himiya tverdogo topliva. 2002. #6. – P. 19–27.

6. Eremina A.O., Golovina V.V., Ugay M.Yu., Stepanov S.G., Morozov A.B. Adsorbtsiya fenolov i nefteproduktov na sorbtsionnyih materialah iz burogo uglya //Himiya tverdogo topliva. 2004. #4. – P. 32–39.

7. Eremina A.O., Golovina V.V., Ugay M.Yu., Rudkovskiy A.V. Uglerodnyie adsorbentyi iz drevesnyih othodov v protsesse ochistki fenolsoderzhaschih vod //Himiya rastitelnogo syirya. 2004. #2. – P. 67–71.

8. Bagrovskaya N.A., Nikiforova T.E., Kozlov V.A., Lilin S.A. Sorbtsionnyie svoystva drevesnyih opilok. //Himiya v interesah ustoychivogo razvitiya. 2006. T.14., #1.– P. 1–7.

9. Knatko V.M., Knatko M.V., Yulin V.A. Sorbent dlya ochistki ob'ektov okruzhayuschey sredyi. //Ekologicheskie sistemyi i priboryi. 2004. #12. – P. 38.

10. Andrievskiy G.V., Klochkov V.K. Gidratirovannyie fullerenyi kak universalnyie bioantioksidantyi i rol v etom osobyih uporyadochennyih struktur vodyi. //Sb. Tezisov UP Mezhdun. Simp. «Biologicheskie mehanizmyi stareniya». Harkov. – 2006. – P. 91–92.

11. Buseck P.R. Geological fullerenes: review and analysis. (angl.)// Earth and Planetary Science Letters. (2002) 203(I 3–4): 781–792.

12. Skorohodov V.F., Mesyats S.P., Ostapenko S.P. Reshenie problemyi ochistki stochnyih vod promyishlennyih predpriyatiy ot mnogokomponentnyih zagryazneniy // Gornyiy zhurnal. 2010. – # 9. – P. 106–108.

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ТЕХНОЛОГІЧНІ АСПЕКТИ ЗАСТОСУВАННЯ ФІТОСОРБЕНТУ З НАНОТРУБКАМИ В ПРОЦЕСІ АДСОРБТИВНОГО ОЧИЩЕННЯ ОЛІЇ

Проаналізовано деякі літературні дані за основними характеристиками ряду сорбційних матеріалів (вуглеводних, природних і сорбентів, отриманих з відходів агро-

промислового комплексу) в результаті термічної обробки. Розглянуто основні сорбційні властивості; гідності та недоліки. Досліджено вплив температури на продуктивність піролізу рослинної сировини і властивості карбонізатов, що утворюються в діапазоні температур 150–600 °С. Тривалість експозиції матеріалів при кінцевій температурі процесу у всіх дослідах була однакова і становила 1 ч. Аналіз експериментальних даних дозволяє зробити висновок, що температура є основним фактором, що впливає на процес карбонізації та виходу кінцевого продукту. Не залежно від атмосфери піролізу вихід продукту з рослинної сировини зі значним збільшенням температури знижується. В даний час основною сировиною для промислового отримання адсорбентів є в багатьох дослідженнях органічні речовини - деревина, копалини вугілля, торф, залишки переробки сільськогосподарської сировини через їх дешевизну і велику кількість. Вирішення проблеми створення сорбентів на основі рослинної сировини з включенням до їх складу гідратованих фулеренів вирішувало питання створення сорбентів і проблеми екології, так як відходи не завжди знаходили корисне застосування. Концентровані водні розчини гідратованого С60, скорочено С60FWS, є молекулярно-колоїдні системи сферичних фрактальних кластерів, структурною одиницею яких є міцний, високогідрофільний супрамолекулярний комплекс, що складається з молекули фулерену С60, укладеної в першу гідратну оболонку, котра містить 24 молекули води: С60 (H_2O) 24-гідратований фулерен С60 (С60HyFn). Гідратовані фулерени створюють в своєму оточенні впорядковану, структурно гетерогенне водне середовище, в якому спрямованість і кінетика хімічних процесів відрізняється від таких, що відбуваються в чистій (невпорядкованій) воді та сприяють утворенню шпарин, необхідних для активної сорбції.

Ключові слова: адсорбенти, пиролиз, відходи агропромислового комплексу, фулерени.

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ТЕХНОЛОГИЧЕСКИЕ АСПЕКТЫ ПРИМЕНЕНИЯ ФИТОСОРБЕНТА С НАНОТРУБКАМИ В ПРОЦЕССЕ АДСОРБТИВНОГО ОЧИЩЕНИЯ МАСЛА

Проанализированы некоторые литературные данные по основным характеристикам ряда сорбционных материалов (углеводных, природных и сорбентов, полученных из отходов агропромышленного комплекса) в результате термической обработки. Рассмотрены основные сорбционные свойства; достоинства и недостатки. Исследовано влияние температуры на производительность пиролиза растительного сырья и свойства карбонизатов, образующихся в диапазоне температур 150–600 °С. Продолжительность экспозиции материалов при конечной температуре процесса во всех опытах была одинакова и составляла 1 ч. Анализ экспериментальных данных позволяет заключить, что температура является основным фактором, влияющим на процесс карбонизации и выхода конечного продукта. Не зависимо от атмосферы пиролиза выход продукта из растительного сырья со значительным увеличением температуры снижается. В настоящее время, ввиду дешевизны и большого количества, основным сырьем для промышленного получения адсорбентов являются во многих исследованиях органические вещества – древесина, ископаемые уголь, торф, остатки переработки сельскохозяйственного сырья. Решение проблемы создания сорбентов на основе растительного сырья с включением в их состав гидратированных фуллеренов решало вопрос создания сорбентов и проблемы экологии, так как отходы не всегда находили полезное применение. Концентрированные водные растворы гидратированного С60, сокращенно С60FWS, являются молеку-

лярно-коллоидными системами сферических фрактальных кластеров, структурной единицей которых является прочный, высокогидрофильный супрамолекулярный комплекс, состоящий из молекулы фуллерена С60, заключенной в первую гидратную оболочку : С60 (Н2О) 24-гидратированный фуллерен С60 (С60HyFn). Гидратированные фуллерены создают в своем окружении упорядоченную, структурно гетерогенную водную среду, в которой направленность и кинетика химических процессов отличается от происходящих в чистой (неупорядоченной) воде и способствуют образованию щелей, необходимых для активной сорбции.

Ключевые слова: адсорбенты, пиролиз, отходы агропромышленного комплекса, фуллерены.

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TECHNOLOGICAL ASPECTS OF APPLICATION OF THE PHYTOSORBENT WITH NANOTUBES IN THE PROCESS OF ADSORPTIVE OIL PURIFICATION

In the present article importance of adsorptive purification of vegetable oils is shown as the most responsible technological stage. Insufficiency of scientific developments in the scope of domestic sorbents in Ukraine is pointed out. The phytosorbent with nanotubes from sunflower peel improving some quality parameters of non-refined sunflower and soybean oils to standard values for refined oils has been offered.

Some literature data on the main characteristics of a number of sorption materials (carbonaceous, natural, fibrous, and sorbents obtained from agricultural waste - Corylus avellana Lambert nuts) as a result of heat treatment are analyzed. The main sorption properties are considered; dignity; limitations. The effect of temperature on the productivity of pyrolysis of plant raw materials and the properties of the resulting carbonizates in the temperature range 150-600 °C was investigated. The duration of exposure of materials at the final temperature of the process in all experiments was the same and amounted to 1 h. Analysis of the experimental data allows us to conclude that temperature is the main factor affecting the process of carbonization of the initial plant material. Regardless of the pyrolysis atmosphere, the yield of the product from plant raw materials decreases with a significant increase in temperature. At present, the main raw material for the industrial production of adsorbents is in many studies organic substances - wood, fossil coal, peat, remnants of the processing of agricultural raw materials due to their low cost and large amount. Solving the problem of creating sorbents based on plant raw materials with the inclusion of hydrated fullerenes in their composition solved the problem of creating sorbents and environmental problems, since the waste did not always find a useful application. Concentration of water solution of hydrated C60, fast C60FWS, є molecular-coloidal systems and spherical fractal clusters, structural unit of which is micro-hydrophilic, high-hydrophilic supramolecular complex, molecules can be folded to fit into) 24-hydration of fullerene C60 (C60HyFn). The hydrated cultivation is set in its own well-ordered, structurally heterogeneous watery middle, in which the directness and kinetics of chemical processes are seen in such, that it is necessary to be washed in order to clean

Keywords: adsorptive purification, sunflower and soybean oil, free fatty acids, peroxide compounds, metals.