Integrated approach in neutralization of the polluted soils and oil-slime

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***Abstract*—** 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. 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.

***Keywords*—** Oil spill, ultrasound, pretreatment, biological degradation.

I. Introduction

At present the most common anthropogenic factors of the environment pollution are still oil and oil refinery products.

As a result of development of new and operation of already functioning oil deposits the environment undergoes considerable changes. Owing to emergency oil products spill on oilfields a considerable amount of oil hydrocarbons and also the chemical reagents used at extraction pollutes the environment.

Oil and oil-slime polluting the environment as a result of emergencies at spilling, extraction, transportation, storage and treatment, are the reason of numerous environmental problems [1,2]. 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 [3,4].

Unfavorable impact of oil on environment and nonrenewaling of hydrocarbonic raw materials make a problem of waste treatment a rather actual.

There are many methods of neutralization of soils and oil slimes. the complex way is represented perspective.

The legislation of many countries, Russia included, encourage the drawing of industrial waste into economic circulation as secondary raw material resources [5]. 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. The main process taking place during the pyrolysis [6] is cracking – destruction of –C–C– bounds of organic molecules chains and also total or partial removal of functional groups with the formation of various organic and inorganic compounds – water, hydrogen, ammonium, carbon oxide and dioxide. One of the possible ways to decrease the power inputs for the implementation of thermal treatment processes of biogenic raw-materials with the production of combustible gases mixture is gasification – heating of biofuels using expulsion by various gases. Traditionally gasification is carried out in the reactors with fixed or pseudo-liquefied bed, with air, oxygen or steam blowing or their combination.

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.

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.

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 % [7].

Applied technologies of soil bioremediation are possible to be divided in two groups: methods in situ and methods ex situ. Bioremediation in situ is based on clearing of spill from pollutants without removal of the polluted soil from pollution area. The most perspective is bioremediation ex situ, which is based on removal of a layer of the polluted soil and its clearing from pollutant outside of a pollution place. Technologies of

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this type have a number of advantages: they demand less time and provide complete control of clearing process.

Use of bioreactors is one of the types applied at bioremediation ex situ technologies. The polluted soil is placed in the bioreactor, necessary nutritious elements and microorganisms are loaded. Optimum conditions of microorganisms cultivation are provided. After completion of the clearing process the soil is dried and returned in environment.

Other approach of bioremediation *ex situ* consists in placement of the removed from a place of pollution soil in certain territory, it is provided with aeration, nutrients and water for stimulation of microorganism growth and a metabolism. In comparison with clearing by means of the bioreactors, this technology demands a lot of place and longer time.

The most effective way of oil hydrocarbonic fraction biodegradation by microorganisms is the method of the continuous cultivation, allowing maintaining a number of process parameters at the set level, and simultaneously carrying out selection of the most active microorganisms-destructors.

The maximal degree of clearing, more than 60-90 %, is observed at use of oil-slime pretreatment and the further additional cleaning by a consortium of not pathogenic petrooxidizing microorganisms [8]. The most perspective method is preprocessing by ultrasound which plays a role of demulsifying agent and a dispergator [9]. As a result of ultrasonic influence in a water solution there is a formation at first the emulsion of direct type which is in a condition of inversion of phases.

Then, starting from critical value of acoustic wave sound pressure, there is a cavitation in a liquid. C-C bonds in paraffin molecules get broken and owing to what there are changes of physical and chemical structure (reduction of molecular weight, temperatures of crystallization, etc.). After ultrasonic pretreatment the steady microemulsion is formed and concentration of an accessible source of carbon and mineral components increases.

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.

II. Experimental

OIL of the Caspian deposit has been used as a model in this study (Table 1).

Table 1. characteristics of oil

Deposit	Paraffin content, %	Sulphur content, %	Minera-lization, g/l	Density (20 ^{0}C), kg/м^3	Dynamic viscosity (20 ^{0}C), мПа*С
Caspian Sea, Russia	10.07	0.2	70	860 ± 2	3.39

In experiments the modeling samples of the polluted soils consisting of soil and oil were used. The sample contained 15 % of oil. Combination of oil with soil spent within three days. Ultrasonic pretreatment of the modeling sample were carried out after that.

As each solvent possesses the characteristic properties, the correct choice of environment is very important for definition of optimum conditions of carrying out sonochemical processes. Selection of a leach, as a rule, is carried out purely empirically; scientific bases of the directed selection are developed in small degree because of a lack of the information about oil-slime structure and character of its interactions with solvents of the various nature.

After analysis of different methods of solvents activity effectiveness research dissolving ability of hydrocarbons for maintenance of the maximum accuracy of received results and an exception of a making error of the experiment caused by possible discrepancy of conditions of carrying out of experiences were defined

Thus for laboratory researches hexane, toluene, chloroform, benzene were used.

Ultrasonic generator IKASONIC U 50 was applied to raw materials treatment, working at frequency of 30 kHz. The device was completed with a nozzle of updating US 50-3 Sonotool with a diameter of 3 mm and maintenance of intensity to 460 Wt/cm^2.

During experiments intensity of ultrasonic processing (from 230 Wt/cm^2 to 414 Wt/cm^2) and extraction time from 1 till 25 minutes were varied. As a control, continuous extraction of hydrocarbons of oil from samples under normal conditions in conical flasks on a rocking chair of type AVU-1.

Samples after ultrasonic extraction by organic solvents subjected biodestructions

The quantity of oil products in the modeling sample were defined by the gravimetric method. Oil qualitative analysis was carried out via GC using chromatograph Kristallux-4000 equipped with FID, and capillary column Zebron ZB-FFAP 50, and GCMS-QP2010.

III. Results and discussion

FOR research of process of extraction of hydrocarbons of oil of samples the following solvents were used: xylol, benzene, chloroform, hexsane, toluene, acetone. 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.

During the experiments it has been established that the fullest extraction of hydrocarbons of oil from samples occurred at leach:oil-slime ratio – 4:1. Experiments were carried out at all rates (from 230 Wt/cm^2 to 414 Wt/cm^2) and in all investigated solvents.

Optimum time of ultrasonic treatment has been also chosen, the range varied from 5 till 10 minutes depending on solvent (Fig. 1).

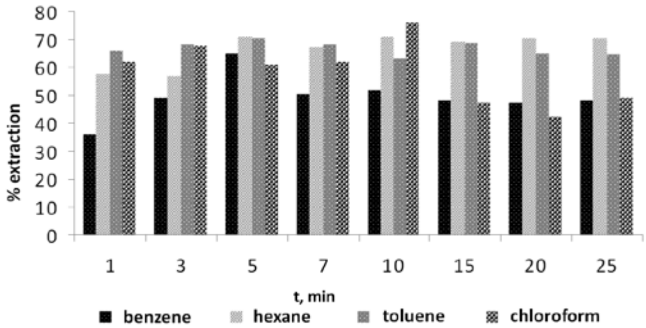


Fig.1 time of oil-slime ultrasonic treatment influence on degree of oil hydrocarbons extraction in solvent

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 there is the most effective extraction of oil hydrocarbons (Fig. 2).

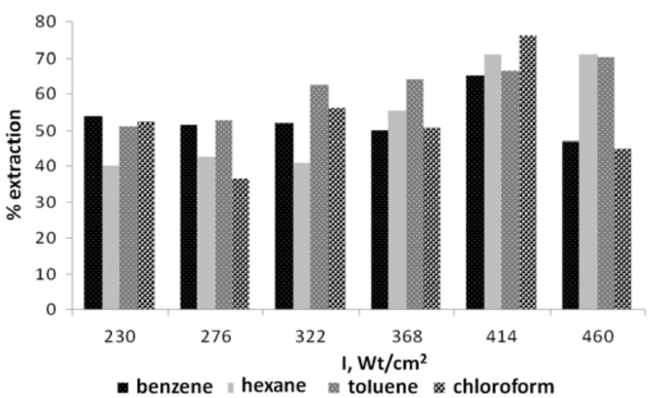


Fig.2 time of oil-slime ultrasonic treatment influence on degree of oil hydrocarbons extraction in solvent

At fractional oil-slime extraction without ultrasonic treatment the maximum degree of oil hydrocarbons extraction has been reached in 1,5-2 hours and was 46, 48, 56, 66 % for chloroform, hexane, benzene and toluene, correspondingly. Thus it it is possible to conclude that ultrasonic treatment intensifies process of oil hydrocarbons extraction from model samples.

It was shown that at ultrasonic influence the mineral oil temperature in the reactor increases on 7-10^{o}C, in comparison with control. It likely occurs because of the acoustic energy dissipation (Table 2.).

Table 2. Influence of ultrasonic treatment intensity on the temperature of the reaction medium (extractant – chloroform)

Intensity, Wt/cm^2	230	276	322	368	414
Temperature, ^{0}C	25	37	32	27	40

During the sonochemical process particles in oil-slime make oscillative motions. Oscillative motion energy increases, in particular, at heating. As a result, the bonding between sand particles and hydrocarbon molecules is destructed, which leads to oil-slime structure weakening, but it is not enough for full extraction.

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

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.

Following stage of the investigation was biodestruction of samples, polluted by oil hydrocarbons during sonochemical process. Collection cultures and the microorganisms secured in «Biotechnologies and chemistry» department of Tver Technical University were used in the study. The phenotypic characteristic of new isolate was studied. It is shown that it concern barmy cultures of Candida genus (DK1, DK2, DK3, B3) and bacterial microorganisms of Bacillus genus.

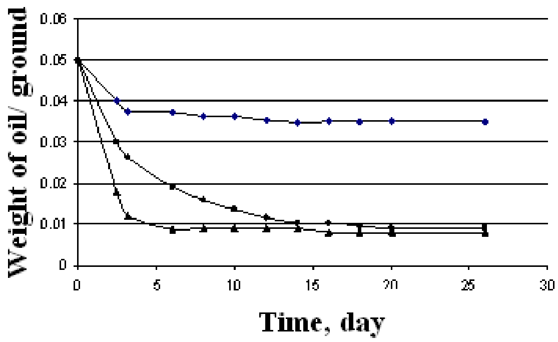
The study of oil-contaminated soil recultivation showed that the use of ultrasound of different intensity resulted in oil hydrocarbons degradation (Table 3.).

Table 3. destruction of pretreated oil (5 days)

Microorganisms	Degradation, %
Native microflora (soil)	10.2
Candida (DK1)	23
Candida (DK1) + native microflora of soil	38.4
- (sterile soil)	2

It was revealed that after 5 days oil (native) destruction in the sterile soil was 2 %, in the soil – 18.5%, in the soil with the introduced monoculture –24 %. 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 (Fig.2). The rate of evaporation is different and depends on the environment properties, meteorological conditions and oil composition.



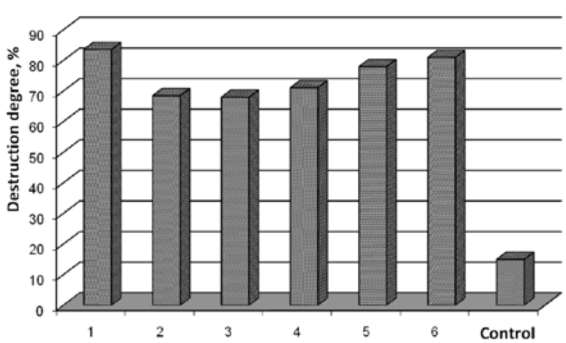
▲ – strain DK2, ■- strain DK3, ♦- control experiment
Fig.2 degradation of the compounded oil-slime

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 (Fig.3).

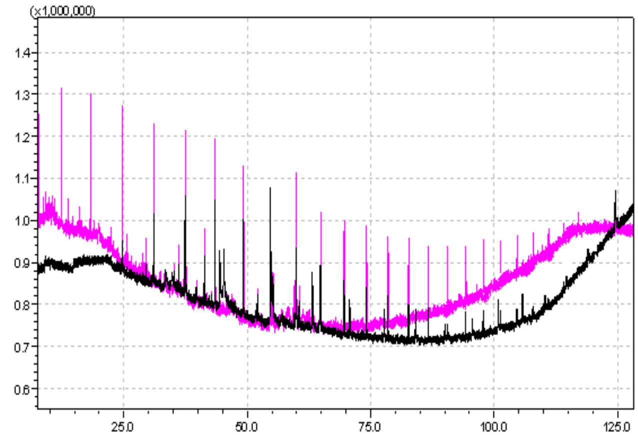
It is clear from graph 7 that microorganisms consortium DK2, DK3 in ratio 1:1 has the most degradation. The worst results were noted in case DK2 and DK3 ratio was not 1:1. The introduction of *Bacillus subtilis* intensifies the process of bioremediation. It is most likely explained by the fact that *Bacillus subtilis* is the producer of surfactants.

Chosen consortium (1) is capable to decompose not only volatile fractions of oil, such as hexadecane, but also diesel fuel and heavier fractions of oil, for example black oil, i.e. destruct a wide spectrum of hydrocarbons (Fig.4). And the consortium doesn't lose the oxidizing activity at the hexadecane, diesel fuel, oil and black oil maintenance at 5% (wt.).



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

Fig. 3 study of oil-slime degradation in different consortia of microorganisms



---- oil after processing consortium(1)
---- oil after processing microorganisms Candida DK3

Fig.4 chromatography oil after destruction

IV. Conclusion

THE Oil spill is a difficult engineering and microbiological problem which demands the complex approach for its solution. The developed method of oil spill recycling combines mechanical, physicochemical and biological methods [10].

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 experimental data optimum conditions of oil-slime ultrasonic pretreatment have been established: duration of process of 5-10 min, ultrasonic influence intensity of 368 Wt/cm^2 – 460 Wt/cm^2. From all studied solvents chloroform possessed the greatest extract ability for used samples. Thus the maximum degree of oil extraction from oil-slime was 75,9 %, at influence with intensity of 414 Wt/cm^2 and time of 10 minutes.

In process of biodestruction of the samples polluted by oil hydrocarbons after ultrasonic extraction, destruction degree has made more than 80 %.

Thus, the complex method of spills and a waste polluted by oil hydrocarbons neutralization, has allowed removing from it more than 85 % of oil hydrocarbons from the initial maintenance in samples within two weeks.

Developed scientific and technical production has advantage in comparison with analogs and includes use of ultrasonic treatment. The basic advantage of ultrasonic treatment consists of its sufficient quickness, profitability and ecological

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