Liquidation of Oil and Petroleum Products Spills Based on Use of NA and CA-Differences of Zeolite

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Abstract. The article discusses the use of ecologically and economically practical proved methods of neutralizing the soil ecosystems in Yakutia after emergency oil spills. Experimental studies have been made to develop a new biosorbent based on a natural sorbent. The natural zeolite Na and CA-differences from the Khonguruu deposit (The Republic of Sakha (Yakutia), Russia) is used as a base for obtaining the biosorbent. The necessary typification of zeolite deposits revealed at the stage of exploration, in order to determine the field of practical application of raw materials in the preparation of the field for industrial development. The types of raw materials according to the cationic composition difference are identified: clinoptilolite-heulandite and heulandite. A brief description of the material composition and averaged physico-chemical characteristics of various types of zeolite raw material is given. We present the results of the experimental application of hydrocarbon oxidizing microorganisms (HOM) immobilized on zeolite (clinoptilolite-heulandite series) from the Khonguruu deposit in oil-contaminated soils. It has been established that the obtained biomimetic compositions provide a significant activation of petroleum hydrocarbons (HIC) biodegradation in the soil. In general, the technology of using zeolite raw materials for cleaning up oil spills from different types of permafrost soils provides a significant ecological and economic effect, thus contributing to the reduction of the time for rehabilitation of disturbed lands and the improvement of the environment in the disturbed territory.

1. Introduction

One of the major environmental pollutants worldwide is oil and petroleum products. Consuming every day about 14 million tons of oil, the industry, in the process of its transportation and processing, due to leaks and environmental incidents of various levels, releases several thousand tons of this raw material into the environment each year [1].

The problem of decontamination of solid and pasty oily production wastes accumulated and regularly formed in production processes, and soil contaminated during emergency oil spills, has been and remains highly relevant. The main way to solve this problem is to increase manufacturability, environmental efficiency and reduce the cost of disposal of such waste [2].
The main problem of restoring disturbed lands on the territory of Yakutia is very acute, which is primarily due to the specific nature and climatic conditions of the region. The duration of the cold period, which lasts 7.5-8.0 months, is practically the period of biogeochemical rest for pollutants. Therefore, it can be assumed that oil pollution in the conditions of the permafrost zone can become a large-scale factor of the negative impact on the environment. For this, it is necessary to create new technologies based on advanced scientific concepts capable of capturing, processing, utilizing pollutants or toxicants, mitigating or preventing the effect of environmentally unsafe enterprise on the environment [3].

For the permafrost soils of Yakutia, the choice of oil destructors that work effectively in the climatic conditions of the North requires special studies and tests [4]. Therefore, the scientific studies of the Institute of Oil and Gas Problems of the Siberian Branch of the Russian Academy of Sciences (IPNG SB RAS, Yakutsk, Russia) aimed at developing biotechnologies for neutralizing oil and petroleum product spills based on the local natural raw material proved to be in demand in modern conditions.

2. Materials
Currently, more than two hundred different sorbents are produced or used in the world to eliminate oil spills, which are divided into inorganic, natural organic and organic minerals, etc. The quality of sorbents is mainly determined by their capacity in relation to oil, the degree of hydrophobicity, buoyancy after sorption of oil, the possibility of desorption of oil, regeneration or utilization of the sorbent [1,5].

Natural sorbents are the most promising type of sorbents for the elimination of oil pollution.

At the end of the twentieth century, a new group of drugs - biosorbents with both absorption and physicochemical activity with respect to petroleum products and biological ones - was used as the basis for a new integrated (combined) technology [1,5].

New biosorbents are built on the basis of the absorption material obtained from natural aluminosilicates (perlite, vermiculite, zeolite, etc.) immobilized by natural bacteria capable of destroying the oil products collected by the preparation in a wide temperature range [1,5].

As source material for the biosorbent production, a natural zeolite from the Khonguruu field (The Republic of Sakha (Yakutia), Russia) and HOM isolated from the permafrost soils of Yakutia was used.

Natural zeolite refers to stable aluminosilicates with a framework structure of the crystal lattice, having a layered structure.

At the stage of zeolite raw materials deposits exploration, first of all, the areas of their practical application should be determined, which is very important in preparing the field for industrial development. For this, it is necessary to distinguish zeolite raw materials types at each of the deposits. In the mineralogical study practice of volcanogenic-sedimentary origin zeolites, the information on the chemical composition of zeolites is mainly obtained on the basis of a gross chemical analysis of the rock. In this regard, the method of calculating the overall composition of the rock as a whole on the crystal-chemical formula of clinoptilolite-heylandite minerals per 72 oxygen atoms $(\text{Na, K})_6^+\text{Al}_6\text{Si}_{30}\text{O}_{72}\cdot n\text{H}_2\text{O} - (\text{Ca, Mg})_2^{2+}\text{Al}_6\text{Si}_{30}\text{O}_{72}\cdot n\text{H}_2\text{O}$ [6].

To isolate the types of raw materials, all the actual material was analyzed at the exploration stage of the Khonguruu deposit with the use of the results of long-term case studies. The results of chemical analyzes, spectral quantitative and semi-quantitative analyzes were used. Each of them was accompanied by the determination of the zeolites content by the PZL (Portable Zeolite Laboratory) and XQPA (X-ray Qualitative Phase Analysis) methods [6, 7, 8, 9].

The bulk of the zeolite rock consists of vitroclastic and crystallo-vitro-clastic tuffs, replaced almost completely by cryptocrystalline isotropic aggregates of clinoptilolite-heylandite. Crystalloclastic material (2-25%) is represented by quartz, feldspar, fragments of siliceous rocks and biotite plates, etc. The thickness of the beds varies from 6.5 to 13 m and is traced to a distance of 8.5 km, their structure has been studied to a depth of 100-160 m. The content of zeolites in the rock is 70-98% [6, 7, 8, 9].
At this stage of study, two types of raw materials are distinguished at the field, differing mainly in cationic composition: clinoptilolite-heylandite composition (mined in quarry 1) and heylandite composition (mined in quarry 2).

In most of the field the first type of raw material clinoptilolite-geylanditovogo composition is distributed. In this area, they folded all four layers.

In the open quarry 1, this type of raw material is a clear interlayering of zeolite rocks of the Na and Ca differences of the zeolite, i.e. clinoptiloliths and geylanditami, and higher in the section gradually move with a wide range of their intermediate differences.

In the north-eastern part of the site the second type of raw material of geylandite composition is represented by the I and IV layers of zeolite rocks.

Throughout the section in a quarry 2 zeolitic rocks consist almost of pure Ca-differences of zeolite i.e. heylandites with aged fractions of contrasting cations of sodium and calcium.

The average chemical composition of two types of raw materials, (%): SiO$_2$ -66.43; TiO$_2$ - 0.18; Al$_2$O$_3$ - 12.03; Fe$_2$O$_3$ - 0.92; FeO - 0.26; MnO - 0.03; MgO: 1.47; CaO - 2.50; Na$_2$O - 1.75; K$_2$O - 1.35; P$_2$O$_5$ - 0.14; pp. - 6.2.

Physicochemical properties of zeolite rocks from the deposits by types of raw materials varies: content of zeolites in the rock, % - 70-98; ion-exchange capacity, mg-eq/g – 0.16-1.91; adsorption properties for water at P/Ps = 1.0, % - 10.34-12.03; thermal stability, °C - 700; the optimum temperature of dehydration, °C - 300-550 [6, 7, 8, 9].

3. Experimental part

Experimental work on testing the combined (physical-chemical and biological) method of cleaning the frozen soils of Yakutia with local Na and Ca-differences of zeolite was carried out on permafrost-taiga soil. Mineral compositions of a sieve fraction of 0.01–1.0 mm were used [10].

At the initial stage of work accumulating cultures of microorganisms (ACM) were received from the oil-contaminated permafrost soils. Obtaining ACM from oil-contaminated soils in a mineral medium with oil allowed for creating elective conditions for preferential growth of microorganisms capable of absorbing and using petroleum hydrocarbons as the sole source of carbon and energy.

The process of accumulation of microorganisms proceeded at room temperature for 3-5 days under conditions of constant aeration. By this time, the disappearance of oil stains, the formation of a turbid emulsion, the pigmentation, the precipitation of flakes, and (or) the saponification and disintegration of the oil layer were noted in the culture flasks.

Sampling and sample preparation were performed according to generally accepted procedures [11, 12]. To isolate HOM, the Muntz method of accumulation cultures on the mineral environment with oil was used [13, 14].

Specific identification of the isolated microorganisms was carried out using the Bergey’s guide [15], using the analysis of the nucleotide sequences of the 16S rRNA gene [16, 17, 18]. The emulsifying activity of the isolated HOM cultures was determined by the Cooper method [19].

Investigation of the sorption properties and petrofluidity of materials was carried out with the Talakanskii field oil (Yakutia, Russia) using the methods of Anufrieva et al. [20]. Determining the content of petroleum products in the soil was carried out in accordance with the generally accepted methods in geochemistry [21-23].

4. Results and discussion

As an example, this paper presents the results of studies of oil-contaminated soils and soils in the emergency section of the Amginsk petroleum depot of JSC Sakhaneftegazsbyt located in the territory of Central Yakutia. The study of the biosorbent based on the Khonguruu deposit zeolite immobilized by accumulative cultures of the aboriginal HOM was carried out in comparison with the industrial biological product “Devoroil” and oil-polluted soil that was not treated with biopreparations.

Experiments:

1. AT-2-08 - soil + biosorbent (zeolite + HOM) + oil;
2. AT-8-08 - soil + industrial biological product "Devoroil" + oil;
3. AT-9-08 - soil + oil.

The test plot was laid on a plot with buried oil-polluted soil. The soil was compacted. The structure is adhesive. The top layer of soil is covered with white salt bloom. On the horizon 0–20 cm, the profile is brownish-gray, heavy loamy, slightly moist, root hairs were absent. The reaction environment is alkaline. Profile at a depth of 20–40 cm and below - sand and gravel, slightly wet.

The soil had an average degree of salinity, insufficiently provided with moisture - 20.0%; nitrate nitrogen (N-NO₃) - 3.63 mg / kg; mobile phosphorus (P₂O₅) - 23 mg / kg; mobile forms of potassium (K₂O) - 94 mg / kg and nitrogen-ammonium (N-NH₄) - 2.3 mg / kg. According to the humus content, the soil is classified as 8.0% of a well-supplied type.

The projective cover was no more than 10%. The toxic effect of oil on plants in this area manifested itself in a change in their morphology. The color of the leaves, in comparison with not polluted plants, was pale, pigmented in some places. Plant stems are thinned. The root system is weak.

As plants that live in an oil-polluted site, timothy meadow (Phléum pratense), meadow bluegrass (Poa pratensis), Devyasil (Inula), wild onion (Allium ursinum), Artemisia ordinary (Artemísia vulgáris) and reed (Scírpus) are noted.

Some crops showed signs of nitrogen starvation and disturbances in the formation of chlorophyll, which were expressed in the lag of growth of the vegetative organs of plants and the appearance of yellow-green leaf color.

The method of biotesting revealed that the soils on the oil-polluted area are phytotoxic. In experiments with “Prilenskaya-19” wheat seeds, the germination in contaminated soil samples was 16%, while in the control variant this indicator corresponded up to 92% (table 1).

| No. of experimental plot | Multiplicity of experience | Numbers of viable seeds, pcs. | Germination percentage, % | Sprout length, cm | Root length, cm |
|-------------------------|---------------------------|--------------------------------|--------------------------|------------------|----------------|
| Before tillage with biological products |                        |                                |                          |                  |                |
| AT-2-08                 | 3                         | 4 ± 0,12                       | 16                       | 17 ± 0,22        | 6 ± 0,12        |
| AT-8-08                 | 3                         | 4 ± 0,10                       | 16                       | 17 ± 0,14        | 6 ± 0,12        |
| AT-9-08                 | 3                         | 4 ± 0,12                       | 16                       | 17 ± 0,23        | 6 ± 0,08        |
| Control                 | 3                         | 24 ± 0,10                      | 96                       | 20 ± 0,16        | 16 ± 0,12       |
| After tillage with biological products |                    |                                |                          |                  |                |
| AT-2-08                 | 3                         | 11 ± 0,24                      | 44                       | 19 ± 0,20        | 8 ± 0,12        |
| AT-8-08                 | 3                         | 9 ± 0,20                       | 36                       | 18 ± 0,20        | 8 ± 0,10        |
| AT-9-08                 | 3                         | 3 ± 0,10                       | 12                       | 8 ± 0,10         | 4 ± 0,10        |
| Control                 | 3                         | 23 ± 0,14                      | 92                       | 22 ± 0,20        | 16 ± 0,14       |

Negative factors affecting the full development of plants in oil-polluted soil were heavy particle size distribution of the soil, disruption of the water and air regimes, and the toxic effect of oxidized oil components.

It was established that despite a relatively high total number of microorganisms (from 1 million to 10 billion cells per 1 gram of dry soil) in soil samples taken from the oil-polluted area, their species diversity is depleted compared to pure soils.

Spore-forming bacteria of the genus Bacillus, non-fermentative bacteria of the genus Pseudomonas, yeast-like fungi of the genus Candida, ascomycetes of the genus Aspergillus, Penicillium and Fusarium were isolated and identified from the soil grounds. At the same time, soil bacilli and pseudomonads performed simultaneously the functions of saprophytes — ammonificators and active destructors of petroleum products.

In oil-contaminated samples, no active forms of azotobacters were detected that trap nitrogen
directly from the air atmosphere. This is apparently due to the reduction of readily available carbon sources in soils. Soils had traces of long-standing pollution (at least 4 years). During this time, during the natural oxidation of petroleum products, a reduction occurred in the composition of oil from readily available paraffin naphthenic low molecular weight hydrocarbons and the exhaustion of biogenic elements. This led to a reduction in the number of nitrogen-fixing microflora.

Among the microorganisms capable of growing on the MacConkey elective medium, were isolated strains that do not ferment lactose, do not form hydrogen sulfide and indole, and stain well by the Ziehl-Nielsen method, which indicated the presence of acid-resistant properties of the cell wall that are not characteristic of sanitary-indicative microorganisms from the bacteria group.

Most of the isolated microorganisms had the ability to assimilate the oil-contaminated substrate.

The field experiment demonstrated the ability of the biomineral composition (BMA) to activate the centers of biodegradation of oil pollution. At the same time, the degree of soil purification from petroleum hydrocarbons (HC) correlated with the degree of HOM accumulation in the experimental plots and decrease in soil phytotoxicity (Table 2).

**Table 2. Biodegradation of petroleum products in soils.**

| No. of experimental plot | NP content,% before cleaning | NP content, % after cleaning | NP degradation, % |
|--------------------------|-------------------------------|-------------------------------|-------------------|
| AT-2-08                  | 14,9547                       | 2,6405                        | 82,3              |
| AT-8-08                  | 11,8362                       | 5,7990                        | 51,0              |
| AT-9-08                  | 23,1900                       | 16,4905                       | 28,88             |

The degradation of oil pollution for 1 year in the experimental section with the use of BFC was up to 82.3%, compared to the control variant, where the degradation of petroleum hydrocarbons under the influence of natural factors was 28.9%, and in the section with the use of the industrial biological product "Devoroil" – 51.0 % for the same amount of time.

5. Conclusion

Thus, the conducted studies have shown that the use of the zeolite Na and CA-differences of theHonguruu deposit in the purification of permafrost soils from oil contamination is an effective and promising method for bioremediation of oil-contaminated soils in the soil-climatic conditions of Yakutia.

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