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ECOLOGY OF OIL AND OIL SORBENTS

Abstract. The article contains materials on oil-sorbents and their application. Methods of liquidation of spills and accidents of oil and oil products on soil and water surface are shown.

Keywords: oil, sorbents, ecology, chemical composition, water, soil, peat, cellulose

1.1. Oil, its composition and properties. The chemical nature and composition of petroleum, petroleum fractions and residues predetermines the entire complex of their physicochemical properties and the colloid-dispersed structure of petroleum systems.

According to the theory of oil formation as a result of long transformations of organic residues, the main part of the oil is made up of hydrocarbons of different structures. However, the oil that coming out to the surface carries with it associated gas, water and mechanical particles of sand, rock, etc. The number of these components for different oilfields is different. These components are insoluble, oleophobic and form a disperse system that undergoes separation. But even after the separation of insoluble components, according to the chemical nature of the oil itself, it is not a molecular solution, or a Newtonian fluid. The presence of heteroatom compounds in the oil, as well as high-molecular compounds, most of which contain sulfur, nitrogen, oxygen and metals, impart oil, oil fractions and residues to the specific properties inherent to colloidal and disperse systems. Depending on the particle size of the dispersed phase, such systems can be either ultraheterogeneous (particle size from 1 to 100 nm) or coarsely dispersed (particle size> 10 nm).

The hydrocarbons and other compounds contained in the oil in one degree or another interact with each other. Physical intermolecular interactions are determined both by the nature and structure of the compounds, and by external conditions [1-3].

1.1.2. Element composition. Oil is a mixture of a very large number of chemical compounds based on hydrocarbons formed from the initial organic matter as a result of prolonged interaction with the environment under the influence of many factors.

Oil is an oily liquid, the complete chemical composition of which is virtually impossible to determine with modern instrumental methods.

The main chemical elements that make up the oil are carbon, hydrogen, sulfur, nitrogen and oxygen. Carbon and hydrogen are contained in various oils in the amount of 82-87% and 11-14%, respectively. They are an integral part of all chemical compounds of oil. Among minerals (excluding petroleum gas), oil has the highest calorific value, since it contains the greatest amount of hydrogen. In connection with this, the combustible properties of oil are usually characterized by the ratio of the quantities of hydrogen and carbon (H: C) in%. Sulfur is a part of heteroatomic compounds. The sulfur content of oil is divided into three classes: in low sulfuric oils, it is up to 0.5%, in sulphurous oils - from 0.51 to 2,0% and in high sulfur - from 2.01%. Nitrogen and oxygen in oil-up to 1,8 and 3,0%, respectively. In oil ash, about 6 metals are found, of which the most common are V, Ni, Te, Zn, Cu, Mg, Al [4, 5].

1.1.3. Group chemical and fractional composition. The composition of oil includes the following groups of compounds: hydrocarbons, heteroatom compounds, resins and asphaltenes. Hydrocarbons of natural oils are represented by three groups-alkanes, cycloalkanes and arenes. The heteroatomic compounds include sulfur-, nitrogen-, oxygen- and metal-containing compounds. Resins and asphaltenes are not a characteristic group of chemical compounds. Heteroatomic compounds are chemical compounds based on hydrocarbons of any group containing one or more different atoms of chemical elements of sulfur, nitrogen, oxygen, chlorine and metals. Heteroatomic oil compounds have a significant impact on the level of environmental pollution. Oil and petroleum products are a complex mixture of hydrocarbons and non-hydrocarbon compounds. Parts are called fractions. The main fractions released from oil at the industrial plant are the following: petrol, kerosene, diesel and the remainder of oil distillation - fuel oil [6].

1.2. Sources of oil pollution and the impact of oil production, transportation and refining on the environment. Among the numerous harmful substances of anthropogenic origin that enter the environment (air, water, soil, vegetation, etc.), one of the first places belong to petroleum products. The work of vehicles and oil refineries and petrochemical industry, gaseous emissions and sewage of industrial enterprises, numerous oil and oil products spills as a result of accidents of pipelines and oil tankers (tankers), accidents and fires at oil storage facilities and oil refineries lead to pollution of air, water and soil with significant amounts of crude oil and products of its processing and create a serious threat to the environment [7].

Anthropogenic pollution of the biosphere, caused by human economic activity, has a negative impact on the state of water, soil, atmospheric air, renewable natural resources.

Oil and its products are one of the most common ecotoxicants. Technogenic pollution appears at all levels - from local to global and poses a serious threat. Oil pollution differs from other anthropogenic influences in that it gives not a constant, but a "volley" load on the environment, causing its rapid response. By the nature of the occurrence of pollution are divided into natural and anthropogenic (figure 1). The main mass of pollution of the World Ocean (about 95%) are sources of anthropogenic origin [8].

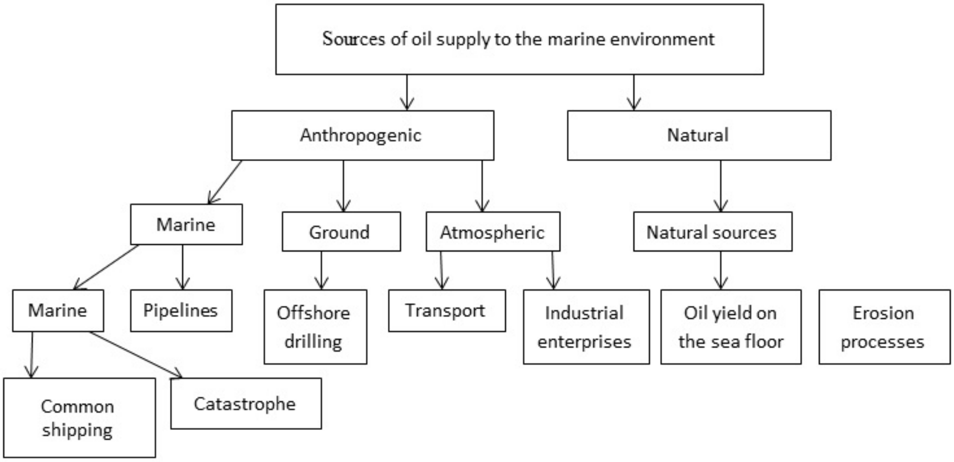

Figure 1 – Sources of pollution

Toxication is very resistant and extends over long distances. Pollution occurs during the extraction, transportation and refining of oil.

The main natural sources of oil pollution of the marine environment are the release of oil at the seabed, and less significant sources are erosion processes. To the most important anthropogenic sources of oil pollution includes:

– marine - marine transport, warships, vessels for various purposes, pipelines, installations and devices used in the development of seabed and subsoil resources;

– ground - rivers, lakes and other water systems, where pollutants enter with groundwater, and also as a result of wastewater discharge from various coastal objects;

– atmospheric - various industrial enterprises, vehicles and other objects from where emissions of hydrocarbon compounds to the atmosphere can occur [9].

There are several groups of sources of pollution of the World Ocean, the classification of which is shown in figure 1.

Oil and gas deposits are in most cases located at a considerable distance from oil and gas refineries. Due to the high fire and explosion hazard during the transportation of oil, and especially natural gas, there are increased requirements for ensuring high integrity, reliability, and fire safety of vehicles.

One of the most economical and technically modern modes of transport oil and gas is the sea and river oil-loading fleet. In the 1970s and 1980s, large-tonnage tankers were put into operation with a carrying capacity of 100-250 thousand tons and giant supertankers - up to 750 thousand tons. A fleet of gas tankers for ocean and sea transport was also created.

On land, oil and gas transportation through pipelines is the most economical. The share of pumping oil and gas through pipelines in our country reaches 85%.

For transportation of oil to areas remote from pipeline magistrates, railroad transport with special oil tankers [10] are used. When transporting is conducted by these methods above, unforeseen accidents and spills on ground and water occur.

1.2.1. Water. The ingress of oil and its components into the environment (air, water and soil) causes a change in the physical, chemical and biological properties and characteristics of the natural habitat, disrupts the course of natural biochemical processes. In the process of the transformation of oil hydrocarbons, even more toxic compounds can be formed than the original ones, which have carcinogenic and mutagenic properties and are resistant to microbiological cleavage.

Any of the classes of petroleum products can become a harmful impurity that pollutes the water. In small concentrations, oil contamination can affect the taste and smell of water, and with large concentrations, they form giant oil spills and cause environmental disasters. The last one occurs during oil spills (for example, in the case of tanker accidents at sea or in oil pipeline breaks) or when large quantities of oil or petrochemical waste streams enter surface and ground water.

Contamination of the world's oceans with oil and oil products is the most vivid example of global anthropogenic impact. Currently in the World Ocean there is practically no such area where oil contamination would not be felt. Background levels of petroleum hydrocarbons in the marine environment vary within very wide limits: 10-5-10 mg/l in water and 10-1-104 mg/kg in bottom sediments, depending on many natural and technogenic factors. Maximum concentrations tend to coastal and inland sea waters, zones of intensive navigation and other economic activities, as well as to areas of hydrocarbons escape from deposits on the shelf.

The problem of oil products pollution is very acute in the Northern Caspian, as a systematic accumulation of a large mass of oil spots is observed in its water area due to imperfect systems and equipment of the oil production complex, as well as an increase in the volumes of crude oil and oil products transportation by tankers. Significant amounts of oil fall into the sea in the event of a ship accident, especially oil-loading [11].

1.2.2. Soil. Sources of soil pollution with petroleum products are the same as in the case of water and air. The main ones are oil and oil products spills, wastewater and emissions from oil refineries and petrochemical enterprises, as well as harmful waste from chemical enterprises that accumulate in landfills.

In soils, Oil and Petroleum products are in the following forms:

– in a porous medium - in a vaporous and liquid easy-moving state, in a free or dissolved aqueous or water-emulsion phase;

– in a porous medium and cracks - in a free motionless state, playing the role of viscous or solid cement between particles and aggregates of the soil, in a sorbed state associated with particles of rock or soil, including humus constituents of soils;

– in the surface layer of soil or soil in the form of a dense organomineral mass;

Both free and inactive sedimentary forms of oil products release volatile fractions to the atmosphere, and soluble compounds into water. This process does not completely stop with time, since the microbiological processes of hydrocarbon transformation lead in partto the formation of volatile and water-soluble products of their metabolism [12].

1.2.3. Analysis of petroleum products in water. Qualitative and quantitative determination of the composition of contaminant sinse wage isnecessary not only for the selection of the technology for their purification, but also for compliance with the norms for dischargingtreate dsewage into water bodies.

It should be recalled that existing standards for the maximumallowable concentration of petroleum products in water in reservoirsaresetat 0.1 mg/l formulti-sulfuroil, 0.3 mg/l forothertypesofoil, 0.1 mg/l forgasoline, tractor (GOST 1843-52) 0.01 ml/l, lighting (GOST 24753-68) 0.05 mg/l, sulfatedwith 0.1 mg/l. The limitingindicatoroftheharmfulnessofalloil products is organoleptic.

Due to the fact that oil and petroleum products are an extremely complex mixture of substances - low- and high-molecular, limiting, unsaturated, aliphatic, naphthenic, aromatic hydrocarbons, oxygen-, sulfur- and nitrogen-containing compounds, asphaltenes and other compounds - In the analysis of waters, "oil products" are considered to be the sum of nonpolar and low-polar hydrocarbons - aliphatic, alicyclic, aromatic, which make up the bulk of oil and are soluble in hexane. Accordingly, methods for determining petroleum products in wastewater should include the concentration and recovery of petroleum products, the separation of the hydrocarbon part from foreign matter and the quantitative analysis of the released substances.

There is a significant amount of specialized literature on sampling methods and analytical methods for determining petroleum products in water. Also there are presented the most widely used methods used in the USSR and abroad mainly for routine analysis.

In our country, depending on the equipment of sanitary laboratories for the determination of petroleum products in effluents, the gravimetric method, IR and UV spectrophotometric, and also gas chromatographic, are used, which, as noted in [13], "give the same exact results if all conditions are met correctly and (GC-MS), the method of high-performance gas chromatography (HPLC), etc. (see / 16, 19-21 (and references therefrom). Nevertheless, when choosing the method for the quantitative determination of petroleum products in waste water, the main requirements are sensitivity and the possibility of wide application in practice. To determine the level of MPC, gravimetric, spectrophotometric (in the IR and UV regions of the spectrum), luminescent and gas chromatographic methods are used. Gas chromatography methods are useful for determining the qualitative and quantitative composition of petroleum products, but their sensitivity largely depends on the type of instrument. When determining the total content, which is stipulated by hygienic standards, gravimetric and optical methods are more convenient, having sufficient sensitivity and expressiveness, the most universal method of infrared spectroscopy, taking into account aliphatic and naphthenic hydrocarbons, the content of which in oil reaches 70-90 % [13, 14].

1.3. Elimination methods of spills and accidents of oil and oil products on soil and water surfaces. Methods of removing oil products from the water surface and soil, which are divided into four large groups:

– mechanical methods, carried out with the help of various constructions and devices for collecting oil;

– physicochemical methods based on the use of physical and chemical phenomena;

– biological methods, carried out with the help of microbiological cultures;

– photochemical, passing under the influence of sunlight and catalysts [15].

For the elimination of the consequences of a spill of oil and oil products, mainly mechanical and sorption methods are used. However, when the thickness of the oil layer is less than 1-2 mm, and also with a small depth of the reservoir, the use of mechanical methods becomes impossible. In such conditions, special oil absorbing materials are most effective. The qualitative removal of oil contamination does not occur without the use of various kinds of sorbents [16].

Currently, the most acute problem is the removal of spilled petroleum products from the water surface. The simplest methods to combat the contamination of the water surface by petroleum products include the way that the spill is localized with the help of booms. The designs and methods of implementing the oil spill (containment) can be very diverse.

1.4. Classification of petroleum sorbents. Classification of oil sorbents [17, 18] by raw materials, table 1; by dispersion, table 2.

Table 1 – Classification of petroleum sorbents by raw materials

Inorganic sorbents		Organic sorbents			
Natural materials	Synthetic materials	Caustobioliths	Natural raw materials vegetable and animal origin and wastes of their processing	Organo-mineral	Synthetic
Disperse silica	Perlite	Coal	Cereal husks	Slates	Polypropylene
Zeolites	Expanded clay	Graphite	Moss, foliage	Sapropel	Polyurethane
Layered silicates	SilicaGel	Peat	Bark, sawdust	Oilsludge	Teflon

Table 2 – Classification of oil sorbents by dispersion

Dispersed		Molded		
Finely dispersed	Large-dispersed	Fibrous	Pressed	Combined
Powders	Crumbs Granule Flakes	Woven and non-woven roll materials	Plates	Sorbing booms Pillows Mats with a shell of permeable material

1.4.1. Inorganic sorbents. *1.4.1.1. Carbon sorbents.* The history of the use of sorbents is associated with microporous carbon materials - active coals.

Active coals are porous solids, the voids of which are interconnected so that their structure resembles the structure of the wood. Depending on the formation conditions, all active carbons have a mono- or polydisperse system. They consist of many randomly arranged microcrystals of graphite formed as a result of a combination of carbon atoms when the carbon-containing raw material is heated. The dimensions of these crystals are 1.8–2.6 nm in diameter and 0.7–1 nm in height.

The ability of charcoal to decolorize solutions is known from the XV century, but only in 1785. T.E. Lovitz took advantage of this property for practical purposes - sorption purification of liquids.

At present, granular and powdered coals, as well as carbon fibers, are used for the sorption of aqueous solutions.

Granulated active carbons have a particle size of 0.07–7 mm. Depending on the size of the pores, they can be successfully used to extract contaminants from the water with a different size of molecules, coarse dispersed impurities and mixtures of polydisperse composition (domestic sewage).

Carbon sorbents with a particle size of 0.07–0.12 mm are classified as powdered active carbons. The main advantages of active coals include their low cost and good sorption kinetics, and a considerable area of the outer surface [19].

Currently, the main directions of the use of carbon sorbents are related to technological processes of adsorption purification, separation, isolation and concentration in gas and liquid media. The role of carbon sorbents in the solution of environmental problems is constantly growing: purification of drinking water, oil effluents, exhaust gases of industrial and energy enterprises.

Porous carbon materials were first obtained predominantly by thermal treatment of wood, then by coal. Now they are produced almost from all types of carbon-containing raw materials: wood and cellulose, stone and brown coals, peat, oil and coal pitches, synthetic polymeric materials, liquid and gaseous hydrocarbons, various organic waste. The modern world production of porous carbon materials (PCM) approximates to one million tons per year. Carbon sorbents are used in various forms: in the form of a powder with a particle size of up to 0.8 mm, granules of a larger size, blocks of various shapes and sizes, films, fibers of tissues. The most common ones are powdery sorbents, which are easy to obtain from crushed raw materials. Porous carbon materials are formed as a result of topochemical reactions during pyrolysis (heating in the absence of air oxygen) of fossil coals, peat, wood, cellulose, carbides. At present, about 36% of carbon sorbents are produced from wood, of coals - 28, of brown coals - 14, of peat - 10, of coconut shells - about 10% [20].

The use of graphite as an oil sorbent is very relevant and has a practical future. Penograft is a well-studied material used in industry and engineering.

It is obtained by very rapid heating (thermal shock) of interstitial compounds in graphite (CSG) of various nature. In mass production, interstitial compounds are used with sulfuric and nitric acids, which are obtained by chemical or electrochemical oxidation of natural graphite powder. After the thermal shock, a product consisting of worm-like carbon particles is formed, the so-called peculiar "black snow". The results of the studies show that the total sorption capacity of STRP and UWRM, depending on the viscosity and on the time of sorption, is 50-60 g of oil per gram of sorbent, then as for commercial sorbents, this value ranges from 3 to 20 g/g [21].

1.4.1.2. Non-carbon sorbents. There is a method for producing a composite cryogel absorbent based on polyvinyl alcohol containing dispersed filler - iron-containing precipitate, isolated at the water intake of Akademgorodok (Tomsk). The sorption properties of the cryogelabsorbant with respect to oil and phenol in the purification of water are investigated. It has been established that cryogel-sorbent possesses the highest phenol-and oil-absorbing capacity on the basis of iron-containing precipitate heat-treated at 250 °C. The degree of water purification in single-stage treatment was 89.5 and 93.5% for oil and phenol, respectively [22].

1.4.1.3. Other natural materials and sorbents on their basis. In connection with the increase in pollution of water basins, the urgency of creating highly efficient sorbents for the removal of oil products (oil and its derivatives) from their surfaces during pollution increases. These sorbents (oil sorbents) must be sufficiently oil-intensive (hydrocarbons absorbability is not less than their own weight), hydrophobic with respect to water and hydrophilic with respect to petroleum products, such as Sorbohole, etc. There are many varieties of oil sorbents from highly porous vegetable materials (peat, sawdust), mineral and artificial origin. These oil adsorbents do not sink, but float on the surface for a long time after absorbing oil products. At the same time, it is recognized that in most situations (fire-danger, excitement, proximity of the coast, lack of special means of collection), it would be advisable to have sorbents drowning after absorbing oil. In this regard, diatomites are natural powder-like nanostructured materials-siliceous rocks consisting of microscopic shells of plankton, 1-5 microns in size with a wall thickness of 50-100 nm of amorphous silicon oxide aggregated in soto-like structures are perspective. Specific high pore volume causes a low specific gravity of dry diatomite - Picu = 0.4-0.6 g/cm^3.

Natural diatomite is equally hydrophilic to both water and hydrocarbons, which does not allow its use in collecting petroleum products from water and wet surfaces. The authors worked out several methods for hydrophobizing diatomite by creating hydrophobic films on the particles with a thickness of about 5-10 nm (estimated evaluation) and obtaining from it an oil sorbent called "Diasorb". The first is to apply a hydrophobizing layer from the vapor of the "high boiling" hydrocarbon to a cold diatomite powder, mixed in a steam-air stream. Hydrophobization of diatomite is achieved by condensation on it of the order of (3-5)% (weight) hydrophobes. Even loose agglomerates of particles with a size of up to 5 mm are hydrophobic. The second method consists in impregnating diatomite (1-2) with a solution of a high-boiling hydrocarbon in a low-boiling hydrocarbon, followed by evaporation of the low-boiling solvent. The advantage of the first method is the relative cheapness for industrial implementation. The second is the possibility of organizing an efficient (due to the microsize of particles) process of demulsification of oil emulsions with the organization of closed component cycling [23].

1.4.2. Cellulose-containing sorbents. *Lignine.* Lignin (from latin *"lignum"* a tree, wood) - the natural polymer which is a part of almost all land plants. Content of lignin in wood of coniferous and deciduous breeds, respectively, is 23–38 and 14–25% on weight. Lignin is located in cellular walls and intercellular space of plants and fastens cellulose fibers. Lignin – amorphous substance from light-cream till dark brown color with a molecular weight from 1 to 150 thousand, with a density of 1250–1450 kg/m^3.

From vegetable fabrics lignin can be emitted in many ways, for example hydrolysis in the presence of mineral acids (chamois).Hydrolytic lignin has the following elementary structure, masses. %:

Carbon – 63,5–65;
Hydrogen – 5,4–5,9;
Oxygen – 29,1–30,1.

In industrial scale lignin is received in the course of cellulose and hydrolytic timber-chemical production. The lignins emitted in various ways distinguish on structure and properties as from a product in a native form (protolignin), and from each other.

Lignin – irregular polymer. His branched macromolecules are constructed mainly of the remains of the replaced phenol alcohols:

I – 3-methoxyhydroxycoric, or coniferyl;
II – 3,5-dimethoxy-4-hydroxycinnamic, or synapic;
III – n-hydroxycinnamic, or p-coumaric.

Lignin of wood of coniferous breeds includes, generally the remains of alcohol I, deciduous breeds - I and II alcohols, grassy plants and some tree species (aspen) - alcohol III.

Large-tonnage waste of bark of a larch can be bricketed without use of the binding and increased temperatures. The coal-raw received from briquettes has the sufficient mechanical durability and other properties allowing to use it in various productions, replacing the charcoal produced from birch stem wood. Sorption properties of the received active coals on iodine and methylene blue are at the level of 67-75% and 265 mg/g respectively that above requirements of the standard, BAU-A and OU-A shown to active coals of industrial brands [24].

Lignin easily is exposed to chlorination, nitridation and oxidation, when processing by acids - to hydrolysis. Development of new types of sorbents is based on these properties of lignin. Hydrolytic lignin absorbs 1,5 kg of oil on sorbent kg. The oil capacity of lignin can be increased by processing of the hydrolyzed lignin by solution of the caustic soda or ammoniac water.

1.4.3. Sorbents based on peat. Destruction of oil in the soil is a difficult physical and chemical and biochemical process which orientation and speed depend on a complex of direct and indirect factors. The climate, properties and the modes of soils, seasonal activity of microflora, humidity, concentration and fractional composition of oil in the soil concern them. The leading role at recultivation is played by biological factors. One of important conditions of biological clarification of the soil from oil is degree of functional activity of soil microflora.

Industrial territories of cold regions are characterized by high extent of oil pollution against the background of extremely adverse soil climatic conditions.

Recently much attention is paid to development of ways of biological recultivation of the petropolluted soils which cornerstone activation of processes of microbiological destruction of oil in the soil is. One of perspective solutions of removal of oil from a surface of the water is use of the sorption and biosorption technologies providing use of the special petroabsorbing materials. The peat processing products used for mitigation of consequences of oil pollution must meet the following requirements: high operational characteristics, rather simple technology of receiving and existence of necessary raw material resources, low cost, biospheric compatibility, i.e. application and utilization of the fulfilled materials shouldn't lead to repeated environmental pollution. There searches conducted by us have shown that sufficiently peat has universality of the properties meeting the above-mentioned requirements. Peat owing to the structure and existence of hydrocarbon-oxidizing microflora (HOM) can serve both as a sorbent of oil hydrocarbons, and their destructor.HOM number in peat by 4-5 times exceeds a similar indicator for soils. Besides, microorganisms of peat aren't antagonists of soil microorganisms.

Peat, owing to the structure and to existence of hydrocarbon-oxidizing microflora (HOM), can serve both as a sorbent of oil hydrocarbons, and their destructor. Sorption capacity of peat in relation to oil depends on extent of decomposition and for riding peat is 8-10, for low-lying – 2-4 g of oil/1 of air and dry peat.

For receiving a peat sorbent, it is recommended to use the riding peat of moss group of low extent of decomposition (5-10%) having the high porosity which was more developed by cellular structure and, respectively, higher sorption ability in relation to oil hydrocarbons. For giving to a sorbent of hydrophobic properties it is modified by, for example, drying at 100-120 °C.

The peat sorbent prepared from riding peat possesses the following characteristics: sorption capacity in relation to oil - 8-10 g of oil/g of a sorbent; saturation time sorbent oil up to the extreme size - 5-10 min.; selectivity in relation to oil in system oil - water - 90-95%; the preservation of oil in volume of a sorbent excluding her spontaneous drain isn't limited on time; buoyancy - more than 30 days.

Utilization of a sorbent is possible in road construction and at production of fuel briquettes [25].

1.4.4. Sorbents based on raw materials of vegetable origin. One of perspective decisions in the field of purification of the petropolluted waters is use of technologies with use as the sorption materials (SM) of vegetable waste. The efficiency of the last is defined, mainly, by their capacity in relation to NP, water repellency degree, buoyancy after sorption and a possibility of a desorption of oil product, regeneration or utilization of a sorbent [26].

By production of sorbents for absorption of oil and oil products as raw materials it is possible to use both pod of buckwheat and sunflower, and a peel of oats and rice, both a cane chaff, and a black shell of walnut, etc.

The petroabsorbing ability of vegetable waste is the main criterion which should be considered by production of this or that type of a sorbent as the oil capacity of the made sorbent on a straight line depends on initial oil capacity of pure raw materials.

Due to the above as SM were studied the following waste of agriculture: wheat peel (WP), barley (BY) and linen fire (LF).Interest in the called materials is connected with a lot of tonnage and an available source of raw materials in the Republic of Tatarstan. For determination of oil capacity of sorbents at a temperature of 200 of C the oil samples got in NGDU “Elkhovneft” of JSC “Tatneft” were used.

Original lyphysicomechanical properties of waste were defined.

The oil capacity of the called sorption materials in static conditions was defined. The obtained data are presented in table 2.It is noted that within fifteen minutes of engagement the oil capacity of WP reaches 4,12 g/g, and BY - 5,95 g/g. The oil capacity in the dynamic conditions determined by transmission of a certain amount of oil through a layer of a sorbent, weighing 1 g, placed in a glass column for WP and BY, didn't exceed the 5th g/g, for linen fires - 9,44 g/g. In static conditions, the greatest values of oil capacity are received when using linen fires. Existence in its structure of large amounts of cellulose (38-40%) while for other SM, no more than 23% and lignin (23-24%) are caused, most likely, by high value of required parameter in comparison with other studied waste [27].

Use of all these materials which are potential local raw materials for production of sorbents allows to combine elimination of waste of agricultural production with nature protection activity.

The petroabsorbing ability of vegetable waste is the main criterion which should be considered by production of this or that type of a sorbent as the oil capacity of the made sorbent on a straight line depends on initial oil capacity of pure raw materials.

The petroabsorbing ability of vegetable raw materials, including rice peel (after special processing) is from 6 to 10 kg.

One more of the major factors characterizing quality of sorbents is absorption of water by them.

Absorbing moisture in a varying degree vegetable sorbents increase the weight therefore their buoyancy and also oil capacity as the part of pore space is occupied by a water phase worsens.

The Kyzylorda region is widely known for the developed rice growing which in turn is also a source of annual large-tonnage withdrawal – the rice peel polluting the environment.

Because a rice peel being silicone polymer of a phytogenesis, doesn't burn and doesn't decay and owing to availability and low cost, it is an irreplaceable source for receiving the biocompass necessary for biodegradation of oil products.

For receiving this compost we have in vitro made experiments according to influence of a rice peel as filler of the polluted soil therefore have come to a conclusion that a rice peel creating airspace in the soil, promotes intensive oxidation of oil products oxygen of air and their degradation and also experiments on destruction of cellulose and lignin structure of a peel by means of soil aerobic and anaerobic microorganisms were made.

For definition of a possibility of purification of the petropolluted waters and soils by means of the rice peel (RP) we have studied her sorption characteristics in dynamic conditions:

– the oil desorption degree characterizing return of oil to a production cycle and a possibility of his repeated use;

– oil capacity;

– moisture absorption;

– buoyancy.

It is known that the sorption capacity of the studied materials depends on viscosity of oil: if oil easy, low-viscous (for example, the viscosity is equal 3,27sst at 20 °C), the full sorption capacity of RP is equal 4,09, if oil – heavy, high-viscosity (for example, the viscosity is equal to 186,5 sst), the full sorption capacity of RP is equal to 8,82.

By a mechanical extraction depending on type of oil and properties of a sorbent it is possible to return from 60 to 95% of collected oil in a production cycle: RP gives from 61,12 to 65,34% of oil. Regeneration is economically inexpedient in the chemical ways since expense of large volume of reagents is required, there is also a problem a further processing of the formed waste. In this plan thermal processing of sorbents with the residual content of oil is of interest.

When determining a possibility of sewage treatment from oil and oil products of a research have shown that the efficiency of cleaning is depending on the speed of transmission of the purified solution through a motionless layer of adsorbent and from concentration of oil in the purified water.

The table 3 – Efficiency of Purification of Waters from oil products depending on the speed of transmission and concentration of oil

Type of a sorbent	Extent of purification of waters (%) of oil products at speeds			Extent of purification of waters (%) depending on concentration of oil		
Sorbenton the basis of RP	6 ml/min	15 ml/min	32 ml/min	1,4 mg/l	27,6 mg/l	60 mg/l
	99,4	99,3	97,7	0,04	0,2	0,8

Being a product of processing of waste of vegetable raw materials, on extent of cleaning the sorbent based on RP provides high extent of purification of waters of oil products. It should be noted one more advantage also: the sorbent contains small amount of impurity, has high content of carbon therefore it is close on the structure to active coals, and the branched structure of dioxide of silicon gives him durability and thermal stability [28].

1.4.5. Synthetic sorbents. Synthetic organic sorbents, thanks to the availability and production commercially, find more and more broad application for collecting the poured oil. Besides, they often are production wastes. The open and cellular structure and high oleophilicity of these materials provide efficiency of their use as petroabsorbers. Application for these purposes of expanded polystyrene, polypropylene, phenol formaldehyde and carboamid of ormaldehyde pitch, a rubber crumb, materials based on polyurethane foam, etc. is well known [29].

In recent years one of the most developing directions of a research is development and use the foamed polymeric of the sorbents microcontainers capable at any weather conditions to make collecting oil and oil products from a surface of the water. At the same time quiet, strict requirements are imposed to foamed polymeric sorbents today: high speed of sorption and sorption capacity on oil and oil products, long buoyancy, water repellency, ability to repeated regeneration, simplicity of technology of collecting sorbents from a water surface and ecologically safe utilization of the fulfilled sorbents. An integrated approach to the solution of this problem the foamed polymeric of sorbents at emergency oil spills opens very perspective opportunities of use. There searches conducted for a row of years in this direction, as a matter of fact, allow us to look a little differently at a problem of development and selection the foamed polymeric of sorbents considering not only their sorption capacity, but also the macrostructure, volume weight (seeming to density), the chemical composition of a polymeric basis, type of oil product, flood scale, etc.

Also, the rubber crumb is applied as a sorbent. Data are provided in table 4.

Table 4 – The Main technical characteristics of an oil sorbent on the basis of rubber powder

Indicators	Value
Bulkweight	350–400 kg/m^3
Oilcapacity, kg/kg	4–4,4
Time of full saturation, min.	5–10
Moisturecapacity	10±1%
Buoyancy	Morethan 96 h.
Utilization	Extraction, as a component in the rubber-bituminous and asphalt concrete mixes

As sorbents use of rubbers in view of variety of their chemical and structural structure and also their physical and chemical properties find more and more wide circulation. As sorbents use rubbers with polar groups, for example nitrilacrylic, methacrylic acids and rubbers without polar groups.

The representative of rubbers without polar groups is butadiene styrene rubber. Received as withdrawal from production of rubber products, material based on this rubber represents a rubber crumb with sizes of 0,5–3 mm. His absorbing ability grows with reduction of the size of a crumb and with increase in time of contact with film oil. Results of researches of these indicators are given in figure 2.

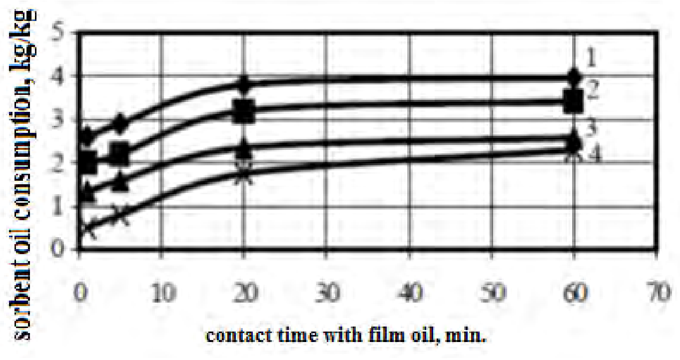

Figure 2 – Dependence of oil capacity of butadienestyrene rubber on time of contact with film oil on a water surface for the size of fractions:
1 – 0,5–1 mm; 2 – 1– 2 mm; 3 – 2–3 mm; 4 – 3– 5 mm

This sorbent can be reused after an extraction. Fractions of a rubber crumb from 0,63 to 2,5 mm in size have the greatest absorbing ability. Application of a shallow crumb, namely less than 0,63 mm, leads to formation of gel weight that considerably complicates her collecting from a reservoir surface. Besides, the fine crumb has very small weight, and even at small wind at sieving bears her that also complicates her use. In view of the above-mentioned reasons the recommended fraction of the rubber crumb used as a sorbent is fraction from 0,63 to 1,5 mm. As a result of oil sorption the sorbent is agglomerated in large agglomerates up to several kilograms which remain on a surface of the water at any her state within several days and easily gather mechanically, without leaving marks even in the form of thin oil films. Rubber powder after collecting oil can be used as filler for a paving. In world practice a significant amount of a rubber crumb is applied in the mixes used at construction of paving (bituminous rubber BITREK mix).The share of mass of rubber powder in bituminous and rubber knitting in paving can make up to 10%.At the same time physic-mechanical characteristics of all covering (the increased crack resistance and the module of elasticity, increases by 20+30% frost resistance coefficient) significantly improve that affects positively a resource (service life of a covering of roads increases by 1,5+2 times).

In all actions connected with removal of pollution from waters of different function it is necessary to proceed from the main principle: not to do to an ecosystem bigger harm, than that which is already put at pollution. One of the main problems of sorption purification of waters is the problem of further utilization of the fulfilled sorbents. The important moment is the solution of the questions connected with utilization of the fulfilled polymeric sorbents after repeated sorption. In our opinion one of effective methods of their utilization is burning in the furnace at rather high temperature over 1273 To at which to zero formation of toxic products during thermal decomposition of a polymeric sorbent practically comes down. Based on the above it is possible to come to conclusion about what in relation to conditions of emergency situations, the received results of researches have not only scientific, but also important applied value. It is established that one of the main advantages the foamed polymeric sorbents their high sorption capacity on oil products, buoyancy and ability to repeated regeneration is. Becomes obvious that the choice of sorbents for cleaning of a surface of the water of oil and oil products must be comprehensively reasonable at which has to be considered not only their sorption capacity, but also oil product type, scale of an emergency flood, thickness of an oil layer on a surface of the water, a macro-structure and morphological features of a sorbent. The same sorbent can't be “panacea from all troubles”, i.e. at the same time to be effective for sorption of various types of oil products. Probably time to speak about a set of polymeric sorbents and selective approach to their use has come for a long time. So, for example, it is established that for cleaning of a surface of the water of oil and fuel oil it is necessary to use sorbents based on foam polyolefins with a volume weight of 80-170 kg/m^3, and for cleaning of diesel fuel sorbents with a volume weight of 500-600 kg/m^3. And, not only foam polyolefins, but also other polymeric materials and their mixes, in relation to these or those conditions, can become highly effective supersorbents for collecting oil and oil products [30-32].

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Резюме

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ЭКОЛОГИЯ НЕФТИ И НЕФТЕСОРБЕНТЫ

Изложены материалы о нефтесорбентах и их применении. Показаны методы ликвидации разливов и аварий нефти и нефтепродуктов на почве и водной поверхности.

Ключевые слова: нефть, сорбенты, экология, химический состав, вода, почва, торф, целлюлоза.

Резюме

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МҰНАЙ ЖӘНЕ МҰНАЙ СОРБЕНТТЕРІ ЭКОЛОГИЯСЫ

Мақалада мұнай сорбенттері және оларды қолдану туралы материалдар берілген. Топырақ және су бетіндегі мұнай мен мұнай өнімдерінің төгілуін және авариясын жою әдістері көрсетілген.

Түйін сөздер: мұнай, сорбенттер, экология, химиялық құрамы, су, топырақ, шымтезек, целлюлоза.