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ECOLOGICAL ASSESSMENT OF USE AND REMEDIATION OF FUEL OILS

Introduction. Oil-contaminated sediments pose serious environmental hazards for both aquatic and terrestrial ecosystems [1]. Contamination by oil and oil products has caused serious harm, and increasing attention has been paid to the development and implementation of innovative technologies for the removal of these contaminants [2]. Innovative and environmentally compatible technologies are urgently required to remove oil-contaminated sediments [1]. Due to tidal and waves actions, the oil spillage affects the shorelines by adhering to the soil, making it difficult for immediate cleaning of the soil. As shoreline clean-up is the most costly component of a response operation, there is a need for effective oil remediation technologies [3]. The remediation of contaminated sites can be achieved by physicochemical or biological methods [2]. Various physical, chemical and biological technologies are investigated for the remediation of oil-contaminated sediments such as flotation and washing, coal agglomeration, thermal desorption, ultrasonic desorption, bioremediation, chemical oxidation and extraction using ionic liquids. A combination of two or more technologies is expected to provide an innovative solution that is economical, eco-friendly and adaptable [1].

Conventional physicochemical methods can rapidly remove the majority of spilled oil, but, in most cases, removal simply transfers contaminants from one environmental medium to another and can even produce toxic byproducts. Moreover, crude oil cannot be completely cleaned up with physicochemical methods. Thus, more attention is being given to biological alternatives [2]. Bioremediation is a promising technology for responding to marine oil spills [4]. Bioremediation is defined as the act of adding or improving the availability of materials (e.g., nutrients, microorganisms, or oxygen) to contaminated environments to cause an acceleration of natural biodegradative processes [5]. A majority of molecules in crude oils and refined products are biodegradable, and they will eventually leave the environment as they are consumed by microbes. Bioremediation aims to stimulate the rate of this process. Successful bioremediation efforts have so far focused on applying fertilizers to aerobic oiled shorelines to at least partially relieve the nitrogen limitation of biodegradation by indigenous microorganisms [4]. It is suggested that bioremediation should now take its place among the many techniques available for the treatment of oil spills, although there is still a clear need to set operational limits for its use [5]. Therefore, the purpose of this study was the development normative and technical documentations and measures for environmental protection in the remediation of waste oil.

Main part. The objects of this study were petroleum products, contaminated during transportation through the pipeline, the remains from the tanks for cleaning of petroleum products, waste products of petroleum refining, oil sludge, substandard oil, oil extracted from the tank during its steaming (GOST 10585-99 "Fuel petroleum. Fuel black oil. Specifications", GOST 21046-86 "Waste oil products. General technical conditions", State Standard 4058-2001 "Fuel petroleum. Black oil"). Elaboration of the normative and technical documentations on utilized and remediated fuel oil was performed according to RD 6-23-84 "Regulations on the production schedules of production at enterprises and organizations of the Ministry of Chemical Industry". Toxicity indices and hazard class of waste fuel oil for remediation were determined in accordance with State standards 2.2.7.029-99 "Hygienic requirements for industrial waste management and the definition of the class of danger for public health". Waste fuel oil by physical and chemical parameters shall meet the requirements and standards specified in the GOST 10585-99 "Fuel petroleum. Fuel black oil.

Specifications”, GOST 21046-86 “Waste oil products. General technical conditions”, State Standard 4058-2001 “Fuel petroleum. Black oil”.

Installation of processing and utilization waste oil mixture (Borislav, Ukraine) with capacity of 12 tons per day, is designed to serve areas in Western Ukraine (customers), for which is advisable to transfer sub-standard petroleum products by road, or use the railroad tank. The recycling process is based on the separation of the mixture of waste oil into fractions and distillates, which are formed at 180°C and within the limits 180—350°C. This residue is obtained and it must comply with the State Standard 4058-2001 “Fuel petroleum. Black oil”. Separation occurs by direct distillation bottoms in heating DC-18584.00.004 (“Cred-mash”, Kremenchug, Ukraine). The technological process consists of several stages: the plums raw materials from rail tank car to ground capacity; downloading of the cub heaters; distillation of the mixture; condensation, cooling and storage of derived distillate and residues; shipment of finished products. The semi-finished 180 and 350 are used for own needs as fuel, and fuel oil 100 brands produced as commodity product.

Component composition of marketable black oil may include atmospheric distillated crude oil, tar — vacuum residue (500°C), vacuum gasoil (vacuum distillate at a temperature of 350-500°C), extracts oil production (350—420°C), oil light fraction — transformer distillates (400—450°C), oil fraction — machine distillates (420—490°C); oil heavy fraction — cylinder distillates (450—490°C), kerosene, gas oil fractions (primary and secondary), heavy gas oil catalytic (thermal) krening and carbonization, bitumen (processed residual lubricating oils and tar), braking remains; heavy pyrolysis resins.

According to State standards 2.2.7.029-99, fuel oils belong to 3 class of toxicity according to LD50, by the threshold limit value (TLV) in the air of the working area — to 4 class of toxicity. Calculation of toxicity index for the individual components of fuel oil (Table 2) showed that the lowest value of its are typical for paraffin ($K_1 = 21.16$), monocyclic low-content sulfur ($K_2 = 25.41$) and monocyclic sulfur ($K_3 = 26.13$) of petroleum. Considering the fact that $K_1 < K_2 < K_3$ and $2K_1 < K_3$, total index of danger not neutralized with glauconite components of oils is $K_\Sigma = 1 / 3^2 \times (21.16 + 25.41 + 26.13) = 7.99$; a mixture according to State standards 2.2.7.029-99 “Hygienic requirements for industrial waste management and the definition of the class of danger for public health” belongs to 3 class of hazard at storage on soils and for oil spill. After sorption of oils with glauconite, content of chemical components (K_1, K_2, K_3) was decreased to 0.003 (paraffin), 0.01 (low-content sulphurous oils) and 0.006 (sulphurous oils). Thus, K_1 is 500.00, K_2 – 242.76, K_3 – 329.46, K_Σ – 117.93 (> 10), that means that a mixture belongs to 4 class of hazard. Experimental mean lethal concentration (LC_{50}) for fuel oil has not been established. Estimated LC_{50} is given by ($LC_{50} = 1.15 \times LD_{50}$ (10 000 mg / kg) – 2.97 = 1.15 × 4.0 – 2.97 = 1.63, ant (1.63) = 5.1 mg / L × 1 000 = 5.100 mg / m^3.

Threshold of acute inhalation action is calculated by the formula: $\lg Lim_{ac} = 0.68 \times \lg LD_{50} - 3.40 = 0.68 \times 4.0 - 3.4 = -0.68$, ant (–0.68) = 0.51 × 1 000 = 510 mg / m^3. TLV of petroleum in the air of the working area is 300 mg per m^3. Clinical signs of acute inhalation action characterized by irritation of the upper respiratory tract with possible development of acute bronchitis and lipid pneumonia. Symptoms of irritation of the mucous membranes are observed at concentrations of 500 to 1 000 mg per m^3. Prolonged contact with fuel oil that could cause the angiotoxic effects, increases the risk of respiratory diseases, liver, kidney and heart. LD_{50} of fuel oils when injected *per os* to white rats include 5.0—10.0 g / kg. LD_{100} (absolute lethal dose) is over 10 g / kg, LD_0 (The maximum inactive dose) – 1 g / kg. The threshold dose is $0.99 \times \lg LD_{50} - 2,83 = 0.99 \times 4.0 - 2.83 = 1.13$, ant (1.13) = 3.1 mg / kg (and in water 3.1 mg / kg × 20 = 62 mg / dm^3). The maximum inactive dose = $0.88 \times \lg LD_{50} - 3.54 = 0.88 \times 4.0 - 3.54 = -0.02$, ant (–0.02) = 0.98 mg / kg (in water 0.98 mg / kg × 20 = 19.6 mg / dm^3). TLV according to organoleptic limiting feature of harm is 0.3 mg / dm^3 (for fuel oils — 4 class of hazard), and in fisheries waters — 0.05 mg / dm^3. LD_{50} *per cut* is more than 2000 mg per kg.

Oils belong to primary skin irritant compounds and are not characterized sensibilization properties, allergenic effects of their actions on the skin is not registered. When working with fuel oil, its concentration on the inner surface clothes on the first day amounts 1.0—10.0 mg / dm^2, during 5—10 days — up to 30—500 mg / dm^2. During working with fuel oil, skin irritation and follicular formation can occur (toxic melanodermatitis, occupational dermatitis, eczema, keratosis, papilloma, warts, etc.). Fuel oil (resinous) containing 0.0015% of 1.2-benzopyrene led to the development of tumors in 9 of the 16 mice, in 7’s — malignant. Fuel oil of direct distillation possesses a weak carcinogenic effect. K_{cum} is not determined, but prolonged exposure to fuel oils can cause black oil hyperkeratosis of skin and even cause skin cancer due to the presence in its compositions 1.2-benzopyren. Heavy oil concentration in the air of the working area and the atmosphere is determined by the nephelometric assay; It consists of hydrocarbons (measured by gas chromatography); water reservoirs (by mass spectrometry, infrared); total hydrocarbons (with the aid of AM-2 or device “Mipran”); in the soil (by the “arbitration” method). During the working with the fuel oil, control of air in working zone for the vapor of aliphatic saturated hydrocarbons C1—C10 in terms of carbon (MPC is 300 mg / m^3) is carry out.

The process of regeneration of waste fuel oil should be as automated and mechanized, and meet the requirements of GOST 12.1.007-76 “Occupational Safety Standards System. Harmful substances. Classification and general safety requirements” and GOST 12.2.003-91 “Occupational Safety Standards System. Production equipment. General requirements for safety”. The microclimate of industrial facilities, ventilation, noise and vibration, natural and artificial lighting and the size of the sanitary protection zone must meet to current health standards and regulations.

The methods of remediation of fuel oils include solvent extraction, bioremediation, phytoremediation, chemical oxidation, electrokinetic remediation, thermal technologies, ultrasonication, flotation and integrated remediation technologies (Lim et al. 2016). In our study, we used environmental sorbent glauconite modified by biosurfactants PS-

17. During spill of raw materials or finished product, they are processed by environmental sorbent glauconite modified by biosurfactants PS-17. The fire on the installation should be extinguished after disconnecting electricity with glauconite modified by biosurfactants PS-17, with carbon dioxide fire extinguishers, water system with fire water supply enterprises, foam, powder, superheated steam, fire blanket, firefighting and others. Containers, tank trucks, sleeves during filling and draining of waste petroleum products regenerated should be grounded. One time per year the soil of enterprise should be regenerated with the ecological sorbent glauconite modified by biosurfactants with normal use 2.2 kg per m^2 at pollution of soil by substances at the level of the MPC, 22 kg per m^2 with significant pollution (10 MAC) or 220 kg per m^2 with high level of pollution (100 MAC). Along the perimeter of the enterprise must create sorption-filtration engineering geochemical 3-ply barrier with thickness of 10 cm for ratio glauconite-grained sand — 30:50; 70:30, and 30:20, respectively. Not allowed to spill the regenerated oil on the ground, in the water and sewerage network.

Conclusions. Technological regulations for regeneration of waste fuel oil include the plums raw materials from rail tank car to ground capacity; downloading of the cub heaters; distillation of the mixture; condensation, cooling and storage of derived distillate and residues; shipment of finished products. The semi-finished 180 and 350 are used for own needs as fuel, and fuel oil 100 brands produced as commodity product. Fuel oils not neutralized by glauconite are belong to 3 class of danger, while after neutralization by glauconite modified by biosurfactants PS-17 — to 4 class of danger.

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COMPARISON OF ACCUMULATION OF NUTRIENTS IN SHOOTS OF HERBACEOUS PLANTS IN FOREST SPRING NICHES

Introduction. Seasonal variability of the environment and different needs of plants during their life span decide about the dynamic character of the relationship plant — environment, especially in ecosystems of marshy land, where underground waters flowing out on the surface create specific conditions for development of the marshy land plants. Specific nature of underground waters introducing a specific ion load to ecosystem [1] and their high level stimulate swamping of the area and development of rich plant species [2]. Plants of marshy meadows by retention, uptake and accumulation of a series of nutritional components, play a very important role in formation of chemical character of waters [3]. In recent years, the composition of species of forest vegetation which in a substantial way modifies physical and chemical properties of waters [4] contributing at the same time to their purification has drawn special attention. Interactions between water, vegetation and the soil in mid-forest spring niches are very close and anisotropic.

The aim of the study was to compare ten species of herbaceous plants of forest spring niches as to accumulation of N, P, K, Mg, Ca, Zn, Cu, Ni, Mn, Fe, Sr and Al. The content of macro- and microelements was analyzed, considering each component separately and in an integrated way, comparing the demand of the examined species for nutritional components.

Main part. The research was done in the upper course of Kamienna Creek which is the left side tributary of River Słupia situated in the northern part of Poland within Leśny Dwór Forest Inspectorate area (54°19'N; 17°10'E). It is the area of average annual precipitation of about 770 mm and average annual air temperature of 7.6°C. The area of the catchments of Kamienna Creek is nearly wholly covered by forests with spatially diverse species composition, with the dominance of beech, pine and spruce trees in its plateau part and common alder (*Ainus glutinosa*) at the bottom of the valley. The 40-86 years' old common alder (*Alnus glutinosa* Gaertn) constituted the layer of trees within a given marshy land, which grew on domed bogs consisting of the wood and sedge peat [5]. In the examined spring niche the

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