UDC 579.695+502.662.2+665.5:628.544+504.06:628.4

Integrated Method for Recovering Oil Sludge

V. S. OVSYANNIKOVA[1], L. I. SVAROVSKAYA[1], L. K. ALTUNINA[1], D. A. FILATOV[1], E. A. FURSENKO[2] and V. A. KASHIRTSEV[2]

[1]*Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademicheskiy 4, Tomsk 634021 (Russia)*

E-mail: varja@ipc.tsc.ru

[2]*Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences, Pr. Koptyuga 3, Novosibirsk 630090 (Russia)*

(Received July 24, 2012; revised January 9, 2013)

Abstract

Results are presented concerning the recovery of an oil sludge model from the contamination by means of a complex microbiological and physicochemical method. It is demonstrated that washing with a detergent composition results in a 55–75 % decrease of soil contamination level. The subsequent biodestruction by native microflora further reduces the contamination by 20–30 % per month. In the case of the mechanical part of the sludge, the microflora is worthwhile for stimulation by nitrogen and phosphorus containing mineral substrates, whereas in the case of spent water the mineral nutrition can be provided by the components of the composition. Changing the structural and group as well as the individual composition of hydrocarbons in the spent water corresponds to the initial stage of biodestruction, whereas that in the washed soil corresponds to the middle stage thereof, which indicates a low activity of the indigenous microflora.

Key words: oil sludge, sludge pits, hydrocarbons, surfactants, detergent compositions, hydrocarbon-oxidizing bacteria, biodestruction, reclamation

INTRODUCTION

At the present time, of extreme urgency is the issue concerning the elimination of oil sludge waste generated in the oil industry almost from the beginning of the development and management of oil fields. The oil sludge involves drilling wastes, soil after oil spills, asphalt-resin-paraffin deposits after the purification of tanks [1]. Basically, sludge represents heavy oil residues containing up to 10–56 % of oil, 30–85 % of water, 1.3–46 % of solid impurities [2].

Solving the problem of utilizing waste oil sludge is complicated due to a high stability thereof, the features of the composition and properties those permanently change under the influence of air when stored in open barns. Over time the waste are "aging" due to the evaporation of light fractions, the oxidation and asphaltization of the oil, the formation of colloidal micelle conglomerates, and an additional contamination of mechanical impurities [3].

For purifying the sludge, the world practice uses technologies based on solvent extraction, electrochemical separation of organic fraction, combustion in special furnaces as well as using the sludge as fuel additives and additives for the materials in road construction. The team from the Institute of Petroleum Chemistry of the SB RAS (Tomsk, Russia) offered an environmentally safe method for the comprehensive remediation of oil sludge and contaminated soils using detergent compositions based on surface-active substances (surfactants) and hydrocarbon-oxidizing microorganisms [4].

At the first stage, the method consists in the physical and chemical separation of oil sludge into its constituent phases (after washing with a composition). The spent washing water with the solution of the composition can

be used at the second washing stage to wash out new sludge portions. At the second stage, depending on the initial level of contamination, the soil and the liquid part of the sludge are subjected to additional microbiological decontamination.

The compositions involve nontoxic biodegradable surfactants and a buffer system to maintain an optimum alkalinity level. The components of the buffer system are involved in the cycle of nitrogen and phosphorus, serving as mineral nutrition for hydrocarbon-oxidizing microorganisms.

Using the compositions allows one to perform bioremediation with respect to sludge with a high level of contamination or to significantly reduce the time bioremediation, with a 50–80 % decrease of the oil content.

The aim of this work consisted in the evaluation of the efficiency of the complex method by the example of a sludge model: washing with the composition and biodestruction of the residual oil contamination with the use of native microflora in the mechanical and liquid parts of the sludge.

RESEARCH OBJECTS AND METHODS

The object for testing the detergent composition was presented by a model of oil sludge with a low level of contamination, similar to the sludge of the Sovyetskoye and Vakhskoye fields in the composition and properties. The composition of the mechanical parts represents sand with a low content of clay. The sludge humidity is equal to 14 %, the initial oil content being of 48 g/kg. Among the components of the initial contamination there prevail hydrocarbons (HC) (84.54 %); the fraction of asphaltenes amounting to 0.25 %, that of resins being of 15.14 %.

The composition for washing represented a mixture of the following components (%): syntanol (surfactant) 0.87, volgonat (surfactant) 1.68, sodium tetraborate 0.65, sodium tripolyphosphate 1.1, urea 1, the rest being water; the acidity of the final composition corresponded to pH 9.1. The surfactants such as syntanol and volgonat exhibit a good biodegradability equal to 85–90 %. Sodium tetraborate and sodium tripolyphosphate produce an alkaline environment, wherein the detergent properties of surfactants can be manifested to he most extent. Urea represents a source of nitrogen nutrition for the microorganisms at the second stage of recovering the sludge. These concentration values for the reagents were chosen basing on the composition operation efficiency and the cost-efficiency when applying the method on an industrial scale [5, 6].

In the course of washing we simulated the possibility of triple using the composition. For this, the took three equal portions of the sludge (200 g); the first portion was mixed with the composition under investigation at a ratio of 1 : 1, settled, and then the supernatant liquid with the washed oil was decanted to the second portion of the sludge. Further, each portion of the sludge was washed twice with water according to the same procedure.

After washing, the supernatant, liquid phase containing washed oil, the solution of the composition and suspended sludge particles were joined together to perform the destruction of residual oil contamination in the liquid phase using indigenous microflora.

The samples of the mechanical part of the sludge (washed soil) were also joined together to perform the biodestruction of the residual contamination in the liquid phase with the help of native microflora.

In the course of biodestruction, we investigated an effect of different mineral nutrition sources on the growth of microflora and the extent of the biological destruction of residual oil contamination (Table 1). In particular, the influence of additional sources of phosphorus,

TABLE 1

Scheme of performing the experiment on the biological destruction of the residual oil contamination in the liquid and mechanical phases of sludge after washing

Samples	Concentration additional mineral substrates, mass %	
	Liquid phase	Mechanical phase
Reference	0	0
Diammofoska	0.03	0.100
NH_4NO_3	0.025	0.025
$K_2HPO_4 + KH_2PO_4$	0.035	0.035

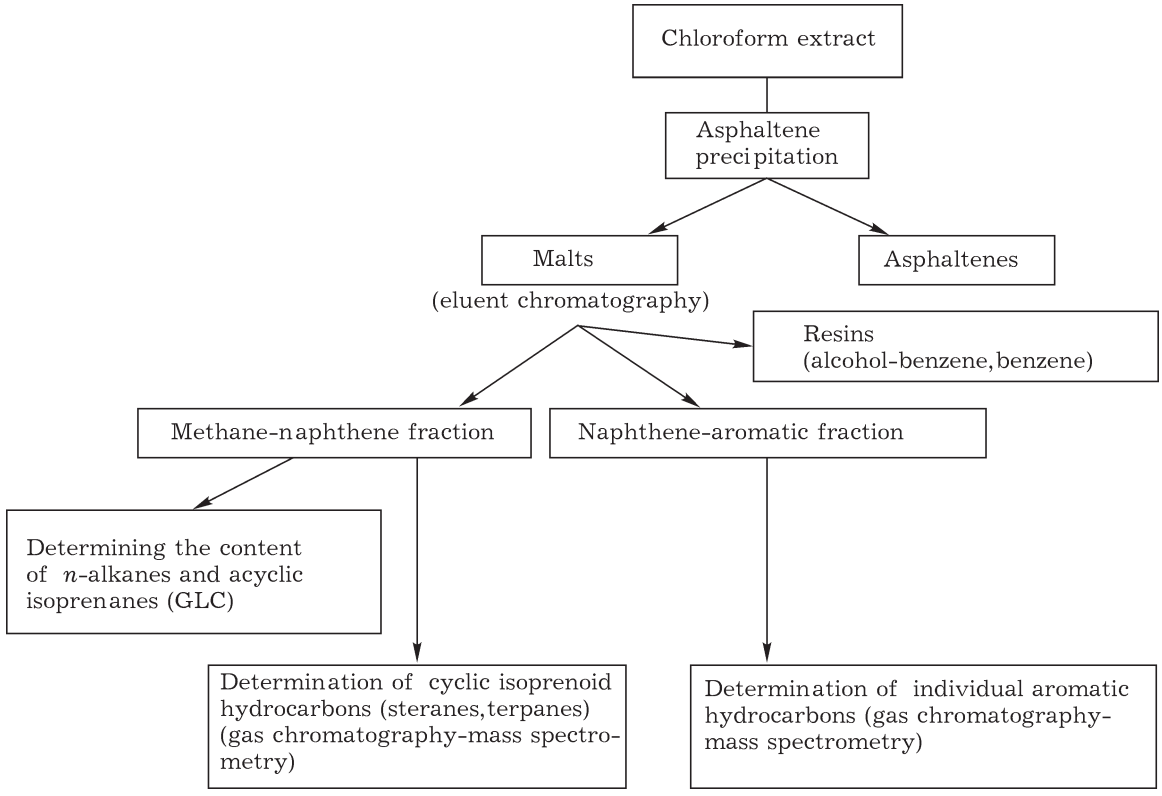

Fig. 1. Schematic diagram of studying the chloroform extracts.

introduced in the form of the mixture of mono- and disubstituted potassium phosphate, nitrogen in the form of ammonium nitrate, and the combination of nitrogen, potassium and phosphorus in the form of commercially available fertilizer "Diammofoska" (ammonium and potassium phosphate). Liquid or mineral sludge with no additional mineral nutrition was used as a reference.

Changing the abundance of microflora was determined using a standard microbiological method of inoculation on dense selective media: heterotrophic microflora was determined using meat infusion agar (MIA), hydrocarbon-oxidizing microflora was determined using agar medium with oil [7].

Changing the content of oil contamination in the mechanical part of the sludge after the washing and biodestruction was determined using gravimetry. The extraction was carried out using chloroform by means of hot method in a Soxhlet extractor.

The residual oil was extracted from liquid phase with chloroform using a separating funnel.

Changing the structural-group composition of the chloroform extracts obtained was studied with the help of FTIR spectrometry according to a set of spectral coefficients with the help of a Nikolet 5700 Fourier transform spectrometer [8].

Further, the chloroform extracts were analyzed according to a scheme adopted at the Institute of Petroleum Geology and Geophysics (IPGG) of the SB RAS (Fig. 1). Data concerning the structural-group composition of chloroform extracts and the corresponding fractions (methane-naphthene, naphthene-aromatic, resins) were obtained with the help of liquid adsorption chromatography (LAC) with a preliminary precipitation of asphaltenes [9].

The distribution of n-alkanes and acyclic isoprenanes was studied by means of GLC method using a Hewlett Packard 5890 chromatograph with a flame ionization detector, a HP5 quartz capillary column in a linear temperature-programmed mode. The identification of individual compounds was carried out with the assistance of a GC ChemStation computer system.

The chromatography-mass spectrometry analysis of individual steranes and terpanes was performed with the use of a Hewlett Packard 5890 chromatograph and a MSD 5972A mass spectrometer with a ChemStation HP G1034 computer system for the registration and information processing. For the separation, we used a HP-5 quartz capillary column; helium was used as the carrier gas. The GC-MS analysis was performed in a TIC mode for characteristic fragmentary ions: m/z 191 for terpanes and m/z 217, 218 for steranes and isosteranes. The identification of compounds was carried out *via* comparison of the retention time values for the fragmentograms obtained with the mass spectra available from the library systems and from the literature.

RESULTS AND DISCUSSION

The initial petroleum product content in the sludge model was equal to 48.6 g/kg. Successive washing with the composition and two-fold washing with water made it possible to reduce the content of oil contamination down to 11.3 g/kg for the first portion of the sludge, to 14.4 g/kg for the second portion, and to 20 g/kg for the third portion, *i. e.* a 60–75 % decrease in the contamination level was achieved.

Washing was accompanied by minor modifying the structural group composition of the contamination: the residual oil contamination exhibited an increase in aromaticity and oxidation level, which indicates the rock particles being predominantly washed out from non-polar HCs (Table 2). The washed-out oil contamination exhibits a decrease in oxidation level.

Initially, in the sludge we determined heterotrophic indigenous microflora in an amount of 300–500 thousand cells/g. The microflora revealed was used for biological destructing the residual oil contamination in the washed mechanical sludge and washing liquid.

The microflora amount in the mechanical and the liquid parts of the sludge after washing was equal to 4.6 and 8 million cells/mL, respectively. In the mechanical part of the sludge, the biodestruction of residual oil contamination was accompanied by a three orders of magnitude increase in the amount of microflora (Fig. 2, *a*). Adding the mineral substrates exerted a positive effect on the growth of microflora, since after twice washing with water,

TABLE 2

Changing the structural composition of oil contamination after washing the sludge and subsequent biodestruction in solid and liquid phases

Samples	Spectral coefficients							
	C_0	C_1	C_2	C_3	A_1	A_2	A_3	A_4
Initial model of sludge	0.60	0.66	1.14	0.29	0.71	0.51	1.60	6.77
After washing by the detergent composition								
1st washing	0.94	0.84	1.15	0.28	0.71	0.55	1.50	5.41
2nd washing	0.85	0.80	1.13	0.28	0.72	0.55	1.50	5.62
3rd washing	0.84	0.79	1.14	0.28	0.71	0.54	1.51	5.74
Biodestruction of the residual oil contamination in the mechanical phase								
Original	0.89	0.82	1.12	0.29	0.74	0.54	1.52	5.36
Reference	1.05	0.91	1.19	0.24	0.79	0.65	1.46	5.77
Diammofoska	0.91	0.99	1.46	0.24	0.75	0.72	1.52	5.28
NH_4NO_3	1.05	0.92	1.25	0.25	0.76	0.64	1.49	5.49
$K_2HPO_4 + KH_2PO_4$	0.86	0.94	1.27	0.24	0.77	0.65	1.52	5.60
Biodestruction of the residual oil contamination in the liquid phase								
Original	0.50	0.74	1.08	0.29	0.77	0.59	1.41	6.06
Reference	0.80	0.89	1.11	0.27	0.73	0.71	1.13	5.26
Diammofoska	0.64	0.79	1.11	0.28	0.73	0.54	1.51	5.68
NH_4NO_3	0.65	0.82	1.11	0.28	0.73	0.58	1.41	5.61
$K_2HPO_4 + KH_2PO_4$	0.71	0.86	1.13	0.28	0.74	0.55	1.52	5.30

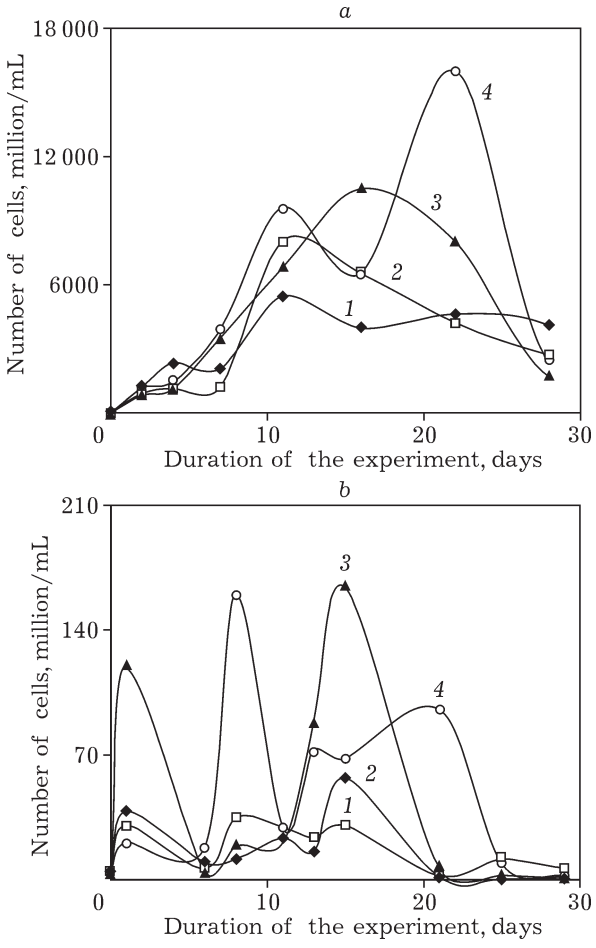

Fig. 2. Dynamics of the abundance of native microflora in the course of the biodestruction of residual oil contamination in the mechanical (*a*) and liquid (*b*) parts of the sludge in the case of introducing additional mineral substrates: *1* – reference, *2* – Diammofoska, *3* – K_2HPO_4, *4* – KH_2PO_4.

from the soil there are nitrogen and phosphorus compounds washed out to cause any deficiency in mineral nutrition. In the liquid phase, which represents a three-fold diluted solution of the detergent composition and washed-out oil, the microflora growth amounted to about 1–1.5 order of magnitude. Introducing the additional mineral substrates exerted a little (30–60 %) stimulating effect on the abundance of microflora (see Fig. 2, *b*). Poor growing the microflora could be explained by a high concentration of oil contamination (about 3 %) and mineral components.

As far as the mechanical part of the sludge is concerned, after 30 days of biological destruction, the content of residual oil contamination therein exhibits a decrease ranging within 21–28 %. As far as the liquid part is concerned, a quantitative decrease of the oil contamination level one could not determine methodically.

The conversion level of oil contamination in the mechanical and liquid parts of the sludge depends on the population of the microflora.

For example, the structural group composition of oil contamination in the mechanical part of the sludge exhibits increasing the proportion of oxygen-containing structures, the aromaticity factor, the branching ratio, whereas there decreases biarene to triarene ratio, which indicates a process of biodestruction to occur. The greatest changes are noted for the experiment with “Diammofoska” (see Table 2).

TABLE 3

Structural-group composition of the chloroform extracts and the ratio between *n*-alkanes and isoprenoid hydrocarbons in the saturated fraction thereof

Samples	Group composition, % of chloroform extract				Ratio values		
	Me–Nn	Nn–Ar	Resins	Asphaltenes	n-C_{27}/n-C_{17}	*n*-alkanes/isoalkanes	(Pr + Ph)/(n-C_{17} + n-C_{18})
Original sludge model	44.08	40.46	15.14	0.25	0.15	3.21	0.84
After washing by the detergent composition							
1st washing	40.57	35.82	21.19	2.42	0.17	3.67	0.77
1st washing	41.08	36.41	20.18	2.53	0.20	3.69	0.79
1st washing	40.49	36.75	20.69	2.07	0.20	3.76	0.76
Biodestruction of the residual oil contamination in the mechanical part of the sludge							
Original	41.36	36.93	20.77	2.94	0.16	3.78	0.71
Reference	41.82	33.74	23.53	0.91	0.16	2.14	1.31
Diammofoska	63.45	15.91	19.89	0.75	0.15	0.73	5.36
Biodestruction of the residual oil contamination in the liquid part of the sludge							
Original	67.58	11.03	18.56	2.83	0.22	3.98	0.72
Reference	63.51	14.18	16.68	5.63	0.18	3.89	0.68
Diammofoska	52.20	21.54	22.38	3.93	0.09	3.42	0.68

After the biodestruction the liquid portion of the sludge exhibit a slight increase in the level of aromaticity and in the fraction of oxygen-containing structures as well as minor changes in the proportion between different classes of aromatic hydrocarbons (see Table 2).

According to LAC, the chloroform extract of the initial oil contamination is characterized by a high concentration of HC (84.54 %) and low asphaltene content (0.25 %) (Table 3).

After washing by the composition the chloroform extracts exhibit reducing the hydrocarbon content and increasing the fraction of resin-asphaltene components (see Table 3). According to data obtained using GLC, the extracts of the samples under investigation (except the extracts obtained from the biodegraded samples of mechanical sludge), and the *n*-alkanes prevail to a considerable extent as compared to acyclic isoprenanes (see Table 3 and Fig. 3).

The molecular mass distribution of *n*-alkanes after washing remains almost unchanged, with slightly increasing the relative content of *n*-alkanes comparing to isoalkanes, whereas the isoprenoid coefficient exhibits a slight decrease (see Table 3).

After the biological destruction, the most significant changes in the composition of the hydrocarbon group were noted for the mechanical part of the sludge such as reducing the content of asphaltenes, changing the molecular mass distribution of *n*-alkanes and isoprenoids toward increasing the relative concentration of the latter, decreasing the ratio between *n*-alkanes and isoalkanes increasing the isoprenoid ratio to a considerable extent. The maximum transformation was observed for the variant with the stimulation of indigenous microflora by means of "Diammofoska": the ratio between *n*-alkanes isoalkanes decreases from

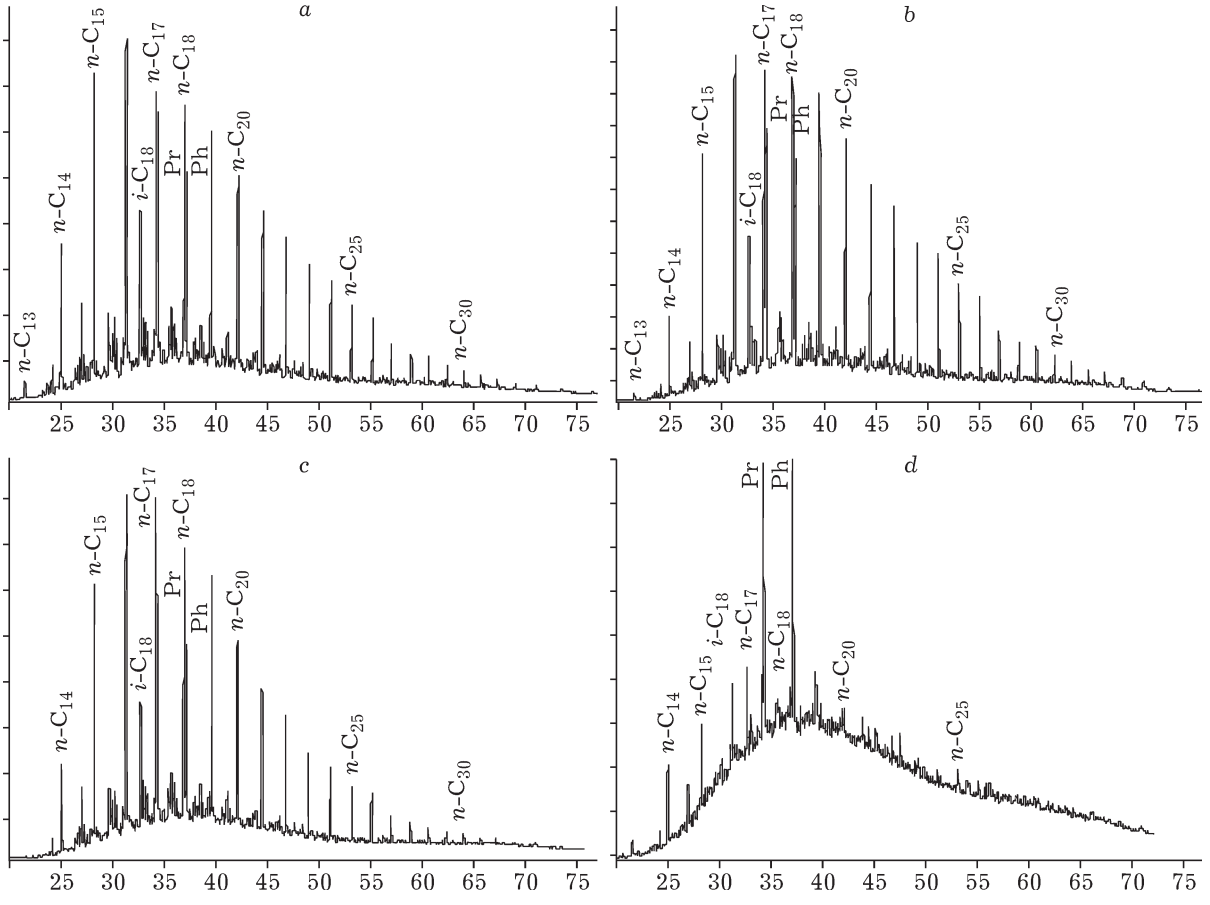

Fig. 3. Chromatographic profiles for the saturated fraction of chloroform extracts. Here and in Fig. 4: *a* – original oil sludge sample, *b* – the sludge after the 1st washing by the detergent composition, *c* – the liquid phase after biodestruction with Diammofoska, *d* – the mechanical phase after biodestruction with Diammofoska.

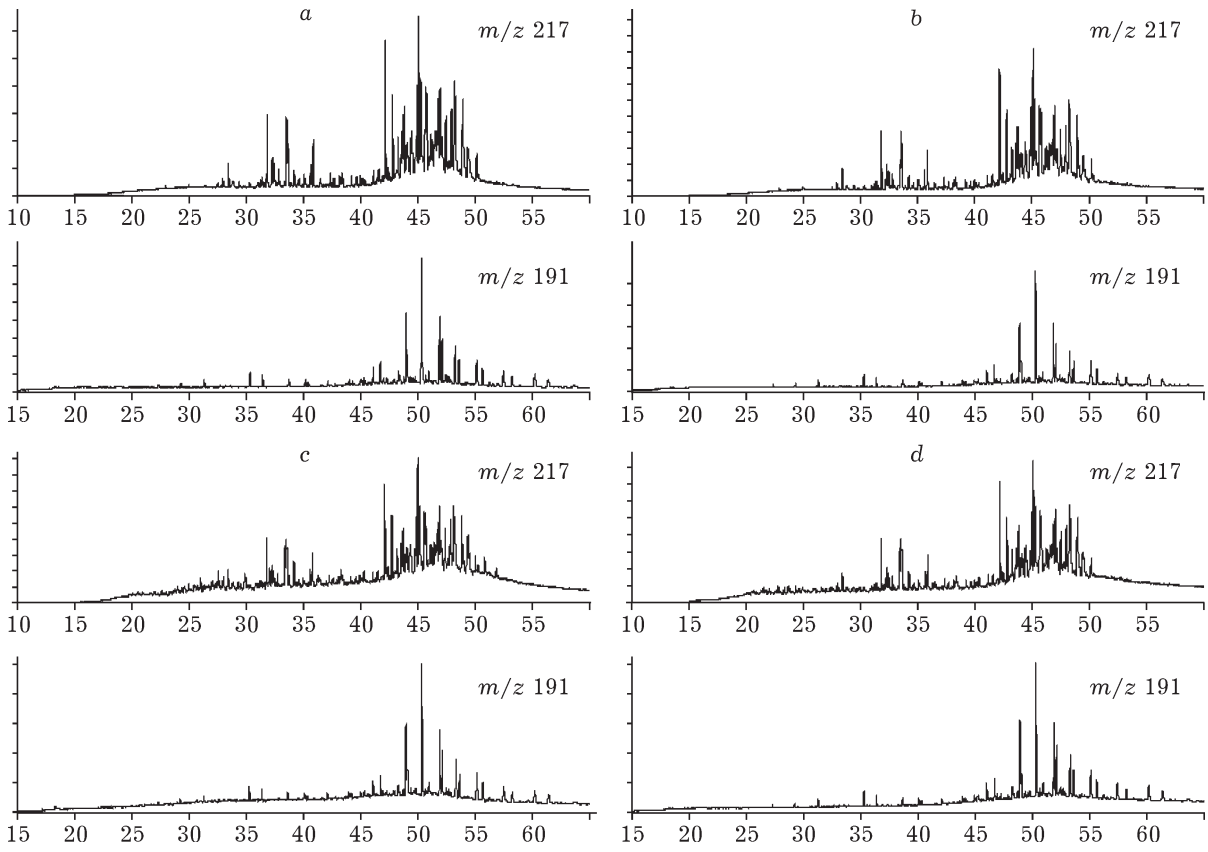

Fig. 4. Mass fragmentograms of steranes (m/z 217) and terpanes (m/z 191). For designations, see Fig. 3.

TABLE 4

Changing the composition of steranes after washing the oil sludge by the detergent composition and subsequent biodestruction of residual oil contamination in the mechanical and liquid parts of the sludge

Samples	Diasteranes/regular steranes	Steranes C_{29}		
		20S/20S + 20R	ββ(20S + 20R)/αα20R	ββ/αα + ββ
Original sludge model	0.58	0.47	3.53	0.54
After washing by the detergent composition				
1st washing	0.58	0.46	3.61	0.54
2nd washing	0.57	0.46	3.50	0.55
3rd washing	0.55	0.46	3.68	0.55
Biodestruction of the residual oil contamination in the mechanical part of the sludge				
Original	0.56	0.46	3.62	0.55
Reference	0.56	0.46	3.63	0.55
Diammofoska	0.57	0.48	3.27	0.51
Biodestruction of the residual oil contamination in the liquid part of the sludge				
Original	0.53	0.48	3.06	0.49
Reference	0.59	0.47	3.12	0.53
Diammofoska	0.56	0.47	3.54	0.54

3.78 to 0.73, the isoprenoid coefficient increases from 0.71 to 5.36, indicating that there occurs a substantial biodestruction of *n*-alkanes (see Table 3 and Fig. 3) [9].

After the biodestruction of the oil contamination in the liquid-phase there are changes observed at the level of group composition: reducing the concentration of both methane-naphthene (Me–Nn), and naphthene-aromatic (Nn–Ar) hydrocarbons; increasing a relative content of resins and asphaltenes. At the level of individual composition, slight decreasing the ratio between *n*-alkanes to isoalkanes is observed (from 3.98 for the original sample to 3.42 after the stimulation by "Diammofoska"). The molecular mass distribution of *n*-alkanes and isoprenoids is close to that observed for the original sample; therefore the isoprenoid coefficient does not change (see Table 3 and Fig. 3).

The chromatography-mass spectrometry study of the saturated fraction demonstrated that the biodestruction does not affect the composition of steranes and terpanes. The mass fragmentographic profiles of steranes and terpanes for the samples under investigation are identical (Fig. 4), whereas 25-*nor*-hopanes have not been identified, while their presence and/or prevailing with respect to the regular hopanes usually indicates an intense biodestruction to occur [10, 11].

The parameters inherent in the composition of steranes used for estimating the level of the biodestruction for oil and organic matter [9] are also close to each other (Table 4), which indicates that there is a low level of biodestruction undergone by the samples in the course of the experiment.

CONCLUSION

Using a detergent composition for washing oil sludge with a low level of hydrocarbon contamination (about 5 %) provides 55–75 % purification level depending on the number of washing cycles. Subsequent biodestruction of native microflora additionally reduces the contamination by 20–30 % per month. In the case of the mechanical part of the sludge, the microflora is worthwhile for stimulation by nitrogen and phosphorus containing mineral substrates (when additionally washing the sludge with water after using the detergent composition), whereas in the case the liquid part of the sludge, the mineral nutrition can be provided by the components of the composition.

Changes in the structural-group and individual composition of hydrocarbons in the liquid part of the sludge corresponds to the initial and in the mechanical part of the middle stage of biodestruction, which indicates the insufficient activity of native microflora. Consequently, a deeper destruction requires either for a longer time, or for the introducing highly active strains, the destructors of hydrocarbons.

REFERENCES

1 Aliev S. A., Gadzhiev D. A., *Izv. AN AzSSR. Ser. Biol. Nauk*, 2 (1977) 46.
2 Yultimirova I. A., Zakonodatel'stvo Tyumenskoy Oblasti: Online Journal, 2003.
URL: http://law.admtyumen.ru/noframe/nic?d&nd=466200921&prevDoc=466200795 (Accessed 2010-10-13).
3 Anderson R. K., Boyko T. F., Bagautdinov F. Ya., *Zashchita ot Korrozii i Okhrana Okruzhayushchey Sredy*, 2 (1994) 16.
4 Svarovskaya L. I., Altunina L. K., *Neftekhim.*, 45, 2 (2005) 157.
5 Filatov D. A., Svarovskaya L. I., Altunina L. K., *Voda: Khimiya i Ekologiya*, 2 (2011) 41.
6 Altunina L. K., Svarovskaya L. I., Filatov D. A., Ovsyannikova V. S., *Bezopasnost' Zhiznedeyatel'nosti*, 11 (2011) 21.
7 Romanenko V. I., Kuznetsov S. I., Ekologiya Mikroorganizmov Presnykh Vodoemov, Nauka, Leningrad, 1974.
8 Bolshakov G. F., Infrakrasnye Spektry Nasyshchennykh Uglevodorodov, part 1: Alkany, Nauka, Novosibirsk, 1986.
9 Bogomolov A. I., Temyanko M. B., Khotyntseva L. I., Sovremennye Metody Issledovaniya Neftey (Handbook), Nedra, Leningrad, 1984.
10 Kashirtsev V. A., Kontorovich A. E., Filp R. P., Chalaya O. N., Zueva I. N., Ivanova I. K., *Geol. Geofiz.*, 42, 11–12 (2001) 1792.
11 Peters K. E., Walters C. C., Moldovan J. M., The Biomarker Guide, 2nd ed., Cambridge University Press, New York, 2005, p. 1155.