Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2020, **30**, 527–530

Mendeleev Communications

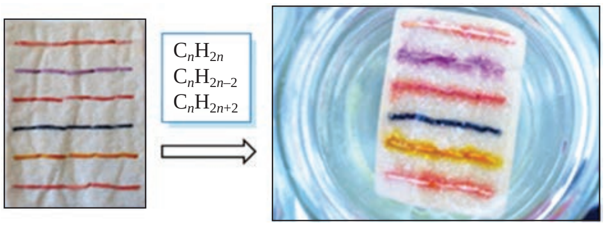
New multifunctional biocomposite material for hydrocarbon detection and reclamation on the surface of water areas

Alexey G. Dedov,*[a,b,c] Dmitry Yu. Marchenko,[a] Ekaterina A. Ivanova,[a] Rafet K. Idiatulov,[d] Delgir A. Sandzhieva,[a,b] Sergey V. Egazaryants,[e] Elena S. Lobakova[f] and Khatira S. Dzhabrailova[a]

[a] *National University of Oil and Gas 'Gubkin University', 119991 Moscow, Russian Federation. E-mail: dedov.a@gubkin.ru*
[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[c] *A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[d] *JSC Research Institute of Synthetic Fiber with the Pilot Plant, 170032 Tver, Russian Federation*
[e] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[f] *Department of Biology, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2020.07.042

Multifunctional biocomposite material BCM-I has been developed for detection, collection and reclamation of hydrocarbon contaminants from the surface of water areas. The material is composed of a nonwoven polymer with the incorporated plant-derived structures and the immobilized associations of hydrocarbon-degrading bacteria. Indicator properties of BCM-I are ensured by formation on its surface of zones from threads impregnated with hydrocarbon-soluble indicator dyes.



Keywords: crude oil, oil products, biocomposite material, solid-phase reagent, indicator threads.

The design of new composite materials is currently an active area of research, these materials being in demand for the construction, mechanical engineering, electronics and other branches of industry. Owing to an increasing anthropogenic impact on the environment there is a need for composite materials with special properties to address ecological issues. Crude oil and oil products are among the large-scale and most serious environmental pollutants.[1,2] Major oil spills, such as the Deep Water Horizon one occurred in 2010 in the Gulf of Mexico, lead to ecological disasters.[3] However, the current water treatment technologies remain multistage, complicated and expensive,[4] they typically require an employment of toxic compounds and/or materials.[5] Besides, a continuous monitoring the water areas with early detection of oil leaks or spills as well as the real-time identification of crude oil and oil products on the water surface represent essential issues, which makes it possible to take measures for minimization of environmental and financial losses. One of the approaches to reduce and prevent an environmental pollution by petroleum hydrocarbons consists in the design of biocomposite materials (BCM),[6–13] including those with indicator properties (BCM-I). These materials allow the monitoring of water areas as well as the extraction of crude oil and oil products from reservoirs or wastewater and their one-step processing into ecofriendly products like water and carbon dioxide.

Earlier, we proposed BCM made of synthetic polymer matrix with incorporated biogenic elements and immobilized hydrocarbon-degrading microorganisms, which could efficiently decompose hydrocarbon molecules.[14] However, the issues of early detection and identification of crude oil and oil products on the water areas surface have not been resolved, the corresponding available methods are still time-consuming and require an expensive equipment.[15] At the same time, convenient express methods have been developed for the detection and identification of many inorganic and organic pollutants. They are based on the employment of solid-phase reagents in combination with modern photometric and colorimetric analytic methods.[16,17]

The use of indicator paper for detection of oil products was proposed, however with low sensitivity or a need for concentrated sulfuric acid in the test.[16,17] An alternative technology may represent sensitive elements on the basis of a set of solid-phase reagents with selectivity to different oil products.

In this work, we have developed a new BCM-I using acrylonitrile–methyl methacrylate copolymer as a matrix capable of adsorbing hydrocarbons from aqueous media. Beet bagasse was used as a plant filler because it created a habitat close to the natural one for microorganisms and provided them with necessary biogenic elements. The associations of hydrocarbon-degrading bacteria *Sphingobacterium multivorum* + *S. mizutaii*, isolated from microbiologically contaminated aviation fuel, were immobilized on the filled polymer matrix. Indicator zones were created on the surface of BCM-I as six threads impregnated with different indicator dyes,[18] thus the threads functioned as the solid-phase chromogenic indicator carriers. They were fixed *via* broaching on the surface of the absorbing filled polymer matrix of BCM-I as the indicator substrate (Figure 1).

BCM-I was prepared from the plant matter-filled acrylonitrile–methyl methacrylate copolymer, which was obtained by aerodynamic spinning.[19] The polymer fibers were modified with beet bagasse as the following. The filler was ground, introduced into

© 2020 Mendeleev Communications. Published by ELSEVIER B.V. on behalf of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.

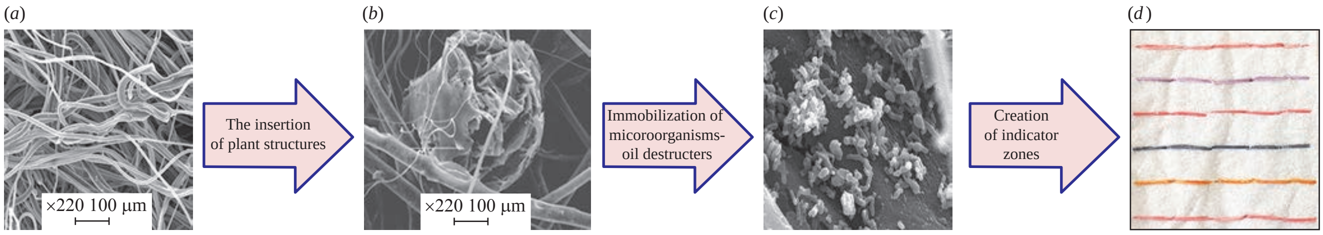


Figure 1 The composition and structure of BCM-I: (*a*) nonwoven matrix of acrylonitrile–methyl methacrylate copolymer, (*b*) the matrix with incorporated plant structures, (*c*) the matrix with incorporated plant structures and immobilized associations of hydrocarbon-degrading microorganisms and (*d*) BCM-I indicator zone containing threads with the dyes Sudan II, tetrazolium violet formazan, zinc ditizonate, Sudan black B, naphthyl red and Sudan IV.

the polymer melt, and the resulting mass was stirred until a uniform distribution of the plant particles in the polymer melt was attained, the beet bagasse concentration in the polymer melt was 25%.

The indicator threads were manufactured by impregnation of cotton ones by the 0.5 g l^{-1} dye solutions in acetone with subsequent drying in air. The dyes represent bright ones well soluble in crude oil and oil product hydrocarbons and insoluble in water, as well as their metal complexes, namely Sudan II, tetrazolium violet formazan, zinc ditizonate, Sudan black B, naphthyl red and Sudan IV. To make the indicator zones, threads functioning as indicator elements were fixed on BCM-I in parallel rows at a distance of 15–20 mm, this prevented overlapping of the colored zones. The dependence of light absorption on the wavelength for the tested dyes was recorded using an i1Pro portable spectrophotometer (GretagMacbeth, Switzerland) according to the technique described[20] (Figure 2).

The isolation and identification of bacterial strains from the infected TS-1 aviation fuel were performed as described.[21] The immobilization of the cells of hydrocarbon-degrading bacteria and their association on the matrix surface were carried out by the adsorption method.[22]

Then, biodegradation of the model hydrocarbons mixture in model seawater using the synthesized BCM-I was investigated for the 21 day period and an analysis of their residual content was performed. GC–MS data revealed, that by the 21st day the concentration of hydrocarbons in the model mixture had decreased appreciably and no other hydrocarbons were detected in the aqueous medium (for details, see Online Supplementary Materials). The experiments demonstrated, that BCM-I was highly active in reclamation of the model seawater contaminated with hydrocarbons. The residual hydrocarbon content in water on the 21st day did not exceed 20% of their initial concentration (Figure 3).

As well, the indicator properties of BCM-I originated from the effect of dyes dissolution in oil products were explored. In the presence of crude oil or oil products in water, the dissolution of a chromogenic indicator occurred accompanied by its transfer from the thread to the surface of the polymeric substrate. As a result, an intense coloration appeared on the substrate surface. The use of various threads impregnated with the solutions of different indicators, selectively soluble in oil products and insoluble in water, makes it possible to identify the types of hydrocarbons in a single quick test (Table 1). The tests were carried out as the following. A strip of BCM-I with the indicator zone was placed in model seawater (0.5 dm^3) with different amounts of liquid hydrocarbons and oil products (50–200 μl) to simulate the interaction of the biocomposite material with pollutants in a contaminated water. The effect of sea waves was imitated using an orbital shaker with a swing speed up to 150 rpm. The experiment lasted one to seven min. The amount of hydrocarbons in the seawater was estimated from a change in the intensity of coloration of the thread and the underlying substrate after contact with the contaminated aqueous medium (Figure 4). The color characteristics were measured in accordance with the technique developed,[20] the difference in color was evaluated using a 6ΔE criterion.[23,24] It has been found, that zinc ditizonate is the universal reagent for all the gasoline and diesel fuel

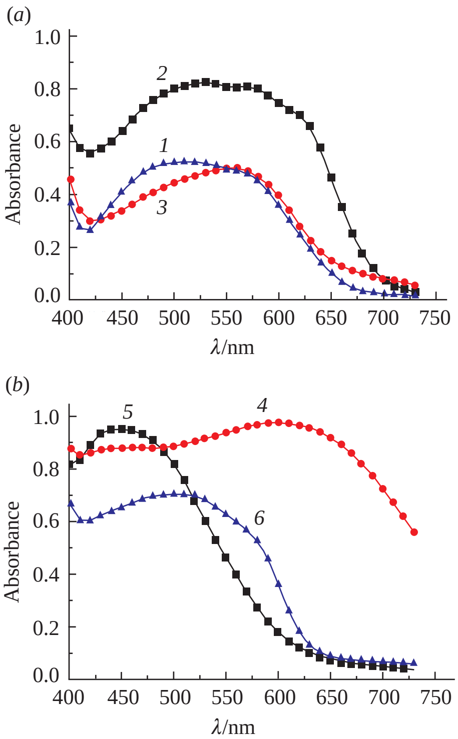


Figure 2 Visible spectra of dyes on the surface of indicator threads: (*a*) (*1*) Sudan II, (*2*) tetrazolium violet formazan and (*3*) zinc ditizonate; (*b*) (*4*) Sudan black B, (*5*) naphthyl red and (*6*) Sudan IV.

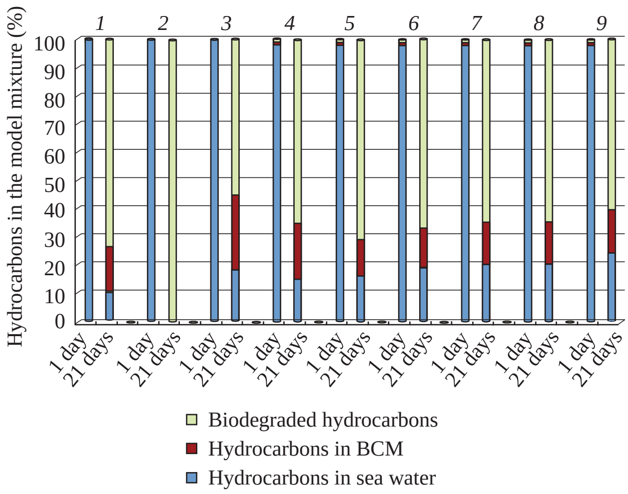


Figure 3 Biodegradation and adsorption of hydrocarbons by BCM-I in the model seawater at 22 ± 3 °C for 21 days: (*1*) isododecane, (*2*) 1,2,4-trimethylbenzene, (*3*) dodecene, (*4*) dodecane, (*5*) 1-tetradecene, (*6*) pentadecane, (*7*) nonylbenzene, (*8*) decylcyclohexane, and (*9*) octadecane.

Table 1 The ability of threads impregnated with indicators to generate an analytical signal in interaction with various hydrocarbons using the solid-phase reagent approach.[a]

Indicator	Benzene, toluene, *o*-xylene, nonyl-benzene, isodecane	1,2,4-Trimethylbenzene	Isopropylbenzene, isooctane	Hexane	Dodecane	Tridecane, pentadecane, hexadecane, dodecene	Decylcyclohexane
Sudan II	+[b]	+	+	–	+	–	+
Tetrazolium violet formazan	+	+	+	+	+	+	+
Zinc ditizonate	+	+	+	+	+	+	+
Sudan black B	+	+	+	–	–	–	–
Naphthyl red	+	–	–	–	+	+	–
Sudan IV	+	–	+	–	+	+	–

[a] For the dye structures, see Online Supplementary Materials. [b] + means analytical signal, – means no analytical signal.

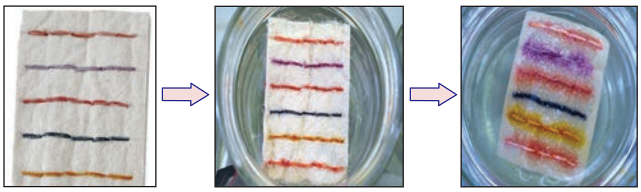


Figure 4 Photos of the BCM-I indicator zone: (*a*) dry material, (*b*) the material soaked in model seawater with 5 ppm diesel hydrocarbons after 1 min exposure and (*c*) the same after 7 min exposure.

samples, while naphthyl red is applicable to all the diesel fuel ones (see Table 1). Other dyes proved to be unsuitable for the determination of diesel fuel and gasoline in water, because their analytical signal did not meet the 6Δ*E* criterion.

According to our results, the indicator threads impregnated with naphthyl red react with some aromatic compounds as well as *n*- and cycloalkanes. The threads with Sudan II are involved in interaction with aromatic compounds and isoalkanes, while the threads containing Sudan IV react with light aromatics, *n*-, iso- and cycloalkanes as well as alkenes. Indicators with Sudan black B interact with all aromatic compounds and isoalkanes, while the threads impregnated with tetrazolium violet formazan and zinc ditizonate react with all the tested hydrocarbons. Note, that zinc ditizonate reveals the most distinct and unambiguous positive effect regardless of the nature of hydrocarbons.

Then, sensitivity of the indicator threads to individual hydrocarbons of different classes as well as their mixtures was examined. For this purpose, microdrops of hydrocarbons and their mixtures (1–20 μl) were applied using a microsyringe to the indicator threads fixed on the fibrous surface. As a result, colored elliptical zones were formed, and their size depended on hydrocarbon content (Figure 5). The 6Δ*E* criterion was applied to estimate the difference between the colored zone and the colored substrate. The geometric characteristics of blurred spots

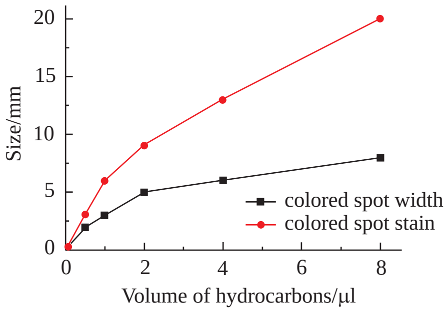


Figure 5 Size of colored zones on the fibrous surface as a function of hydrocarbon amount.

originated mainly from the sorbent–sorbate interaction, these parameters were similar for different oil products.

Our experiments demonstrated the high sensitivity of hydrocarbon detection using the colored zones, that appeared during the transfer of dye from indicator threads into the polymer substrate. The value of analytical signal was at least four to six mm in detection of 0.5 μl amount of hydrocarbons.

Thus, the synthesized BCM-I allows one the following: (i) real-time detection of hydrocarbon contaminants in water; (ii) extraction of hydrocarbon contaminants from water *via* their absorption by a polymer matrix; (iii) biodegradation of hydrocarbons within BCM-I due to hydrocarbon-degrading bacteria associations in its composition; (iv) decontamination procedure with no secondary pollution and no need for the BCM-I disposal; (v) control over the degree of water purification using the indicator zones and (vi) retention of microorganisms on the polymer matrix with no need for their extraction from water after completion of the treatment. Note, that the existing water biotreatment techniques rely on the use of the free-living microorganisms associations, which are not removed from the water areas after the purification. This may result in an uncontrolled propagation of the microorganisms in water and a change in the biocenosis.

The results of this investigation allow us to state, that BCM-I provides an opportunity to combine three functions in one material, namely monitoring of water areas (one stage) as well as adsorption and microbiological treatment of contaminated water (two stages of water decontamination). No doubt this new material will considerably simplify the water area cleaning.

This work was supported by National University of Oil and Gas ‘Gubkin University’ as well as the Ministry of Science and Higher Education of the Russian Federation [State Assignment no. FSZE-2017-0008 (4.6718.2017/6.7, 10.5422.2017/8.9)], the Russian Foundation for Basic Research (project no. 18-29-05067) and the Presidium of the Russian Academy of Sciences (program no. 34 ‘Topical issues pertaining to the physical chemistry of the surface and the creation of new composite materials’). UV-VIS spectral studies were supported by the Russian Science Foundation (project no. 17-13-01468).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.07.042.

References

1 M. Schrope, *Nature*, 2011, **472**, 152.
2 S. E. Chang, J. Stone, K. Demes and M. Piscitelli, *Ecol. Soc.*, 2014, **19**, 26.
3 R. S. Kurtz, *Review of Policy Research*, 2013, **30**, 366.
4 H. R. Walther, III, *Master Thesis*, University of San Francisco, 2014.

5 G. Goodbody-Gringley, D. L. Wetzel, D. Gillon, E. Pulster, A. Miller and K. B. Ritchie, *PLoS One*, 2013, **8**, e45574.
6 S. J. Varjani and N. V. Upasani, *Int. Biodeterior. Biodegrad.*, 2017, **120**, 71.
7 T. Shen, Y. Pi, M. Bao, N. Xu, Y. Li and J. Lu, *Environ. Sci.: Processes Impacts*, 2015, **17**, 2022.
8 Y.-C. Lee, H.-J. Shin, Y. Ahn, M.-C. Shin, M. Lee and J.-W. Yang, *J. Hazard. Mater*., 2010, **183**, 940.
9 X. Zhao, Y. Wang, Z. Ye, A. G. L. Borthwick and J. Ni, *Process Biochem*., 2006, **41**, 1475.
10 C. J. Cunningham, I. B. Ivshina, V. I. Lozinsky, M. S. Kuyukina and J. C. Philp, *Int. Biodeterior. Biodegrad*., 2004, **54**, 167.
11 A. R. Gentili, M. A. Cubitto, M. Ferrero and M. S. Rodriguéz, *Int. Biodeterior. Biodegrad*., 2006, **57**, 222.
12 S. P. Costa, A. L. Angelim, M. d. F. V. de Queiroz Souza and V. M. M. Melo, *Int. Biodeterior. Biodegrad.*, 2014, **87**, 122.
13 K. Tong, Y. Zhang, G. Liu, Z. Ye and P. K. Chu, *Int. Biodeterior. Biodegrad.*, 2013, **84**, 65.
14 A. G. Dedov, E. S. Lobakova, P. B. Kashcheeva, E. A. Ivanova, R. K. Idiatulov, D. A. Sandzhieva, S. G. Vasil'eva, V. M. Bouznik and M. P. Kirpichnikov, *Dokl. Chem.*, 2015, **462**, 160 (*Dokl. Akad. Nauk*, 2015, **462**, 435).
15 I. V. Kumpanenko, A. V. Roshchin and B. V. Myasoedov, *Khimicheskaya Bezopasnost'*, 2017, **1**, 10 (in Russian).
16 R. K. Chernova, L. M. Kozlova, N. B. Shestopalova and Yu. O. Ryanova, *Izvestiya Saratovskogo Universiteta. Seriya: Khimiya, Biologiya, Ekologiya*, 2008, **8**, 15 (in Russian).
17 Yu. A. Zolotov, V. M. Ivanov and V. G. Amelin, *TrAC, Trends Anal. Chem.*, 2002, **21**, 302.
18 A. G. Dedov, E. A. Ivanova, D. Yu. Marchenko, D. A. Sandzhieva and Kh. S. k. Dzhabrailova, *RU Patent 2696982 C1*, 2019.
19 A. G. Dedov, E. E. Belousova, P. B. Kascsheyeva, E. I. Belyaeva, E. O. Omarova, E. C. Lobakova, E. A. Ivanova, R. K. Idiatulov, A. V. Genis and V. M. Buznik, *Theor. Found. Chem. Eng.*, 2014, **48**, 706 (*Khim. Tekhnol.*, 2013, **14**, 606).
20 E. I. Belyaeva, L. V. Zrelova, D. Yu. Marchenko and A. G. Dedov, *Pet. Chem.*, 2015, **55**, 74 (*Neftekhimiya*, 2015, **55**, 78).
21 T. N. Shapiro, G. A. Dolnikova, N. V. Nemtseva, D. A. Sandzhieva and E. S. Lobakova, *Zh. Mikrobiol., Epidemiol. Immunobiol.*, 2018, 107 (in Russian).
22 E. Lobakova, S. Vasilieva, P. Kashcheeva, E. Ivanova, G. Dolnikova, K. Chekanov, R. Idiatulov, M. Kirpichnikov, V. Buznik and A. Dedov, *Int. Biodeterior. Biodegrad.*, 2016, **108**, 99.
23 E. A. Reshetnyak, Yu. V. Kholin and V. N. Schevchenko, *Metody Ob'ekty Khim. Anal.*, 2011, **6**, 188 (in Russian).
24 S. V. Khimchenko and L. P. Eksperiandova, *J. Anal. Chem.*, 2014, **69**, 322 (*Zh. Anal. Khim.*, 2014, **69**, 363).

Received: 5th December 2019; Com. 19/6077