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SYNTHESIS OF HIGHLY EFFICIENT SORBENTS FROM PLANT WASTE

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Keywords: sorption, coal, oil, water, ecology, sunflower husk with nanotubes.

Introduction

As materials in the production of sorbents for the absorption of oil and oil products, a significant number of types of plant and natural raw materials were used: buckwheat and sunflower husks, walnut, pine and other nut shells, oat and rice husks, corn cobs (waste), grass processing waste, straw, reed cut, reed inflorescences. The use of all materials that are potential local raw materials for the production of sorbents makes it possible to link the disposal of agricultural waste with environmental protection [1–2]. The sorbent based on husk and nanotubes is a porous material, consisting of 5–10 % silicon oxide and 80–90 % carbon (by weight). Full-scale tests of sorbents were carried out in a mock laboratory environment.

Experiment

Results Getting sorbents. To obtain sorbents with different ratios SiO_2: C, a batch of sunflower husks was selected. After appropriate washing with 10% sulfuric acid followed by By washing with distilled water, the washed batch was burned in a muffle furnace in an air atmosphere to remove volatiles at a temperature of 400–500 ^oC in the interval of 30 and 60 min, since at this temperature, according to a literature source, adsorption centers are formed. At the stage of carbonization, the framework of the future activated carbon is formed - primary porosity and strength [4]. According to thermal analysis data, the main part of the organic component of the husk is removed already at a temperature of 400–500 °C. A necessary part of carbonized organic substances is the determination of the carbon content, since the degree of water purification from oil and oil products depends on the carbon content. For this purpose, we carried out studies on the carbon content in the obtained sorbent. Study of sorbents for carbon content. In order to determine the carbon content and ash content of the obtained sorbent, they were heat treated at 450 °C; the processing time was 2 hours. At this temperature, there is complete combustion of carbon and practically remains the whitish ash of carbonized waste. The data on the modes of obtaining sorbents with different SiO_2: C ratios are summarized in Table 1.

Table 1 – Modes of obtaining sorbents

№	Carbonization temperature, °C	Carbonization time, min	Carbon content, %	Ash content, %
1	400	30	95	2.5
2	400	60	90	4,0
3	500	30	80	3,5
4	500	60	60	3,0

As you can see from the table 1, the most effective coal is No. 1. For further research on water purification from oil, the sorbent with the highest carbon content was selected, i.e. the sorbent obtained at 400 °C in the pyrolysis interval of 30 minutes. As you know, the main indicator characterizing the efficiency of sorbents is their sorption capacity, that is, the ability to absorb the maximum possible amount of sorbate per unit mass of the sorbent [5]. For this purpose, studies were carried out on the complete absorption of oil and oil products (gasoline) by sorbents (Table 2).

Table 2 – Full sorption capacity of sorbents

Sorbent obtained at temperature:	Sorption time, hour	Full sorption capacity	
		For oil	For gasoline
400^{0}C	1	0,39±0,03	0,22±0,01
	2	0,57±0,04	0,18±0,01
	24	0,81±0,07	0,21±0,02
500^{0}C	1	0,33±0,03	0,18±0,01
	2	0,35±0,03	0,21±0,02
	24	0,72±0,06	0,21±0,01

In the conducted studies of oil capacity within an hour, it was shown that 1 g of sorbent is capable of absorbing 0.39 g of oil with a further increase with increasing sorption time. The sorption capacity for gasoline also increases with an increase in the sorption time. The kinetic dependences of the sorption capacity of the obtained sorbent were studied. This dependence is shown in Fig. 1.

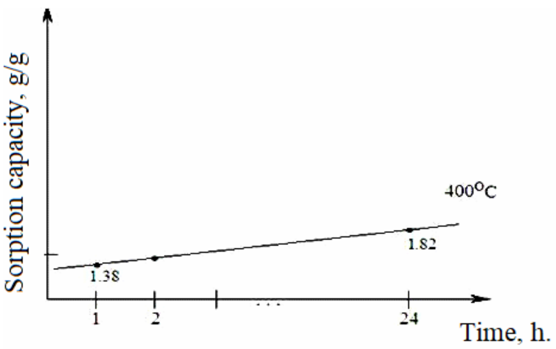

Fig. 1 – Dependence of the sorption capacity of the sorbent on the carbonization time

As shown in the data table. 2, the total sorption capacity of the obtained coal is very low, which will not allow using them for collecting spilled oil products, however, as is known from the literature, the use of carbonized carbon-containing substances in wastewater treatment is the most effective sorption method. Based on the data obtained, we decided to increase the sorption capacity of the sorbent due to the presence in it of nanotubes obtained by pyrolysis of coke. Study of the dynamic capacity of sorbents. After additional processing (granulation, chemical modification), high-quality sorbents can be obtained from activated carbons, similar in parameters to activated carbons. To control the quality of the obtained activated carbon, careful studies are also required on the requirements for activated carbons, for example, the total porosity in accordance with GOST 17219 and the determination of the adsorption activity of coal in terms of methylene blue in accordance with GOST 4453. In order to determine the possibility of wastewater treatment from oil and of oil products using the obtained sorbents based on vegetable matter, their sorption characteristics were studied under dynamic conditions after filtration of the solution to be purified through a fixed bed of adsorbent.

When determining the characteristics of sorption under dynamic conditions, the rate of water transmission and the concentration of oil in the treated water were taken into account.

The initial concentration of oil in water was determined by the gravimetric method [7], based on the separation of oil products from water by extraction with hexane, chromatographic separation of oil products from compounds of other classes in a column filled with aluminum oxide. Sorbent efficiency studies were evaluated for water contaminated with oil concentration of 23 mg / l. Preliminary studies were carried out to assess the degree of water purification depending on the rate of passage through the layer of the studied stationary sorbent. The volumetric flow rate of water through the fixed bed of the sorbent was (5, 15, and 30 ml / min). A column 50 cm high and 3 cm in diameter was filled with a 20 cm high sorbent, the initial solution was fed from above, and it passed by gravity through the sorbent layer.

The purified water was collected in a collector in portions of 250 ml. At the outlet of the column, the water is transparent – it corresponds to GOST 3551-46, the purified water is odorless. It is no longer possible to carry out the residual content of small amounts of oil in water using the gravimetric method. It is used, as a rule, in the analysis of heavily contaminated samples and cannot be used in the analysis of samples containing petroleum products at the MPC level, since the lower limit of the measurement range is 0.3 mg / dm^3 with a sample volume of 3–5 dm^3. Maximum allowable concentration of oil for drinking water is 0.05 mg / l. The main methods of quantitative chemical analysis currently used in the determination of oil products in waters are gravimetric, IR spectroscopic, gas chromatographic and fluorimetric. For this purpose, the analysis of water for residual oil content in water was carried out by the fluorimetric method on a fluid analyzer "Fluorat-02". The obtained data on the concentration of oil in purified water are shown in Table 3, which indicate that the concentration of oil in water is at the MPC level when water is filtered at a rate of 5 and 15 ml / min (the volumetric filtration rate is selected).

Table 3 – Concentration of oil in water when using sorbents

Name of sorbent	The concentration of oil in water at various filtration rates, mg/l		
	0 ml/min	15 ml/min	35 ml/min
The sorbent obtained from 450 °C for 30 min	0.045	0.07	0.25

At a filtration rate of 30 ml / min. the concentration of oil is 0.25 mg / l, which is lower than the MPC for fishery waters, the MPC of which is 0.5 mg / l.

In water purification, the filtration rate plays an important role, since the duration of the contact of water with the sorbent is seconds, and it is very important that in this short time the water has time to be completely cleared of oil. The dependence of the purification of contaminated water on the filtration rate is shown in Fig. 2.

Chemical regeneration is understood as the treatment of a sorbent with liquid or gaseous organic or inorganic reagents at a temperature usually not higher than 100 °C. Regeneration of the above sorbents by chemical methods is not economically feasible, since it requires a large amount of reagents, and further processing of the resulting waste becomes a problem. In order to clean up the contaminated coal, the methods of the most efficient and cheaper. The regeneration of the used sorbent was carried out by mixing the spent sorbent with gasoline; after its purification, the sorbent was subjected to heat treatment at 500 °C for complete removal of oil products. Thus, it was found that, due to its high strength, it can be regenerated many times.

Separately, it should be noted the results on the sorption characteristics of the sorbent based on carbonized sunflower husk and nanotubes obtained by pyrolysis of coke. As a product of processing waste of plant materials and carbon-containing substances containing nanotubes, the sorbent provides a high degree of water purification from oil products [8]. The discussion of the results Effective removal of undissolved, dispersed oil products from water is also achieved due to the ability of the impurity to adhere to the surface of the filter material. Therefore, oil sorbents, the physicochemical properties of which meet the technical requirements for filter media, can be used to remove oil products from wastewater at the filtration stage.

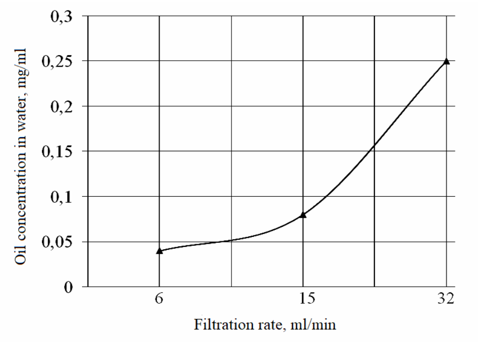

Fig. 2 – Dependence of contaminated water purification on the filtration rate through a sorbent layer with an initial concentration 23 mg/l

The obtained coals from sunflower husks, used at the stage of deep post-treatment, provide the ability to remove dissolved oil products if the parameters of the porous structure of the sorbent correspond to the size of the impurity molecules. Active carbons can be used as filter media if they are properties meet the requirements for such materials. As you know, oil products in wastewater can be in free, bound and dissolved states. Coarse, free oil products are removed as a result of sedimentation. To remove finely dispersed and associated petroleum products, flotation cleaning methods, electrocoagulation and electroflotation methods are used. As a result of these processes, oil products remain in the water up to 20 mg/l. Deeper purification from finely dispersed, especially emulsified, oil products up to 10 mg/l is achieved in filtration processes. Removal of dissolved impurities up to 0.5–1 mg/l occurs at the stage of sorption post-treatment.

Conclusion

Analysis of the results on the dynamic sorption of petroleum products showed that maximum sorption is achieved when using a sorbent obtained at 450 °C in the interval of 30 minutes. Optimized temperature regimes for obtaining a sorbent from sunflower husk and nanotubes obtained by pyrolysis of coke with different carbon content, common to all these materials is the hydrophobicity and oleophilicity of their surface. The total sorption capacity of sorbents for oil and oil products has been determined. The processes of adsorption capacity of sorbents have been studied under dynamic conditions. The efficiency of sorption and the specific capacity of the sorbents have been determined. The investigated sorbents can be returned to the technological cycle after cleaning.

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Ельнаггар Е.

СИНТЕЗ ВИСОКОЕФЕКТИВНИХ СОРБЕНТІВ З РОСЛИННИХ ВІДХОДІВ

Можливість створення широкого асортименту вуглецевих адсорбентів суттєво полегшується різноманітністю вихідної вуглецевмісної сировини та технологій її переробки. В даний час основною сировиною для промислового отримання адсорбентів є деревина, викопні вугілля, торф, залишки переробки сільськогосподарської сировини, деякі полімерні матеріали. Значно рідше застосовуються лігнін та технічний вуглець (сажа). Однак потенційно вуглецеві адсорбенти можуть бути отримані з набагато більшого асортименту твердих, рідких та газоподібних вуглецевмісних речовин, багато з яких розглядаються в даний час лише як непотрібні побутові та промислові відходи. Так адсорбенти з задовільними характеристиками, активні в конкретних технологічних процесах, можуть бути синтезовані з відходів деревини та деревної кори, лігніну та целюлозно-паперової промисловості, активного мулу, попутних газів, і т.д. Зола лушпиння соняшника при спалюванні при нестачі кисню, також має сорбційну активність. Її використовували при отриманні сорбенту, здатного вловлювати нафтопродукти. Місткість його в лабораторних умовах становить 1,5–3 г/г, але ефективність очищення може досягати 90 і більше %. Чорна зола, отримана при піролізі лушпиння соняшника, має чудові сорбційні властивості і не поступається за якістю кращим маркам активного вугілля. Обробку поверхні води або стічних вод пропонованим сорбентом здійснюють за температури від 0 до 100 °С. Регенерацію використаного сорбенту можна проводити обробкою вуглеводневими розчинниками органічними розчинниками (спирти тощо) або їх сумішами.

Ключові слова: сорбція, вугілля, нафта, вода, екологія, лушпиння соняшника з нанотрубками.

Эльнаггар Э.

СИНТЕЗ ВЫСОКОЭФФЕКТИВНЫХ СОРБЕНТОВ ИЗ РАСТИТЕЛЬНЫХ ОТХОДОВ

Возможность создания широкого ассортимента углеродных адсорбентов существенно облегчается разнообразием исходного углеродсодержащего сырья и технологий его переработки. В настоящее время основным сырьем для промышленного получения адсорбентов являются древесина, ископаемые угли, торф, остатки переработки сельскохозяйственного сырья, некоторые полимерные материалы. Значительно реже применяются лигнин и технический углерод (сажу). Однако потенциально углеродные адсорбенты могут быть получены из гораздо большего ассортимента твердых, жидких и газообразных углеродсодержащих веществ, многие из которых рассматриваются в настоящее время лишь как бесполезные бытовые и промышленные отходы. Так адсорбенты с удовлетворительными характеристиками, активные в конкретных технологических процессах, могут быть синтезированы из отходов древесины и древесной коры, лигнина и целлюлозно-бумажной промышленности, активного ила, попутных газов, и т.д.

Зола шелухи подсолнечника при сжигании при недостатке кислорода, также обладает сорбционной активностью. Ее использовали при получении сорбента, способного улавливать нефтепродукты. Емкость его в лабораторных условиях составляет 1,5–3 г/г, но эффективность очистки может достигать 90 и более %. Черная зола, полученная при пиролизе шелухи подсолнечника обладает превосходными сорбционными свойствами и не уступает по качеству лучшим маркам активного угля. Обработку поверхности воды или сточных вод предлагаемым сорбентом осуществляют при температуре от 0 до 100 °С. Регенерацию использованного сорбента можно проводить обработкой углеводородными растворителями органическими растворителями (спирты и т.п.) или их смесями.

Ключевые слова: сорбция, уголь, нефть, вода, экология, шелуха подсолнечника.

Elnaggar E.

SYNTHESIS OF HIGHLY EFFICIENT SORBENTS FROM PLANT WASTE

The possibility of creating a wide range of carbon adsorbents is greatly facilitated by the variety of the initial carbon-containing raw materials and technologies for its processing. At present, the main raw materials for the industrial production of adsorbents are wood, fossil coal, peat, remnants of processing of agricultural raw materials, and some polymeric materials. Lignin and carbon black (soot) are used much less frequently. However, potentially carbon adsorbents can be obtained from a much wider range of solid, liquid and gaseous carbonaceous substances, many of which are currently considered only useless domestic and industrial waste. Thus, adsorbents with satisfactory characteristics, active in specific technological processes, can be synthesized from waste wood and bark, lignin and the pulp and paper industry, activated sludge, associated gases, etc. On the basis of it was received by the sorbent capable to catch oil. Its capacity is 1–2 g/g, but the cleaning efficiency can reach 90 %. The black ash walnut shell has excellent absorption properties and is not inferior in quality to the best brands of activated carbon. Surface treatment of water or wastewater proposed sorbent was carried out at 0–100 °C. Regeneration of used sorbent spend its processing hydrocarbon solvents (gasoline, kerosene, etc.) or organic solvents (alcohols, etc.) or mixtures thereof.

Keywords: sorption, coal, oil, water, ecology, sunflower husk with nanotubes.