Complex Approach to Oil Spill Utilization

E.M. Sulman, M.G. Sulman, E.A. Prutenskaya, E.V. Selivanova, M.Yu. Rakitin
Tver Technical University
Tver, Russia
e-mail: sulman@online.tver.ru

***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. 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.**

Keywords-oil spill, ultrasound, pretreatment, biological degradation

I. INTRODUCTION

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

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 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 [4]. The most perspective method is preprocessing by ultrasound which plays a role of demulsifying agent and a dispergator. 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.

Preprocessed oil-slime destruction is 10-30 %.

Thus the aim of this study is development of neutralization method of spills and a waste polluted by oil hydrocarbons.

II. EXPERIMENTAL

Oil of the Caspian deposit has been used as a model in this study. Some of the major characteristics of oil are the density and viscosity. The density of oil is 860 kg/m^3. Oil

Copyright (c) IARIA, 2011. ISBN: 978-1-61208-138-0

with relative density 0.86 is called average. Dynamic viscosity of oil ranges from 1.4 to 4.5 mP·s and depends on chemical and fractional structure, in our case viscosity of oil makes 3.39 mP·s.

Observable oil contains about 10 % of paraffin. Hence, it concerns to highwaxy substances. From ecological positions components sulfur presented in oil (elementary, hydrosulphuric, sulphidic, sour sulfur) are important compounds of it. Used oil contains 0.2 % of sulfur, therefore is low-sulphur. Mechanical impurity was also defined in the oil. Its general maintenance in the investigated sample doesn't exceed 0.01 %.

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.

The quantity of oil products in the modeling sample were defined by the gravimetric method. 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.

Extraction degree (W, %) of oil hydrocarbons from oil-slime were defined under the equation:

$$W = \frac{A*100}{B},$$

where

A – amount of the producing hydrocarbons from oil-slime solvent quantity (g);

B – content (wt.) of oil in oil-slime (g).

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

Determination of leach:oil-slime optimum ratio the first investigation stage. 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 (Figure 1). Experiments were carried out at all rates (from 230 Wt/cm^2 to 414 Wt/cm^2) and in all investigated solvents.

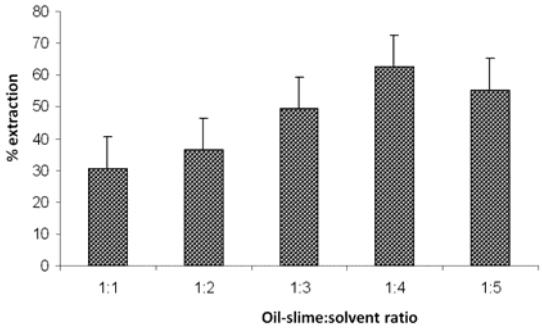


Figure 1. – Oil-slime hydrocarbons extraction degree at various oil-slime:solvent ratios
(Solvent is chloroform, intensity of 414 Wt/cm^2)

Optimum time of ultrasonic treatment has been also chosen, the range varied from 5 till 10 minutes depending on solvent (Figure 2).

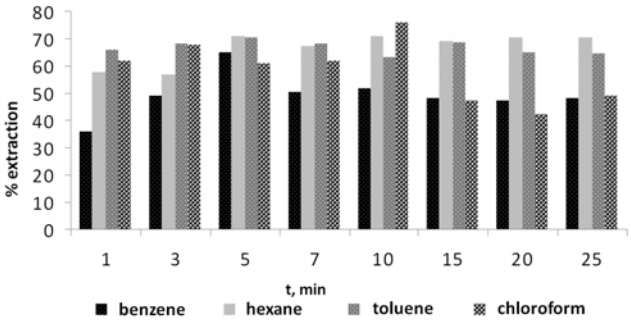


Figure 2. – Time of oil-slime ultrasonic treatment influence on degree of oil hydrocarbons extraction in solvent

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 (Figure 3).

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.

Copyright (c) IARIA, 2011. ISBN: 978-1-61208-138-0

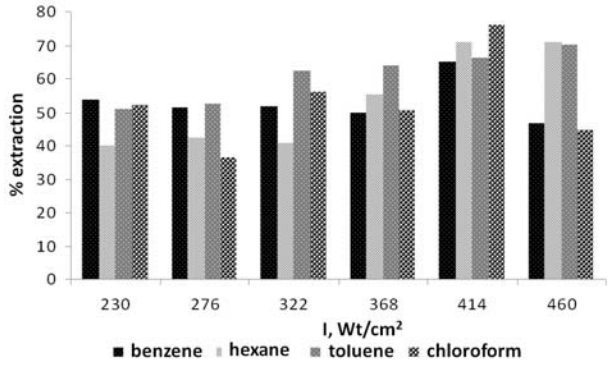


Figure 3. – Time of oil-slime ultrasonic treatment influence on degree of oil hydrocarbons extraction in solvent

It was shown that at ultrasonic influence the mineral oil temperature in the reactor increases on 7-10°C, in comparison with control. It likely occurs because of the acoustic energy dissipation (Figure 4).

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.

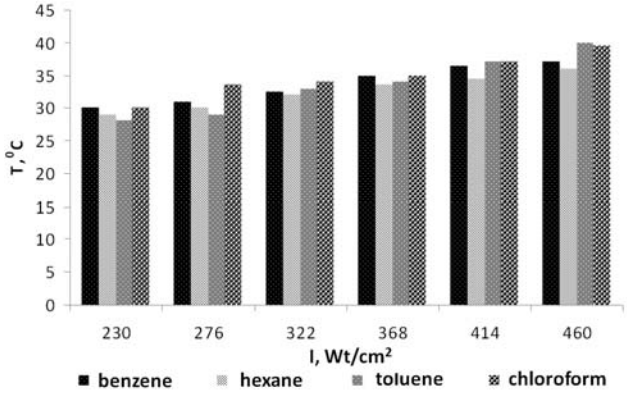


Figure 4. – Influence of ultrasonic treatment intensity on extraction temperature

However, even at higher temperature changes, limiting gradients of pressure can be reduced maximum in two-three times [5] (not in degrees, as it is necessary in many cases) since during the increase of the amount of free particles the probability of its collision and dynamic balance between process of hydrocarbons structure destruction and its restoration also increases. 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.

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. Oxidizehydrocarbon ability of studied microorganisms has been found (Figure 5).

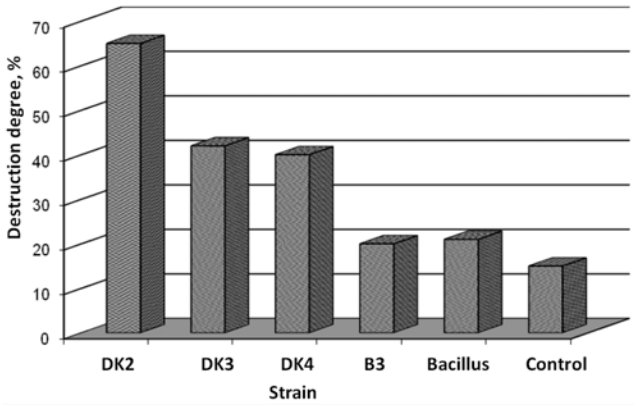
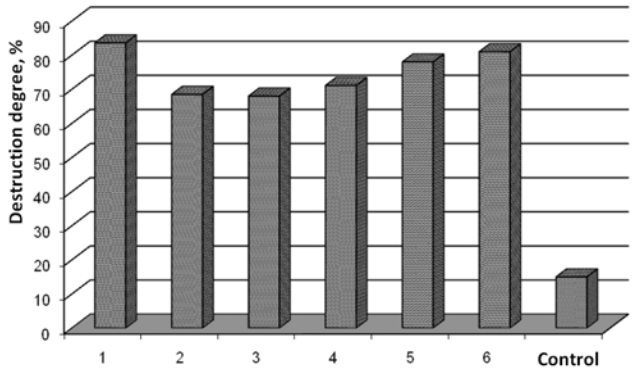


Figure 5. – Degree of oil hydrocarbons destruction by pure cultures

Optimum conditions of oil-slime biodestruction (temperature; pH; organic solvent, mineral salts and oil hydrocarbons concentrations) were chosen. It was shown that yeasts are the most effective destructor.

Further the consortium from allocated isolate was developed (Figure 6).



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 6. – Oil hydrocarbons destruction in associations of microorganisms

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. And the consortium doesn't lose the oxidizing activity at the

Copyright (c) IARIA, 2011. ISBN: 978-1-61208-138-0

hexadecane, diesel fuel, oil and black oil maintenance at 5% (wt.).

CONCLUSIONS

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.

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 destruction 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 harmlessness. Besides, it allows destroying C-C bonds in paraffin molecules.

REFERENCES

[1] M. Kumar, V. Leon, A. Materano, O.A.Ilzins, Enhancement of oil Degradation by Cop-Culture of Hydrocarbon degrading and Biosurfactant Produciong Bacteria, Polisch Journal of Microbiology.-2006.-A(2).-P.139-146.

[2] G.G. Yagafarova, S.V. Leontjeva, A.H. Safarov, I.R. Yagafarov, M.V. Golovtsov, Complex technology of oil-slime purification, Oil-treatment-2008: international scientific-practical conference. – Ufa, 2008. – P. 330-331 (in Russian).

[3] T.V. Mikhailova, S.V. Leonova, Problems of oil-slime treatment, Industrial ecology.-2009.-1. –P.10 (in Russian).

[4] Isolation of autichthonous non-white rot fungi with potential for enzymatic upgrading of Venezuelan extra-heavy crude oil./ Naranjo, Urbina H., Leon V// Biocatal Biotransformation.-2007.-F(25).-P.341-349

[5] R. Baldev, V. Randjendran, P. Palanichami, Ultrasound application, Moscow: Technosphere.-2006.-576 pp. (in Russian).

Copyright (c) IARIA, 2011. ISBN: 978-1-61208-138-0