

Methods for cleaning soil from benzopyrene in the territory allocated for construction

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Abstract. The article examines the harm caused by benzopyrene to the environment and human health. Being a carcinogen, accumulating in human body, it has a mutagenic, embryotoxic, hematotoxic effect. Regulations require the removal of contaminated soil from the construction site with subsequent disposal. The disinfection methods are analyzed.

1 The influence of benzopyrene on the environment and humans

The most important indicator in assessing a territory suitability for development is soil contamination with various substances harmful to human health: oil products, radioactive gases, heavy metals, etc. Therefore, great attention is paid to their content control. The indicator is benzo(a)pyrene (C₂₀H₁₂), as the most toxic representative of polycyclic aromatic hydrocarbons.

Benzopyren is one of the most powerful and widespread carcinogens. Being chemically and thermally stable, possessing the property of bioaccumulation and once in the body accumulates, acts constantly and powerfully.

In addition to carcinogenic, **benzopyrene** has a mutagenic, embryotoxic, hematotoxic effect. It belongs to the substances of the first hazard class.

At present, due to the large number of technogenic processes, as a result of which carcinogenic and toxic substances enter the environment, great attention is paid to control over the content of harmful substances in water, soils, etc.

Benzopyrene causes significant damage to human health, getting into groundwater, contaminating the soil.

In this regard, when carrying out environmental surveys during the construction of facilities, a hygienic assessment of the quality of soils is carried out for compliance with the requirements SanPiN 2.1.7.1287-03 "Sanitary and Epidemiological Requirements for Soil Quality" (1).

If the benzopyrene content in soil does not exceed 0.02 mg / kg in total, taking into account the background level, then according to HR 2.1.7.2041-06 "Maximum Allowable Concentrations (MAC) chemicals in the soil" (2) the studied soil meets the safety requirements. Otherwise, the soil is recognized as unsuitable for use in landscaping and

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must be replaced or decontaminated directly at the construction site or with removal to the landfill and further disposal.

2 Methods used for cleaning soil from oil products

Documentation, in accordance with which it is necessary to determine the degree of danger, algorithms for the placement and disposal of soil:

SanPiN – №4266-87 и №2.1.7.1287-03.

- Order of the Ministry of Natural Resources and Environment of the Russian Federation – No. 536 MNR from 04.12.2014.
- GOST No. 17.4.3.04-85.
- Hygiene regulations – 2.1.7 2041-06 and 2.1.7.2511-09.
- Sanitary rules – 2.1.7.1386-03.
- Natural regulations, including measurement procedures – NR F T14.1:2:3:4.10-04 and NR F T14.1:2:3:4.12-06 (T 16.1:2:2.3:3.9-06).

The bulk of the existing regulatory framework was developed between 1999 and 2010.

The soil is taken from the construction site at several points, then transferred to the analytical laboratory, where, as a result of special sample preparation, the extract necessary for measurements is obtained. Further, using the method of liquid chromatography with fluorimetric or spectroscopic detection and gas chromatography (GCH) with mass selective, flame ionization, electron capture or photoionization detection, the concentration of benzo(a)pyrene in the obtained extract is determined, and then its concentration in the sampled soil is calculated.

After the increased volume of research on benzopyrene, the question about the disposal of the remnants of standard samples arose. There is only a note in GOST about oxidation with a strong solution of potassium permanganate. But since it is a precursor, it is necessary to accurately prescribe its amount. Benzopyrene is oxidized by an acidic solution of potassium permanganate to carbon dioxide and water.

The methods of disposal used to clean the soil from petroleum products, including benz(a)pyrene, include:

2.1 Chemical

The method is based on the choice of substances that promote the decomposition of materials into components. To speed up the process, materials containing oil are dissolved. This creates the conditions for the formation of solid, liquid impurities. They can be reapplied.

2.2 Combined

The most effective methods are those that simultaneously affect different components in the composition of oily waste.

Available options:

1. Extraction. Various types of solvents are used: liquids, liquefied gas, etc. They must react with petroleum products that are disposed of. When heated, the process develops faster.
2. Flotation. The waste is affected by hot water, which promotes the separation of the material – the components are released from the mixture.

3. The use of drum separators. The main purpose is to collect poisonous substances from oil spills in water bodies. Such installations operate in an aquatic environment, attract oil, which enters and is retained in drums.

2.3 Thermal

Available options:

1. Combustion with the subsequent formation of carbon dioxide, water.
2. Combustion in fluidized bed (boiling) ovens. As a result of the movement of the flow of the gaseous substance, a large amount of heat is released. The boiling liquid effect is created by the vortex turbulent movement of particles.
3. Pyrolysis. Incineration takes place in an oxygen-free environment. As a result, the formation of products of a different aggregate state occurs: liquid, gaseous.

All of the above-listed methods of disposal involve the removal of soil from the construction site. But, often the volume of the removed soil is very large and significant costs are required.

Despite numerous works on the development of various technologies for cleaning the environment from benzo(a)pyrene, more and more attention, due to economic efficiency, is paid to carbonaceous and mineral sorbents capable of binding benzo(a)pyrene and reducing its toxic effect. Complexes for high-temperature waste disposal have proven themselves well abroad, which is confirmed by operating experience in many port cities and large settlements of Russia, such as St. Petersburg, Murmansk, Novosibirsk, an oil terminal in Primorsky, etc. and operate in various institutions of the city five incinerators of IN-50 type.

Environmental pollution by hydrocarbons has become the most important environmental problem of our time.

Currently, the search for funds and the development of technologies are being actively carried out, allowing the most quickly and safely eliminate the consequences of the ingress of hydrocarbons into the environment. Of all the methods of cleaning the soil from oil and oil products, the most environmentally friendly and economical is in situ bioremediation, based on the oxidation and mineralization of hydrocarbons by specific microorganisms- destructors directly on the contaminated site. However, (4) bioremediation technologies still do not always bring the desired results [Alvarez, Illman, 2006]. This is due to the high site-specificity of the methods, the duration of cleaning (usually more than 1-3 years), inhibition of oil destructors in highly contaminated soils, and a high probability of groundwater contamination by pollutants. Improvement of methods for bioremediation of oil-contaminated soils is the most important problem of our time [Kuznetsov et al., 2009; Slyusarevsky, 2018] (3).

Research carried out in the laboratory Institute of Physicochemical and Biological Problems of the Russian Academy of Sciences, allowed to develop a highly environmentally friendly method of sorption-biological cleaning of soils heavily contaminated with organic pollutants, including chloroanilines and their derivatives, herbicides, 2,4,6 - trinitrotoluene, polychlorinated biphenyls, as well as oil and oil products [Vasilyeva et al., 2003, 2006, Strizhakova, Vasilieva, 2004; Vasilieva et al., 2008, 2012]. It has been shown that the use of granular activated carbon (GAC) can accelerate the bioremediation of soils contaminated with diesel fuel, used engine oil and crude oil [Vasilieva et al., 2013; Semenyuk et al., 2014; Yatsenko et al., 2014]. The use of sorbents expands the possibilities of soil bioremediation by reducing their toxicity and localizing toxicants in the cleaned layer. However, due to the relative high cost of activated carbon, a search is underway for cheaper materials that could replace this sorbent in the sorption bioremediation technology development.

The main mechanism of action of sorbents in soils heavily contaminated with hydrocarbons is associated with the predominantly reversible sorption of hydrocarbons and their toxic and mobile metabolites in the pore space and on the sorbent particles' surface. This provides more favorable conditions for the life of microorganisms-destructors by reducing the toxicity and hydrophobicity of soils, as well as by increasing soil moisture and the availability of biogenic elements.

Of all the sorbents studied, the highest absorptive capacity (4-6 g / g) in relation to oil and oil products is possessed by sorbents capable of swelling - vermiculite, biochar and peat.

For sawdust, granular activated carbon, diatomite and zeolite, this value ranges from 1-3 g/g.

Kaolinite cannot be used to collect oil due to its ability to be dispersed in it.

The introduction of natural sorbents of different classes can significantly increase the rate of decrease in the concentration of hydrocarbons in gray forest soil contaminated with oil products - a mixture of weathered used motor oil and diesel fuel. With an initial concentration of hydrocarbons of about 5%, the optimal doses of mineral sorbents fluctuate within 0.2-1%, and for carbonaceous and organic ones, 0.5-2%.

A comparative ecological assessment of the sorption bioremediation method, carried out under the conditions of a 3-year micro-field experiment, freshly contaminated with weathered oil of medium density (about 5% of hydrocarbons), showed that the use of various mineral sorbents significantly increases the efficiency of the bioremediation method provided that the dose of applied mineral fertilizers is optimized (the ratio C:N:P:K=100:1:0.5:1) and pH soil within 6.0-7.5.

The general mechanism of action of sorbents is based on a decrease in the phyto- and micro-botoxicity of the soil due to the predominantly reversible sorption of hydrocarbons and their toxic metabolites, an increase in the moisture capacity and porosity of the soil, as well as a decrease in its hydrophobicity, which provides favorable conditions for the development of oil destructors (aboriginal or inoculated) and the growth of phyto-ameliorants.

With the introduction of optimal doses of sorbents, there is no significant accumulation of environmentally hazardous benzo(a)pyrene in the soil compared to the control, and its accumulation in the mass of phyto-meliorants at the stage of additional treatment does not exceed 0.2-0,4 MAC.

The listed cleaning methods can be used to clean the surface layers of soils. We are interested in methods for cleaning the soil from bin (a) perennial at a sufficiently large depth.

The underground method of soil cleaning ("insitu" method) can be considered when the soil is processed at the place of infection (at the place of natural occurrence), i.e., without its notch. When using the methods outside of natural bedding ("exsitu" methods), the soil is subjected to excavation. For dredging methods, a distinction is made between on-situ and ofsitu methods. With on-situ methods, the treatment of contaminated soil is carried out after it has been excavated in the immediate vicinity of the sanitation site, while the "ofsitu" treatment involves transporting it to a soil cleaning plant. Thus, microbiological sanitation can be carried out either by underground methods or with dredging by means of "onsitu" or "ofsitu".

Factors influencing the success of the refurbishment are as follows:

- Soil permeability. The permeability determines the head loss and thus the "radius of action" of the pneumatic measure. Based on the detailed exploration results, it is possible to give an initial estimate of the permeability coefficient (PC) value along the grain size distribution curve. The possibility of applying Darcy's law to assess the flow of ground air was confirmed (5). When air penetrates through the ground, water also moves in the form

of a film flow. Due to the intense contact of air with the hydration shell, oxygen dissolves in water and the metabolic product CO₂ is removed, as well as volatile harmful components.

- Type and number of pollutants, volumetric distribution of contamination. Pollutants tend to spread according to the geometrical structure of reservoir packs or sediment piles. Sedimentological conditions have a significant impact on the mechanical dispersion of harmful substances in the underlying rocks. Thus, also anthropogenic disturbances such as foundations or boreholes can cause pneumatic and hydraulic methods to shorten the path of propagation.

Sanitation can be carried out using modified sorbents from waste of local plant materials. Corn cobs, walnut shells and sunflower stalks were selected as a raw material study. For comparison, a thermally split graphite sorbent adsorbent is taken being developed by LLC "Ingush National Engineering Center of Innovations and Technologies".

Water is pumped into the ground to any depth with injections. Then the pumping unit rises to the surface and is purified by passing through a filter. To analyze the wastewater purification from oil products, including benz(a)pyrene, a simple laboratory setup was assembled, shown in Fig. 1.

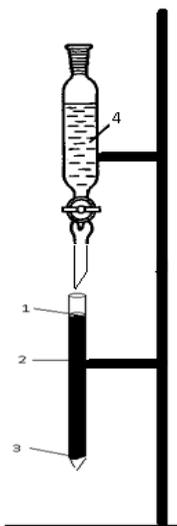


Fig. 1. Installation for filtering contaminated water through a fixed bed of sorbent: 1,3 - fiberglass pads, 2 - sorbent, 4 - contaminated water.

Sorbent efficiency studies were evaluated for water contaminated with oil concentration: 29 g/l.

Purified water with a volume of 1000 ml was collected in a collector in portions of 250 ml.

The obtained data on the concentration of oil in the treated water are given in table. 3.

Table 3. The obtained data on the concentration of oil in the treated water

Initial concentration of oil products, mg/l	Type of modified sorbent	Concentration OP in filtered water, mg/l	Type of unmodified sorbent	Concentration OP in filtered water, mg/l
	sorbent based PC	0.037	sorbent based PC	0.24

6.72	Thermally split graphite sorbent adsorbent	0.015	Thermally split graphite sorbent adsorbent	0.07
	sunflower stem sorbent	0.042	sunflower stem sorbent	0.36

The data obtained indicate that the concentration of oil in water is below the level MAC. (MAC oil in water for fishery waters is 0.5 mg/l).

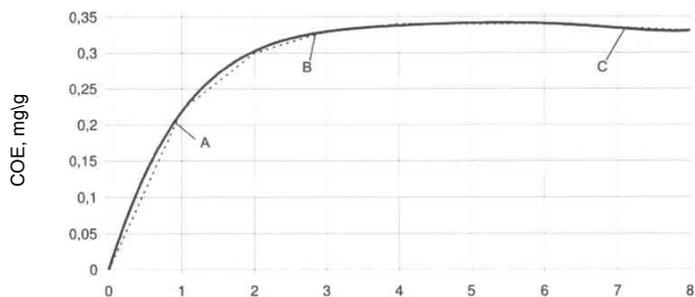


Fig. 2. Isotherm of petroleum products sorption by sorbent based on corn cob

The constancy of the adsorption value at high concentrations (BC segment) is explained by the fact that the adsorption surface of the sorbent is occupied by hydrocarbon molecules, that is, the adsorption limit has been reached.

The laboratory studies presented in this figure show that the treatment of waste water containing high concentrations of zinc, copper and lead under static conditions and in the presence of dissolved petroleum products can be carried out using a modified sorbent based on corn cobs.

3 Conclusion

Construction on a contaminated area without replacing soil can be carried out using the technologies for cleaning and remediating contaminated soil. They are based on the following methods' implementation:

- ventilation of contaminated soil masses and removal of volatile substances using a device of vacuum wells, including the treatment of contaminated groundwater;
- neutralization of toxic substances contained in the soil mass using chemically active substances;
- ventilation of contaminated soil dumps using microorganisms;
- cleaning the soil from benzopyrene using a modified sorbent based on corn cobs waste.

References

1. SanPiN 2.1.7.1287-03 Sanitary and Epidemiological Rules and Regulations. Resolution of the chief state sanitary doctor of Russian federation from 17 April 2003. No. 53
2. HR 2.1.7.2041-06 "Maximum Allowable Concentrations (MAC) chemicals in the soil".
3. L.V. Zinnatshina, Environmental assessment of the effect of natural sorbents on the efficiency of oil-contaminated gray forest soil bioremediation, PhD Thesis Abstract. Moscow, 2019.

4. P.J.J. Alvarez, W.A. Illman, *Bioremediation and natural attenuation: Process fundamentals and mathematical models* (New Jersey, Wiley InterScience, 2006).
5. Yu.V. Shuvalov, E.A. Sinkova, D.N. Kuzmin, *Cleaning of soil from oil and oil products pollution* (MSEU, Moscow).
6. O.G. Dolgikh, S.N. Ovcharov, *Bulletin of the North Caucasus State Technical University* **1** (**22**), 156-162 (2010).