DOI: 10.6060/ivkkt.20236602.6729

УДК: 504.064.2

СТАБИЛИЗАЦИЯ ЭМУЛЬСИЙ «МАСЛО-В-ВОДЕ» ВЫСОКОДИСПЕРСНЫМИ МИНЕРАЛЬНЫМИ ЧАСТИЦАМИ: БИОДЕГРАДАЦИЯ И ТОКСИЧЕСКОЕ ВОЗДЕЙСТВИЕ НА ГИДРОБИОНТЫ

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Для процессов естественного самоочищения водных экосистем от разливов нефти существенное значение имеет наличие в толще воды минерального тонкодисперсного взвешенного вещества, способного к формированию так называемых нефтеминеральных агрегатов с последующей их миграцией в придонные слои и биодеградацией нефтяного загрязнения. В литературе имеется достаточно большое количество публикаций, посвященных условиям образования нефтеминеральных агрегатов и возможности их применения в технологиях ликвидации разливов нефти. Однако влияние нефтеминеральных агрегатов на морские экосистемы и их представителей мало изучено. Отсутствие систематических исследований, направленных на оценку экологического риска влияния нефтеминеральных агрегатов на морские экосистемы и эффективности биодеградации нефти с образованием нефтеминеральных агрегатов, приводит к весьма противоречивым выводам. В данном обзоре предпринята попытка обобщить имеющиеся данные об экологическом риске воздействия нефтеминеральных агрегатов на водные экосистемы и оценке влияния образования нефтеминеральных агрегатов на биодеградацию нефти. Описаны факторы, влияющие на токсичность нефтеминеральных агрегатов для гидробионтов, обитающих в водной толще и донных отложениях и перспективы дальнейших исследований в области их воздействия на окружающую среду с целью более активного использования в технологиях ликвидации разливов нефти. В данном обзоре использовался анализ 70 научных публикаций по ключевым словам «биодеградация» и «токсичность для водной среды» для систем «тонкодисперсное взвешенное вещество – нефтяные капли – морская вода», размещенных в базе данных научной периодики ScienceDirect с 1999 по 2021 гг.

Ключевые слова: дисперсия нефти, тонкодисперсные минеральные частицы, нефтеминеральные агрегаты, токсичность, биодеградация, оценка экологического риска

STABILIZATION OF OIL-IN-WATER EMULSIONS WITH HIGHLY DISPERSED MINERAL PARTICLES: BIODEGRADATION AND TOXIC EFFECT ON AQUATIC ORGANISMS

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For the processes of natural self-purification from oil spills, the presence of suspended solids in the water column is essential to form so called oil-mineral aggregates (OMA) followed by their migration to the bottom layers and subsequent oil biodegradation. The literature contains a sufficient number of publications devoted to OMA formation conditions and feasibility of their application in oil spill response technologies. However, the impact of OMAs on marine ecosystems and their representatives is poorly studied. The lack of systematic studies focused on the estimation of ecological risk of the consequence OMAs entail for marine ecosystems, and the efficiency of oil biodegradation involving OMA formation, leads to quite contradictory conclusions. This review presents an attempt to summarize the available reports on the ecological risk of OMAs for aquatic ecosystems and estimations of the effect of OMA formation on oil biodegradation. Factors that influence the toxicity of OMAs for suspended and benthic aquatic organisms, and the prospects for further research in the field of environmental impact of these structures with a view to use them more actively in oil spill response technologies are described. This review are based on the analysis of scientific publications over a period of 1999 to 2021 by ScienceDirect search tool.

Key words: dispersed oil, fine mineral particles, oil-mineral aggregates, aquatic toxicity, biodegradation, ecological risk assessment

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Для цитирования:
Гречищева Н.Ю., Королев А.М., Заворотный В.Л., Стародубцева К.А., Али М.С. Стабилизация эмульсий «масло-в-воде» высокодисперсными минеральными частицами: биодеградация и токсическое воздействие на гидробионты. *Изв. вузов. Химия и хим. технология*. 2023. Т. 66. Вып. 2. С. 23–35. DOI: 10.6060/ivkkt.20236602.6729.
For citation:
Grechishcheva N.Yu., Korolev A.M., Zavorotny V.L., Starodubtseva K.A., Ali M.S. Stabilization of oil-in-water emulsions with highly dispersed mineral particles: biodegradation and toxic effect on aquatic organisms. *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*]. 2023. V. 66. N 2. P. 23–35. DOI: 10.6060/ivkkt.20236602.6729.

INTRODUCTION

The oil transportation, storage and refining industry has unfavorable effect upon the environment. By the beginning of the 21st century the accidents with tankers and oil-producing platforms have shown that the humanity still cannot prevent the catastrophic impact of petroleum hydrocarbons on Earth's hydrosphere. Earth remote sensing systems have shown that 30% of the world's oceans are covered with an oil slick, and the coastal waters of Russia contain oil hydrocarbons in a concentration of the maximum allowable concentration (MAC) multiplied by a factor of 0.5 to 13 [1].

For the processes of natural self-purification from oil spills, the presence of suspended solids in the water column is essential to form so called oil-mineral aggregates (OMA) followed by their migration to the bottom layers and subsequent oil biodegradation [2]. Inside OMA, oil is incorporated in a network of suspended mineral particles [3], which provides the ability to stabilize the dispersed oil. OMAs formation prolongs and enhances the oil weathering processes such as dissolution, evaporation and biodegradation [4]. At the same time, the biodegradation processes of oil, associated with particles in the form of OMAs prevail over dissolution, evaporation and weathering processes. Thus, the reduction rate of polycyclic aromatic hydrocarbons (PAH) in OMAs due to biodegradation was 36.8%, while due to evaporation, merely 29.7% [5].

In order for OMAs to form, spilled oil is to be dispersed into the water column as small droplets, then the droplets is to interact with and adhere to fine suspended mineral solids [6]. In this case, adsorption of hydrocarbons by mineral particles can occur, along with their binding to cations, polar components of oil and charged surfaces of mineral particles contained in seawater, as well as penetration of small minerals into oil droplets at various depths with the formation of cohesive aggregates [6-8]. The fine particles can be considered as a natural dispersant, the use of which excludes toxic effects on the environment, in contrast to chemical dispersants based on molecular surfactants. The specific feature of the adsorption of colloidal particles at the interface is irreversibility, which significantly distinguishes it from the adsorption with surfactants [9, 10]. Currently, the use of finely dispersed solid particles as stabilizers of oil dispersions is highly relevant from the point of view of the development of environmentally friendly and cost-effective methods to minimize the impact of oil spills, based on natural-cleansing processes, the use of which reduces the risk of secondary contaminations, in contrast to the use of chemical dispersants [6, 11-13]. Thus, oil combined with a chemical dispersant (Corexit 9527 and 9500A) is more toxic than either oil or the dispersant alone due to intense contamination of the water column with toxic low soluble components such as PAH [14-17]. During chemical dispersion, the PAH content in the water column can increase up to 10 times [18-20].

The literature contains a sufficient number of publications on the use of finely dispersed suspended matter for the recovery of oil-contaminated water areas [11, 12, 21-24]. However, the OMA impact on marine ecosystems is poorly studied, as evidenced by the limited number of the relevant reports. In addition, the available data on the effectiveness of degradation and risk assessment are very contradictory and based on laboratory studies only. So, there is evidence that due to negative buoyancy, OMAs can accumulate in sediments, causing negative impacts on the plankton and benthos [25-31]. Such a negative impact may be due to OMA associated contaminants, especially PAH [2]. At the same time, there are some reports that oil bound up inside OMAs may be diluted to below toxicity threshold limits [32] and become more available for biodegradation [33]. In addition, the OMA size (50-250 μm) is comparable to the size of potential food sources for zooplankton, and is an additional factor contributing to the accumulation of OMAs in the food chain [34].

Earlier, we published a review, which described in detail the conditions for the formation of OMAs, methods of stabilizing aqueous oil emulsions with highly dispersed solid particles, factors affecting the efficiency of their formation, and the prospects of using them in oil spill response technologies, in both open water areas and coastal zones [35]. This review attempts to summarize the information in the literature available to date on the environmental risk of OMAs for aquatic ecosystems and to estimate the impact of

OMAs formation on oil biodegradation, based on the analysis of scientific publications over a period of 1999 to 2021 (about 80 selected literatures with the keywords “biodegradation" and "aquatic toxic" for the systems "suspended mineral substances - oil droplets - sea water" by ScienceDirect search tool).

EFFECT OF OMAS ON DISPERSED OIL BIODEGRADATION

There are numerous publications on the impact of OMA formation on biodegradation of dispersed oil [5, 36-50], which indicate that OMA formation clearly facilitates rapid biodegradation of oil compared to other forms of oil. It has been reported [5] that oil biodegradation rate is maximum in OMAs (51.4%) followed by chemically dispersed oil (33.5%), oil film (21.6%), and dissolved oil (14.3%). The authors [41] report enhanced degradation of spilled oil in the presence of mineral particles even at low temperatures. There are two main mechanisms that make this possible [51]. First, due to the fact that oil that is trapped in OMAs is in a form of micrometer-scale droplets, the area of oil-aqueous medium surface increase making the oil more available for biological degradation. Second, OMA-entrained oil is associated with suspended particulates that typically host greater numbers of more metabolically active microbes than the surrounding water.

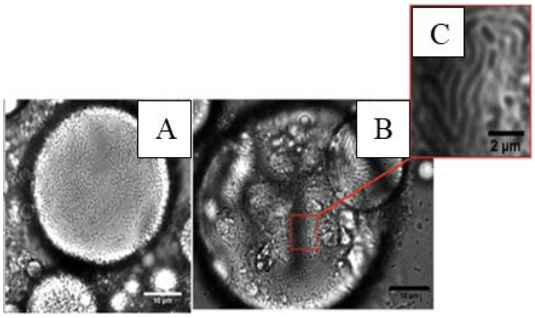

Fig. 1. Growth of a colony of bacteria *A. borkumensis* on the surface of oil droplets: A – a single natural dispersed oil droplet with bacterial cells attached to it formed after 3 days of continuous shaking at 30 °C and 175 rpm; B – dispersed oil formed with 1 wt.% of hydrophobized halloysite. C – enlarged portion of the image demonstrating filamentous growth of bacteria [47]

Рис. 1. Рост колонии бактерий *A. borkumensis* на поверхности масляных капель: A – одиночная капля естественной дисперсии нефти с прикрепленными к ней бактериальными клетками, образовавшимися после трех суток непрерывного встряхивания при 30 °C и 175 об/мин; B – дисперсия нефти с массовым содержанием гидрофобизированного галлуазита 1%; C – увеличенная часть изображения, демонстрирующая нитевидный рост бактерий [47]

Fig. 1 shows tedvisualization of the growth of the colonies of *Alcanivorax borkumensis* bacterium on the surface of naturally dispersed oil droplets (A) and oil emulsion droplets stabilized by the presence of hydrophobized halloysite (B, C) according to [47]. The bacteria were spread and formed a biofilm as they grew between halloysite aggregates (Fig. 1B, C). The biofilm density increased fivefold three days after the start of the experiment: from 0.3 to 1.5 number of cells/μm^2.

At the same time, after three days of the experiment (Fig. 2), no similar increase in A. *borkumensis* colony count was observed on oil droplets of chemically dispersed oil.

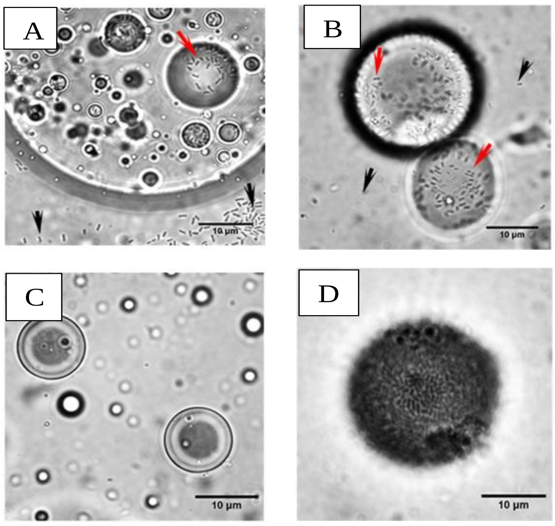

Fig. 2. Optical microscopy images of crude oil emulsions formed with 1 wt.% of dispersant blend (A, C) and presence 1% (wt.) of hydrophobized halloysite (B, D): A, B – through 1 day after inoculation of *A. borkumensis*; C, D – through 3 days after inoculation of *A. borkumensis* [47]

Рис. 2. Оптическая микроскопия изображений эмульсий сырой нефти, образованных в присутствии смеси диспергаторов с массовым содержанием 1% (A, C) и присутствии гидрофобизированного галлуазита с массовым содержанием 1% (B, D): A, B – через один день после инокуляции *A. borkumensis*; C, D – через три дня день после инокуляции *A. borkumensis* [47]

The authors [49, 50] provided evidence of an increase in microbiological activity and a corresponding increase in the rate of oil biodegradation in OMA structures. The results of model experiments showed a decrease in the content of n-alkanes after 56 days down to 25% in mineral/oil flasks compared with the controls, where the concentration of total n-alkanes reduced down to mere 48%. At the same time, a significant growth of oil-oxidizing and heterotrophic microorganisms was observed: more than 7 times after the first 7 days of the experiment. For aromatics, the corresponding values were 8% and 25%. A significant decrease in the content of *n*-alkanes and aromatic fraction of oil contamination of rocky beaches located in the surf zone was also linked by the authors [36, 40, 42] to an increase in the rate of biodegradation of OMA-associated oil.

Recently, the prospects of the co-presence of dispersants and mineral fines in the purification of oil-contaminated water areas were reported. In most cases, this contributed to both formation of more stable oil emulsions in water and acceleration of the natural dispersion of oil (including high-viscosity) due to OMA formation and minimizing the amount of dispersants to eliminate spills [35, 52]. At the same time, data on the effect of dispersants on the rate of biodegradation of oil in the presence of mineral particles are quite contradictory. The authors [44] observed an increase in the biodegradation rate of oil in a system with mineral fines in the presence of both chemical and the rhamnolipid bio-dispersants. Both dispersants had a positive effect on some PAH and their alkylated homologues, resulting in 8%-23% and 25%-42% reduction, respectively. When analyzing field samples of the Deepwater Horizon oil spill, the authors [45] observed a similar reduction in levels of particulate-bound PAHs and alkanes in surface waters. However, other authors [48], who analyzed the consequences of the Deepwater Horizon oil spill, observed an increase in the contents of a number of some aromatic hydrocarbons (benzene, toluene, ethylbenzene and *o*-, *m*-, and *p*-xylene) up to the toxic levels in the presence of both clay particles alone and Corexit, which caused a delay in oil biodegradation. At the same time, kaolin clay and Corexit had a synergistic effect in increasing aromatic concentrations in the water. Opposite results of the effect of dispersants on the rate of oil biodegradation in the presence of mineral particles are evidently due to both different nature of the dispersants and mineral particles used, and different properties of the oil. It is worth noting that the co-presence of dispersants in the system facilitated the formation of negative buoyancy OMAs due to the elevated density. As mentioned above, this fact can lead to an increase in the accumulation of OMAs in bottom sediments and cause a negative impact on the plankton and benthos. Thus, according to [53] total petroleum hydrocarbons in the sediment phase increased from 6.9% to 90.1% in the presence of Corexit EC9527A, and PAHs increased from 11.4% to 86.7%.

The authors [54, 43] reported an acceleration of the biodegradation processes of oil dispersed through OMA formation after adding nutrients (NH_4Cl, $NaNO_3$, and KH_2PO_4). However, the introduction of nutrients less contributed to stimulating the activity of microbial flora than the level of dispersion of the suspended matter [54-56]. Furthermore, adding nutrients promoted formation of negative buoyancy OMAs in the same way as the introduction of dispersants.

TOXICITY OF OMAS TO AQUATIC ORGANISMS

Analysis of literature data for a period of 2000 to 2021 revealed a limited number of publications assessing the toxic effects of OMAs on marine ecosystems. In total, the authors reported that, in addition to increasing the availability of oil to microorganisms, OMA formation could also reduce the oil bioavailability and toxicity to aquatic organisms in the affected environment [2]. At the same time, environmental risks of the oil dispersed by OMAs are mainly estimated for benthic organisms, which are considered to be more susceptible to the adverse effects. It was shown [57] that the highest risk of toxicity had areas where up to 34.10% of the oil was potentially trapped in OMAs, offering a risk of up to 27.20% of the oil dispersed to benthic organisms, and up to 3.60% for the organisms inhabiting the water column.

When assessing the risks of OMAs to the benthic organisms, various mathematical models were used that taken into account the factors affecting the parameters of OMA-spill transfer process, sediment properties, oil type, water depth, and the hydrodynamics. As a rule, the risks from the various scenarios studied were generally low and not persistent [27]. However, existing modeling approaches do not take into account the whole variety of possible factors affecting fates for OMAs in the water column and, therefore, do not allow to assess their potential risks to marine ecosystems with high accuracy [26, 27]. An important ecological consideration is closely linked to the turbulent energy of the environment with more risk associated with submerged OMAs in depositional or low energy marine environments.

Thus, the authors [26, 27] used a hydrodynamic model that takes into account the wave activity and the intensity of sea currents to assess the risks related to OMAs. The potential risk of settled oil on benthic organisms was assessed in terms of Hazard Quotient (HQ) (as the ratio of a contaminant’s environmental concentration to a screening value selected for risk assessment of that substance). If HQ is greater than 1.0, harmful effects can be expected; if HQ is less than 1.0, harmful effects are unlikely to occur. It can be seen from these studies that the risk of OMAs on benthic organisms occurs only for the case with very weak current (0.16 m/s) without wave activity at the end of 9 days. Thus, the risks of OMAs may increase in an environment with very weak currents. However, the modeling approach used did not include such an important process as biodegradation, and therefore the researchers’ conclusions might not be entirely correct. The development of an improved model [26], taking into account the biodegradation of OMA-associated oil in the water column and sediment, showed that the risks of OMAs in terms of the impacted area decreased significantly.

The sources note that such models should take into account the oxygen depletion process, which leads to a slowdown in oil degradation in sediment. Failing to include the processes may cause underestimation of oil content in sediment more than threefold. Thus, the calculated amount of oil remaining in sediment, with only taking into account the biodegradation of OMA-trapped oil in the water column was 28%, while it was 88.8% with considering the oxygen depletion process as well.

Table 1

Correlation coefficients between acute sediment toxicity test results and analytical variables using *Chironomus dilutus.* Highlighted cells indicate a statistically significant correlation at $\alpha = 0.05$ [2]

***Таблица 1.* Коэффициенты корреляции между результатами испытаний на острую токсичность отложений и аналитическими переменными с использованием *Chironomus dilutus*. Выделенные ячейки указывают на статистически значимую корреляцию при $\alpha = 0,05$ [2]**

Variables	*Chironomus dilutus*		
	Survival	Growth	Biomass
Sum LMW-PAH (μg/kg)*	-0.53	-0.47	-0.51
Sum HMW-PAH (μg/kg)*	-0.45	-0.36	-0.40
Total PAH (μg/kg)	-0.49	-0.43	-0.47
TEH (mg/kg)**	-0.52	-0.53	-0.54
% Total organic carbon	-0.67	-0.35	-0.42
% Gravel	-0.08	0.02	0.03
% Sand	-0.56	0.40	0.41
% Silt	-0.54	-0.52	-0.52
% Clay	-0.53	-0.21	-0.25

Notes: *Low molecular weight (LMW) PAHs include Naphthalene to Benzo(b)fluorine (38 analytes), whereas high molecular weight (HMW) PAHs include Fluoranthene to Benzo[g,h,i]perylene (26 analytes). ** Total extractable hydrocarbons (TEH)

Примечания: *ПАУ с низкой молекулярной массой (НММ) включают от нафталина до бензо(b)флуорантена (38 веществ), тогда как ПАУ с высокой молекулярной массой (ВММ) включают от флуорантена до бензо[g,h,i]перилена (26 веществ). ** Всего углеводородов (УВ)

Risks from individual hydrocarbon groups and combined hydrocarbons in the settled OMAs were evaluated by authors [2, 26, 27], which showed that the toxicity of OMAs (in terms of HQ) on benthic organisms was mainly due to the presence of aromatic hydrocarbons. For aromatic hydrocarbons, the highest HQ of 0.86 is from the alkyl PAHs [26]. At the same time, no toxic effects were observed from individual hydrocarbon groups. The HQs from the two lower molecular weight hydrocarbon groups (C6-C8 and C9-C12) and the two higher molecular weight parent PAH groups were all smaller than 1.0.

The relationship between the PAH content in OMAs accumulated by bottom sediments and the vital activity of benthic organisms is shown in Table 1-2 [2].

Table 2

Correlation coefficients between acute sediment toxicity test results and analytical variables using *Hyalella Azteca.* Highlighted cells indicate a statistically significant correlation at $\alpha = 0.05$ [2]

***Таблица 2.* Коэффициенты корреляции между результатами испытаний на острую токсичность отложений и аналитическими переменными с использованием *Hyalella Azteca*. Выделенные ячейки указывают на статистически значимую корреляцию при $\alpha = 0,05$ [2]**

Variables	*Hyalella Azteca*		
	Survival	Growth	Biomass
Sum LMW-PAH (μg/kg)*	-0.44	-0.18	-0.17
Sum HMW-PAH (μg/kg)*	-0.36	-0.20	-0.17
Total PAH (μg/kg)	-0.39	-0.22	-0.21
TEH (mg/kg)**	-0.47	-0.29	-0.39
% Total organic carbon	0.04	-0.65	-0.65
% Gravel	0.01	0.07	0.18
% Sand	0.23	0.41	-0.54
% Silt	-0.36	-0.44	-0.55
% Clay	-0.13	-0.41	-0.53

Notes: *Low molecular weight (LMW) PAHs include Naphthalene to Benzo(b)fluorine (38 analytes), whereas high molecular weight (HMW) PAHs include Fluoranthene to Benzo[g,h,i]perylene (26 analytes). ** Total extractable hydrocarbons (TEH)

Примечания: *ПАУ с низкой молекулярной массой (НММ) включают от нафталина до бензо(b)флуорантена (38 веществ), тогда как ПАУ с высокой молекулярной массой (ВММ) включают от флуорантена до бензо[g,h,i]перилена (26 веществ). ** Всего углеводородов (УВ)

Negative correlation coefficients indicate that survival, growth, and biomass reduced in sediment with growing concentrations of low molecular weight PAHs and TEHs. Increases in sand, silt and clay, which act as accumulators of OMAs settled, can also increase the toxicity of OMAs for benthic life.

The paper [26] reported a dependence of risk to the benthos from aromatic hydrocarbons on physical properties of sediments. Thus, in the presence of OMAs formed with sediments, characterized by the presence of coarsely dispersed fractions, with a size of greater than 400 μm, a density of 2510 to 2570 kg/m^3, and an organic matter content of 6.8% to 7.0%, the risk from aromatic hydrocarbons increased by a factor of 7 to 8 compared to aliphatic hydrocarbons. In total, OMAs formed with sediments having the above properties showed greater potential toxicity to benthic organisms compared to OMAs formed with fine particles less than 200 µm in size, with a density of 2410 to 2730 kg/m^3 and an organic matter content of 10.5% to 10.7%. At the same time, the presence of a chemical dispersant increased by 132% the risks to benthic organisms from OMAs formed with coarse sediments and decreased by 6.3% the risks from OMAs consisting of finely dispersed particles of a higher density. The corresponding HQ were 3.58 and 1.54 for coarse sediments with and without chemical dispersant, respectively, and 0.66 и 0.71 for sediments formed by finely dispersed particles. Apparently, the dependence of the toxic effect of OMAs on the physical properties of sediments is caused by a difference in particle size distribution and sedimentation rates, which affect the nature of the transfer of oil to OMAs.

The sediment type can also be a contributing factor to the toxicity of OMAs. It is a known fact that surface modification of nanoparticles may increase or decrease the cytotoxic effect of the particles [58, 59]. Thus, pristine halloysite in oil-clay nanotube emulsions slowed down the growth rate of bacteria *Alcanivorax borkumensis* as compared to the control. There was no significant difference in the culture growth rates in the presence of hydrophobized halloysite [47]. However, microtoxicity test of the water phase after oil-sediment interactions demonstrated that sediment type did not affect significantly the aqueous toxicity. The toxicity changed depending on the oil type and was maximum for samples with relatively high levels of light toxic components dissolved in the water phase [60, 61].

It should be noted that, as a rule, all experiments to assess the toxicity of OMAs were performed in the laboratory conditions. In this regard, the findings cannot fully reflect the processes occurring in real water conditions. However, such factors as sediment characteristics, oil composition, water depth, biodegradation rate and hydrodynamic conditions are significant in assessing the potential risk of OMAs to benthic organisms. At the same time, the amount of oil due to sediment affects the potential risks of OMAs on benthic organisms to a lesser extent than the above factors [27].

The introduction of OMAs to living organisms may occur through ingestion, microbial activity, food web transfer, transdermal exposure, and/or bioaccumulation [62]. It is believed that accumulating inside living organisms and their metabolic products, OMAs can have toxic effects [63]. The degree of impact will be proportional to the order of the trophic level a living organism occupies. Thus, when analyzing the consequences of the Deepwater Horizon oil spill, it was shown that, due to trophic transfer, OMAs actively accumulated along the chain: surface plankton - shrimps - fish living at a depth of over 600 m [63-65]. This led to lesions of scales in 9% of bottom fish and bivalves. This pathology was most clearly reflected in pelagic, tile fish and hake [64, 65]. Up to 70% of OMAs migrating from the water surface to the bottom areas can have direct toxic effects on zooplankton [30].

According to [66], residual OMAs in coastal areas had toxic effects on coastal birds and sea turtle eggs. However, there are currently no direct studies of this effect. There is evidence of neurotoxic effects of OMAs on human body [67, 68]. An analysis of the consequences of the Deepwater Horizon oil spill showed that an increased concentration of OMAs was likely to lead to the formation of reactive oxygen species, causing disruption of the integrity and permeability of cell membranes, as well as promoting the transformation of DNA molecules produced by the cell nucleus [69]. OMAs can also pose a threat to epithelial cells, kidneys and neurons [70]. It should be noted that in the above-mentioned works, the impact of chemicals trapped from tarmats, also known as submerged residual oil mats (SRMs) were studied. SRMs can approximately be a special case of OMAs. It can be assumed that since oil as part of OMAs is subjected to continuous weathering processes like dissolution and biodegradation, only highly weathered and persistent oil fractions may end up on the seabed [38]. Heavy metals nickel and chromium were found in OMA samples collected in coastal areas with a content of about 4,8% to 8,5%. However, ingestion of these metals by the oral route into the body of marine animals is not believed to have a significant toxic effect, due to their low absorption in the gastrointestinal tract of organisms [71].

CONCLUSION

Thus, we analyzed scientific publications for a period of 1999 to 2021 to study the impact of OMAs on the biodegradation of dispersed oil and on the assessment of their potential negative effect on marine ecosystems. The published data unambiguously indicate an enhancement in biodegradation of oil associated with mineral particles in the form of OMAs compared to non-dispersed oil. At the same time, there is no unambiguous opinion on the demonstration of toxicity of OMAs to aquatic organisms in the current literature. Apparently, this is due to, firstly, the abundance of different factors affecting fates for OMAs in the water column and, therefore, hindering to assess with high accuracy their potential risks to marine ecosystems, and secondly, the fact that most studies were carried out on model systems that did not reflect the real water conditions. Nonetheless, the following conclusions can be drawn on the base of the published reports.

Because of the fact that oil associated with OMAs may be diluted to below toxicity threshold limits, the process of OMA formation could reduce the oil toxicity to aquatic organisms in the affected environment.

The oil is incorporated inside OMAs in a network of suspended mineral particles, thus reducing the ecological risks of the oil to aquatic organisms.

The major factor causing the negative impact of OMAs on representatives of marine ecosystems is the high capacity for biological accumulation. The degree of exposure in this case will be proportional to the order of the trophic level of living organisms.

The risk from OMAs for suspended and benthic aquatic organisms is largely determined by the high concentrations of PAHs capable to exert toxic effects on the inhabitants of marine ecosystems after accumulating in their bodies. Nevertheless, the question of the extent of the spread of this effect to the representatives of various types of marine life is open now, since the analyzed sources are characterized by an extremely narrow sample of research objects.

The environmental risks of the oil dispersed by OMAs are mainly assessed for benthic organisms, which are considered to be more susceptible to the adverse effects due to the negative buoyancy OMAs.

When assessing the risks of OMAs to benthic organisms, mathematical models are used taking into account such factors as spill amount, sediment properties, oil type, water depth, hydrodynamics, and the rate of oil biodegradation. As a rule, the risks from the various scenarios studied were generally low and not persistent. In total, the use of mathematical models allows us to draw the following conclusions:

- the settable amount of oil by sediment has less influence on the potential risks of OMAs on benthic organizations than sediment properties, oil type, water depth, hydrodynamics and other factors;
- the risks of OMAs may increase in an environment with very weak currents;
- OMAs formed with sediments characterized by the presence of coarse particles showed greater potential toxicity to benthic organisms compared to OMAs formed with fine particles;
- sediment type did not affect significantly the aqueous toxicity. The toxicity changed depending on the oil type and was maximal for samples with relatively high levels of light toxic components dissolved in the water phase;
- the presence of chemical dispersant increased the potential risks from OMAs to benthic organizations formed with coarse sediments and reduced the risk by for OMAs formed with sediments formed by fine particles;
- an increase in the content of sand, silt and clay acting as accumulators of deposited OMAs may cause an increase in the toxic effects of OMAs on benthic organizations.

However, to establish a more detailed picture, it is necessary to conduct additional studies based on mathematical modeling, taking into account a wider range of relevant factors.

It is the method of mathematical modeling that is preferred in the literature when conducting research on quantitative assessment of the risk arising from the sedimentation of OMAs in various water areas with an acceptable level of accuracy. As mentioned above, the models developed and tested currently do not allow making a complete account of all available factors and, accordingly, minimizing the error of the results obtained. Today developing and building models with higher variability is the task of prime importance for the estimation of the environmental risk of OMAs. Optimization of the chemical properties of OMAs to minimize their environmental impact is another important challenge. The answer to the questions about the safe application of OMAs will directly affect their further use in oil spill response and other prospects.

DECLARATIONS

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

The authors declare the absence a conflict of interest warranting disclosure in this article.

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Поступила в редакцию (Received) 19.09.2022
Принята к опубликованию (Accepted) 15.11.2022