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Development of an Integrated Approach to Neutralisation of Oil-Slime

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In the course of oil extracting on oilfield, and also at oil transportation inevitably there are oil spills leading to ecological balance disruption and bringing a doubtless loss to natural ecosystems. Bioremediation is the safest way of neutralization of the soils polluted with oil spill products. The highest degree of polluted soil clearing is observed while using of oil-slime pretreatment and its further additional cleaning by a consortium of not pathogenic petrooxidizing microorganisms. Complex method of neutralization of spills and wastes polluted by oil hydrocarbons allows converting more than 85 % of oil hydrocarbons from the initial concentration in samples within two weeks. Developed scientific and technical production has advantage in comparison with analogs and includes the use of ultrasonic pretreatment. The basic advantage of ultrasonic processing is its sufficient quickness, profitability and ecological harmlessness, and possibility to destroy C-C bonds in paraffin molecules.

1. Introduction

At present the most common anthropogenic factors of the environment pollution are still oil and oil refinery products. A lot of papers on the development of natural sites cleaning from oil hydrocarbons have recently appeared, but the fact that oil of each region is characterized by its unique composition and behaves in a different way in each climatic zone should be taken into consideration (Repečkienė et al.,2013).
A lot of modern biopreparations used for biological treatment (bioremediation) of oil-containing natural sites are chemically multicomponent. The literature data show that microorganisms consortia can fully and quickly degrade hydrocarbon substrates comparing to individual strains. It has been shown that the hydrocarbon-oxidative activity of isolated strains to black oil was 13.1-17.3 %.The hydrocarbon-oxidative activity of associations of the strains isolated from other regions was 24.0-30.0 % (Shkidchenko,2004).
The legislation of many countries, Russia included, encourage the drawing of industrial waste into economic circulation as secondary raw material resources (Ibrahim et al., 2013). In Russia the development of industrial technologies and equipment for the obtaining of ecologically safe products from waste is in the initial stage, in a stage of pilot plants design. The processes suggested are very expensive and in spite of the low price of the initial raw material are not economically effective.
Therefore, the organization of scientific research and development of the methods of waste recycling and detoxification by the local governments and business are among the high-priority tasks.
Thus, the development of the compound method of oil-slime neutralization with the help of physical and biological methods is important and has scientific novelty.

2. Experimental

In the experiments the modelling samples of oil-slime consisting of river sand and oil of the Caspian deposit were used. The sample contained 15 % of oil. The combination of oil with sand took three days. Ultrasonic pre-treatment of the modelling sample were carried out after that.

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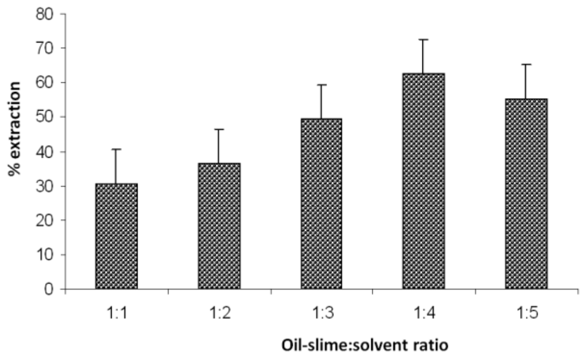


Figure 1: Influence of the solvent quantity on the degree of hydrocarbons extraction from oil-slime (chlorophorm)

As each solvent possesses the characteristic properties, the correct choice of environment is very important for the definition of optimum conditions of carrying out sonochemical processes.

Ultrasonic generator IKASONIC U 50 was applied to treat raw material, it works at a frequency of 30 kHz. The device was completed with a nozzle US 50-3 Sonotool with a diameter of 3 mm. The intensity of ultrasound treatment was up to 460 Wt/cm^2.

The quantity of oil products in the modelling sample was determined by the gravimetric method. During the experiments the intensity of ultrasonic processing (from 230 Wt/cm^2 to 414 Wt/cm^2) and the extraction time (from 1 to 25 minutes) were varied. As a control, continuous extraction of oil hydrocarbons from oil-slime was used.

After being treated with the organic solvent, oil-slime was biodegraded.

3. Results and discussion

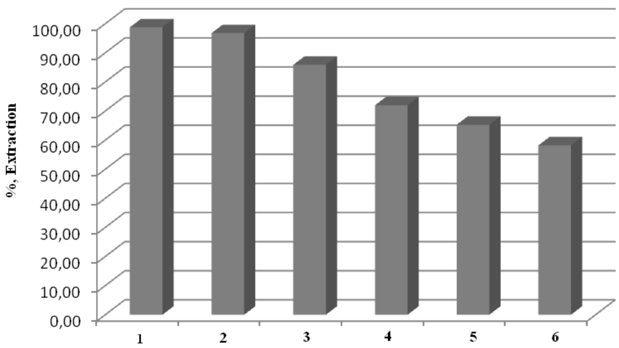
The determination of extractant: oil-slime optimum ratio was the first investigation stage. In the Figure 1 the data on oil hydrocarbons extraction with chloroform are presented.

During the experiments it was revealed that the fullest extraction of hydrocarbons of oil from the samples take place at extractant:oil-slime ratio – 4:1 Similar data were obtained for the other solvents.

Then organic solvents were chosen. Xylene and benzene can extract oil products from oil-slime the best.

As xylene is extremely toxic and expensive compound, acetone is not effective further research was carried out with benzene, chloroform and toluene.

Then the influence of the time of ultrasonic extraction on the degree of oil extraction from oil-slime in all the above-named solvents (Table 1).



1 – xylene, 2 -benzene, 3- chloroform, 4- hexsane, 5 -toluene, 6 -acetone

Figure 2: Extraction of oil-slime hydrocarbons with different solvents

Table 1: Results of ultrasonic extraction of oil-slime

Time of extraction, min	Intensity of treatment, Wt/cm^2	Degree of oil-products extraction from a modelling sample with the organic solvent, %			
		Benzene	Hexane	Toluene	Chloroform
1	230	32.3	19.0	47.1	38.0
3		45.1	47.7	39.0	40.8
5		45.2	40.1	45.9	41.2
7		45.7	23.0	38.9	32.0
10		53.9	35.6	50.9	52.2
15		30.8	43.8	56.9	47.3
20		46.1	13.4	50.9	39.4
25		48.5	30.0	64.4	35.3
1	276	35.7	44.5	64.1	36.3
3		41.2	47.4	52.0	31.4
5		51.4	35.8	47.6	31.2
7		44.7	40.6	49.8	39.6
10		37.8	42.3	52.6	33.2
15		48.3	44.5	43.0	33.2
20		40.8	34.4	52.8	42.3
25		42.3	25.5	51.8	39.2
1	322	35.8	27.9	51.1	36.7
3		37.5	29.6	57.6	38.1
5		42.6	34.9	62.4	56.1
7		50.4	40.6	47.0	48.9
10		51.9	40.2	56.9	49.3
15		45.9	54.0	68.5	36.8
20		44.7	45.8	55.1	37.3
25		41.0	43.7	42.2	49.3
1	368	33.0	28.1	59.8	61.8
3		44.0	35.2	63.3	67.6
5		49.8	48.4	61.0	50.5
7		45.3	55.3	63.9	32.2
10		36.0	39.4	52.8	37.9
15		39.0	47.0	58.2	34.7
20		39.3	64.2	56.0	27.5
25		43.4	31.3	61.7	28.2
1	414	34.6	47.7	62.8	48.0
3		39.8	56.8	68.8	46.3
5		**65.2**	47.9	66.2	61.0
7		41.8	63.5	62.7	61.7
10		28.4	**71.1**	59.7	**75.9**
15		34.0	64.2	68.2	32.7
20		47.2	55.1	64.8	37.5
25		41.4	70.5	63.1	39.2
1	460	33.7	57.5	66.0	42.0
3		49.5	47.7	65.8	50.3
5		46.7	**71.1**	**70.3**	39.9
7		39.9	67.1	68.2	49.9
10		37.5	70.3	63.1	34.7
15		33.7	69.2	60.5	41.9
20		34.0	70.4	62.7	32.1
25		31.0	59.0	42.9	32.7

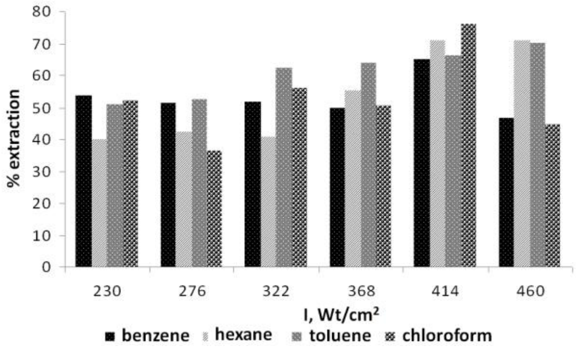


Figure 3: Influence of the intensity of oil-slime ultrasonic treatment on the degree of oil hydrocarbons extraction

On the basis of the obtained results it is possible to find an optimum range of ultrasonic extraction intensity (414 Wt/cm^2 – 460 Wt/cm^2) at which the most effective extraction of oil hydrocarbons takes place (Figure 3).

At fractional oil-slime extraction without ultrasonic treatment the maximum degree of oil hydrocarbons extraction was reached in 1.5-2 hours and made 46, 48, 56, 66 % for chloroform, hexane, benzene and toluene, correspondingly. Thus, it is possible to conclude that ultrasonic treatment intensifies the process of oil hydrocarbons extraction from model samples by 1.2-1.5 times.

The study shows that at ultrasonic influence the oil-product temperature in the tube increases by 7-10^{o}C, in comparison with the experiment without ultrasonic treatment. It is likely to occur because of the acoustic energy dissipation.

However, the, temperature rise owing to acoustic energy dissipation isn't the basic mechanism of oil-slime cleaning from paraffins though it plays a subsidiary role.

Chromotographic analysis of the extract obtained showed that during the ultrasonic treatment higher hydrocarbons are destructed, but for the complete destruction of hydrocarbons structural network the treatment applied is not enough. It is possible that the growth of the number of free particles results in the probability of their collision and thus there is a dynamic balance between the process of hydrocarbons structure destruction and its recovery.

So out of all the solvents studied chloroform had the most extracting ability for the samples used. The maximum degree of oil extraction from oil-slime was 75.9 %, at the treatment intensity 414 Wt/cm^2 and time 10 minutes.

The following stage of the study was biodestruction of samples, polluted by oil hydrocarbons and ultrasonically treated. The collection cultures and the microorganisms preserved at the Department of Biotechnology and Chemistry of Tver Technical University were used in the study. The phenotypic characteristics of a new isolate were studied. It is shown that it belongs to barmy cultures of *Candida genus* (DK1, DK2, DK3, B3) and bacterial microorganisms of *Bacillus genus*. The ability of the studied microorganisms to oxidize hydrocarbons was found.

The study of oil-contaminated soil recultivation showed that the use of ultrasound of different intensity resulted in oil hydrocarbons degradation.

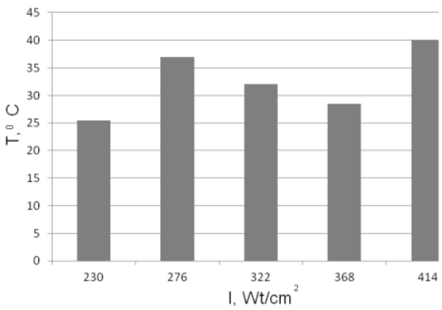


Figure 4: Influence of ultrasonic treatment intensity on the temperature of the reaction medium (extractant – chloroform)

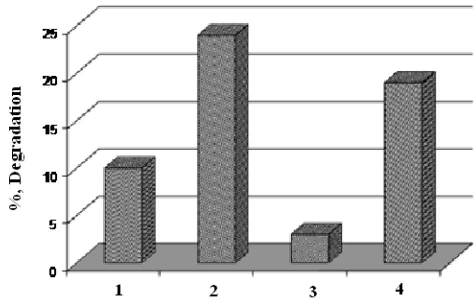
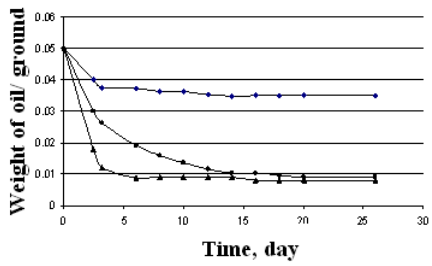


Figure 5: Degree of oil biodestruction in soil



▲ – strain ДК2, ■- strain ДК3, ♦- control experiment

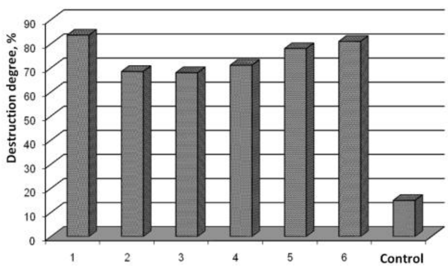
Figure 6 :Degradation of the compounded oil-slime

It was revealed that after 5 days oil destruction in the sterile soil was 5.3 %, in the soil – 10.2 %, in the soil with the introduced monoculture – 38.4 %. The results of the experiments showed that destruction is the most effective in the non-sterile soil with the introduced monoculture. Destruction without monoculture takes more time. Therefore the use of microbial consortium, consisting of microorganisms – oil-destructors and accompanying microflora intensifies the process. Soil can be used to accelerate bio-destruction process due to its composition and the presence of hydrocarbon-oxidizing microflora for oil-slime compounding.

During the first days of oil pollution of soil physical processes of hydrocarbons migration and dispersion mostly take place as a result of evaporation and leaching. The rate of evaporation is different and depends on the environment properties, meteorological conditions and oil composition.

As the result of oil evaporation the viscosity of the remaining part increases and the migration rate decreases, the quantity of hydrocarbons with the chain length of more than C_{20}, aromatic and cyclic hydrocarbons increases because low-grade hydrocarbons mostly evaporate. The removal of the most toxic volatile hydrocarbons lessen the harmful effect of the remaining mixture on microorganisms-destructors. It facilitates the following microbiological degradation and increase the share of the components resistant to degradation.

The strains-destructors studied differ much in the growth specific rate, thus different consortia were developed.



1 – strains DK2, DK 3, Bacillus subtilis in the ratio 1:1:1; 2- strains DK2 и DK3 in the ratio 2:1; 3- strains DK2 и DK3 in the ratio 3:1; 4- strains DK2 и DK3 in the ratio 1:3; 5- strains DK2, DK3, Б3 in the ratio 1:1:1; 6- strains DK2 и DK3 in the ratio 1:1

Figure 7: Study of oil-slime degradation in different consortia of microorganisms

It is clear from graph 7 that microorganisms consortium DK2, DK3 in ratio 1:1 has the most degradation. The worst results were noted in case DK2 and DK3 ratio was not 1:1. The introduction of *Bacillus subtilis* intensifies the process of bioremediation. It is most likely explained by the fact that *Bacillus subtilis* is the producer of surfactants.
The consortium chosen (1) is capable of decomposing not only volatile fractions of oil, such as hexadecane, but also diesel fuel and heavier fractions of oil, for example black oil, i.e. it destructs a wide spectrum of hydrocarbons. The consortium also doesn't lose the oxidizing activity at 5% (wt.) content of hexadecane, diesel fuel, oil and black oil.

4. Conclusion

Oil spill is a difficult engineering and microbiological problem which demands complex approach to its solution. The developed method of oil spill recycling combines mechanical, physicochemical and biological methods.
Mechanical method means removal of oil spill from the polluted area and transferring it to the reactor for ultrasound extraction. Physicochemical method (ultrasound extraction) of oil spill pretreatment allows decreasing concentration of oil hydrocarbons up to atoxic level for microorganisms. Biological method allows destructing the remaining oil hydrocarbons up to maximum permissible concentration.
On the basis of the experimental data optimum conditions of oil-slime ultrasonic pretreatment were determined: duration of the process 5-10 min, ultrasonic treatment intensity 368 Wt/cm^2 – 460 Wt/cm^2. Out of all the solvents studied chloroform possessed the greatest extraction ability for the samples used. Thus the maximum degree of oil extraction from oil-slime was 75.9 %, at ultrasonic treatment intensity 414 Wt/cm^2 and time 10 minutes.

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