Chapter 10

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Ecologically important properties of bio-oils

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ABSTRACT

Environmental monitoring was carried out in the Caspian Sea's Oil Rocks and 28 May areas. First, the composition of crude oil taken from these regions was determined based on gas chromatography. Then, 15 polycyclic aromatic hydrocarbons and representatives of 11 phenolic organic compounds were analyzed based on mass spectroscopy in seawater. The physico-chemical properties of sea waters were also studied. As the examined seawater samples were exposed to petrogenic pollution, many PAHs and phenolic organic compounds exceeded the permissible concentration limit. Later, in laboratory conditions, the crude oil taken from these two areas was used for the absorption of bio-oils of natural origin to purify drinking and seawater, and it was determined that, oil sorption occurs effectively when the process is carried out in an organic solvent (hexane or heptane). The sorption process was investigated with different oils of natural origin and oil collection on seawater and drinking water for three hours at room temperature was better with soybean and castor oils.

Keywords: Oil Fields; Bio-Oil; Sorption; Hexane; Heptane.

INTRODUCTION

It is known that recently, as a result of anthropogenic effects on the biosphere, as well as due to the effect of the greenhouse effect, the Earth's atmosphere, hydrosphere and lithosphere are being polluted with various types of toxicants.[1,2,3] From this point of view, it is important to conduct new research methods and modern analyzes in order to find solutions to the ecological crisis and ecological complications.[4,5,6,7,8]

According to the researchers, if the ecological imbalance is not prevented, the temperature of the Earth's crust is expected to increase by 40C in the last century, which will lead to ecological disasters.[9,10,11,12] It is important to maintain the temperature of the ground at a maximum of 1,50C. It is known that the main factors influencing the creation of the greenhouse effect are the increase of industrial enterprises, various anthropogenic effects, as well as the environmental damage caused by automobile transport.[13,14,15,16] The main components of gases that cause the greenhouse effect are carbon dioxide, methane, freons, nitrous oxide, and ozone and traces of water to a lesser extent [17-19]. In an era of nanotechnology development, the growth of industrial and chemical enterprises, as well as the negative impact of conventional fuel-powered automobiles on the environment, are driving the deepening of the environmental threat that will be considered global.[20,21,22,23] This eventually leads to global pollution of the

atmosphere, lithosphere and hydrosphere, which interact with each other.[24]

Currently, the problem of pollution of the world ocean and water shortage is one of the main environmental problems.[25,26,27,28] Due to global pollution, the problem of droughts, depletion of fresh water resources, mixing of wastewater with other water resources and polluting them is currently relevant. These problems are also relevant in our country.[29] So, since the extraction of oil from the Caspian Sea and its transportation to different countries is carried out by land, as well as by waterways, various injuries are caused to the hydrosphere layer.[30,31,32,33] In this case, the protection of the hydrosphere layer is currently considered as an urgent environmental issue of the day, and it is important to investigate efficient ways to implement water treatment.[34,35,36,37]

It is known that various natural and synthetic sorbents are used in chemical cleaning. The sorption method is a classic method, and it is widely used in cleaning the oil layer accumulated on the water.[38]

From this point of view, experiments were carried out in laboratory conditions for the effective collection of oil collected on the water surface with oils of natural origin in hexane or heptane environment.

Experimental part

Chemical analysis of the crude oil taken from the two areas examined by us was carried out. Based on the results of gas chromatography analysis, it was conducted to determine which organic hydrocarbons the composition of crude oil consists of (figure 1 and figure 2).

Table 1. Analysis of crude oil taken from two points of Oil Rocks

	Oil Rocks (point I)		**Oil Rocks (point II)**	
Alkanes	***Area***	***Ratio %***	***Area***	***Ratio %***
nC 10	28518	1,02	27851	0,99
nC 11	27630	0,99	27647	0,98
nC 12	28438	1,02	28369	1,00
nC 13	27575	0,99	26380	0,93
nC 14	21991	0,79	21159	0,75
nC 15	17601	0,63	12477	0,44
nC 16	6091	0,22	5972	0,21
nC 17	5078	0,18	5190	0,18
Pristane	19617	0,70	18677	0,66
nC 18	2705	0,10	2673	0,09
Butane	15656	0,56	15243	0,54
Total amount of hydrocarbons	2799090	100	2826610	100
Area ratio of isoprenoid hydrocarbons				
17/pristane	0,259		0,278	
18/butane	0,173		0,175	
Pr/B	1,253		1,225	

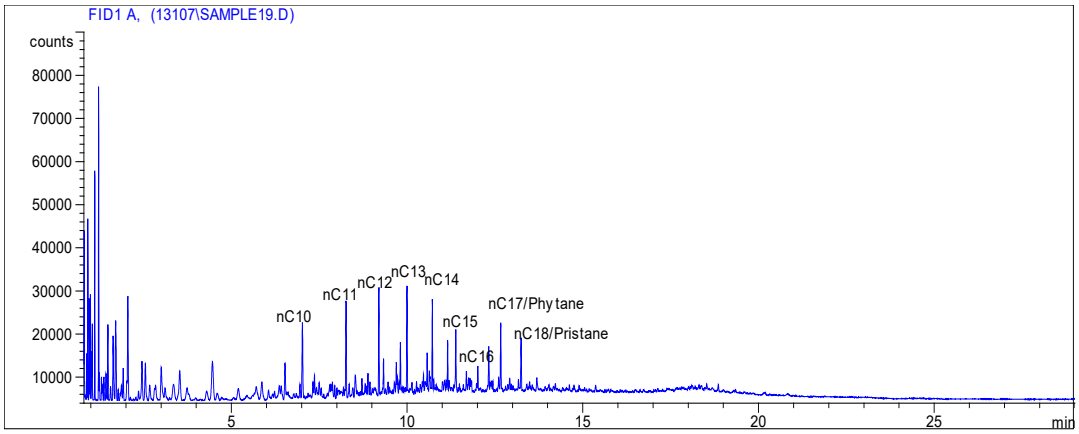

Figure 1. General view of the chromatogram of crude oil taken from Oil Rocks (point I)

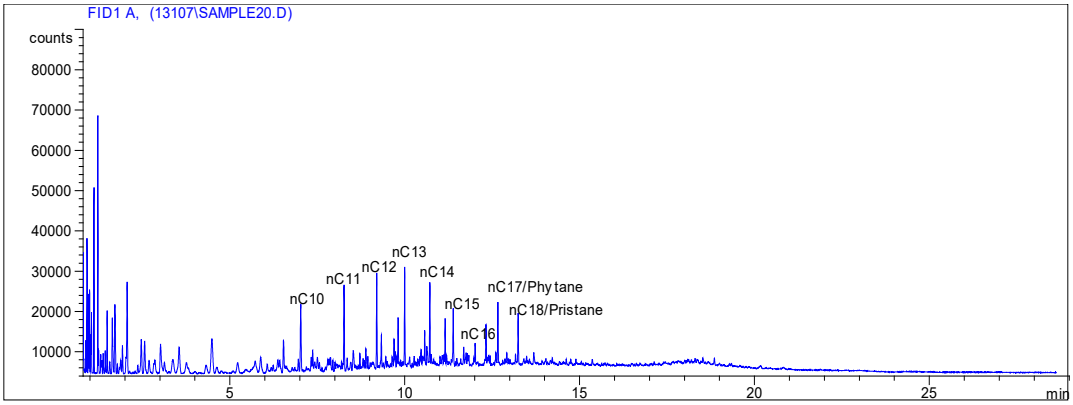

Figure 2. General view of the chromatogram of crude oil taken from Oil Rocks (point II)

Table 2. Composition of crude oils taken from 28 May area

Substances	**28 May oil**	
Alkanes	***Area***	***Ratio %***
nC 10	50149	0,92
nC 11	48948	0,90
nC 12	51185	0,94
nC 13	49362	0,91
nC 14	40799	0,75
nC 15	32639	0,60
nC 16	10899	0,20
nC 17	5133	0,09
Pristane	33157	0,61
nC 18	3848	0,07
Butane	31326	0,58
Total amount of hydrocarbons	5430940	100
17/pristane(Pr)	0,259	0,155
18/butane(B)	0,173	0,123
Pr/B	1,253	1,058

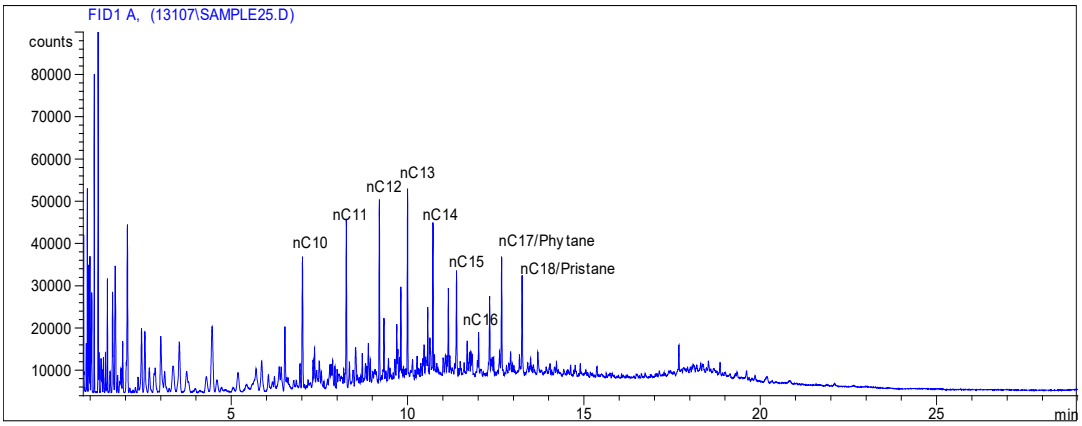

Figure 3. General view of the chromatogram of crude oil taken from 28 May area

Sunflower, olive, castor and soybean oils were used as natural absorbents of biological origin. Based on the comparative analysis of all four containers, it can be said that the property of these substances to collect oil on water occurs only with the presence of hexane (heptane) in that medium. The petri dishes were monitored for several days. Vegetable oils of different origins were taken and compared in the experiments. Better results were obtained with soybean and castor oils in vessels II and IV (table 1). At this time, only 20-30 % of the total area of the vessel remained untreated. Thus, the ability of these natural oils to collect oil was 60-70 %. The diameter of the oil spheres obtained on the water layer and the thickness of the oil layer were measured, and based on this, a graph of dependence between oil collection was constructed depending on time. Then, in laboratory conditions, four petri dishes were separated, 40-50 ml of drinking water was added to two of them (I, II) and sea water was added to the other two (III, IV). Then 0,4-0,6 ml, about 2-3 drops of crude oil taken from two regions of Azerbaijan with oil field (28 May and Oil Rocks) are added to the water in each container, and the solutions remain in a calm state for 1 day. After 1 day, after the oil has completely spread over the water layer, 2,5 ml of hexane (or heptane) was added to the containers with drinking and sea water (I, III), and 2,5 ml to the other containers with drinking water and sea water (II, IV). 5 ml of 50 % solution of oil in hexane is added and kept for some time (2-3 days).

Discussion and interpretation of results

Chemical analysis of crude oils was carried out before experiments. Oil was taken from two regions of Azerbaijan (Oil Rocks and 28 May oil) and its chemical composition was determined. The composition of Azerbaijani oil is mainly rich in paraffins and naphthene, and the amount of sulfur is low. This is one of the unique features of our oil. As the number of higher hydrocarbons in the oil increases, so does its absorption. Table 3 below shows the chemical parameters of crude oils taken from the oil fields of Azerbaijan.

Table 3. Some chemical properties of oils taken from the regions of Azerbaijan

Type of crude oil	Chlorine salts (mg/l)	Sulphur (%)	Paraffin (%)
Oil Rocks	39,2	0,21	1,65
28 May	31,7	0,27	1,27

After that, sea water samples were taken from the examined areas and polycyclic aromatic hydrocarbons and phenolic organic compounds were determined in them (table 4 and table 5).

Table 4. PAH content in seawater sampled from two regions of the Caspian Sea

PAH (mcg/l)	28 May	Oil Rocks
Naphthalene	0,07	0,12
Accented	0,03	0,05
Acenaphthene	0,04	0,04
Fluorene	0,24	0,03
Phenanthrene	0,29	0,05
Anthracene	0,04	0,05
Fluoranthene	0,03	0,02
Pyrene	0,05	0,02
Benz (a) anthracene	0,01	0,01
Khrezen	0,02	0,02
Benz (b + j + k) fluoranthene	<0,01	0,02
Benz (a) pyrene	<0,01	0,02
Indene (1,2,3-cd)pyrene	<0,01	<0,01
Benz perylene	<0,01	0,01
Diphenanthrene	0,02	0,02

Table 5. Amount of phenolic organic compounds in seawater sampled from two regions of the Caspian Sea

Phenol (mcg/l)	28 May	Oil Rocks
phenol	0,13	0,16
o-cresol	0,04	0,45
2-nitrophenol	0,10	0,13
2,4-dimethylphenol	0,11	0,13
2,4-dichlorophenol	0,03	0,04
2,6-dichlorophenol	0,07	0,08
4-chloro-3-methylphenol	0,14	0,08
2,4,5-TCP	0,07	0,10
2,4,6-TCP	0,07	0,10
2,3,4,6-tetrachlorophenol	0,10	0,12
pentachlorophenol	0,12	0,16

The reviewed chemical analyzes were carried out at the Caspian Ecological Laboratory based on mass spectroscopy equipped with Agilent series gas chromatography.

The physico-chemical properties of seawater taken from the areas considered in table 6 below were also investigated.

Table 6. Some physicochemical characteristics of seawater samples

Areas	Tem. °C	pH	salinity, %	Electrical conductivity, mS/cm
28 May	26,3	8,2	11,0	18,7
Oil Rocks	25,9	7,9	10,5	17,7

After the ecological monitoring of sea waters taken from two regions of the Caspian Sea, oil sorption from these sea waters was examined in laboratory conditions. The concept of rapid accumulation was used to determine the collecting (dispersing) property of oils of biological

origin. The rapid collection constant (K) is based on the faster action of the reagent and its ability to collect oil more quickly. K is equal to the ratio of the total area of the container (S_1) to the area of the oil circle (S) collected after the reaction of the reagent: $K=S_1/S$

The more effective the reagent, the smaller the numerical value of S and the larger the numerical value of K. Here, the total area of the vessel is S_1, and the area of the oil spheres spread over the water layer is denoted by S. As the thickness (h) of the oil layer in the Petri dish increases, the ability of oil to accumulate (disperse) on the water surface decreases. The thickness of the oil layer was calculated according to the following formula: h=V/S

Here, h-thickness of oil layer (cm); V-volume of added oil (ml); S is the area of the oil sphere (cm^2).

However, the best results were obtained with soybean and castor oils. Thus, in the presence of hexane (heptane), almost complete accumulation of oil on sea and drinking water was observed. At this time, the obtained oil balls were completely collected on the water surface (table 7).

Table 7. Main indicators of absorption of oil from sea water and drinking water by bio-oils

Castor oil	Drink. Water ml	40	50
	h, ml	0,014	0,013
	S, sm^2	34,2	37,4
	K	3	2
Castor oil	Seawater, ml	40	50
	h, ml	0,016	0,013
	S, sm^2	31,25	38,46
	K	2,5	2,1
Soybean oil	Drink water, ml	40	50
	h, ml	0,02	0,02
	S , sm2	26,3	29,4
	K	2,4	3,7
Soybean oil	seawater	40	50
	h, ml	0,01	0,01
	S, sm2	27,2	27,7
	K	2,2	2,5

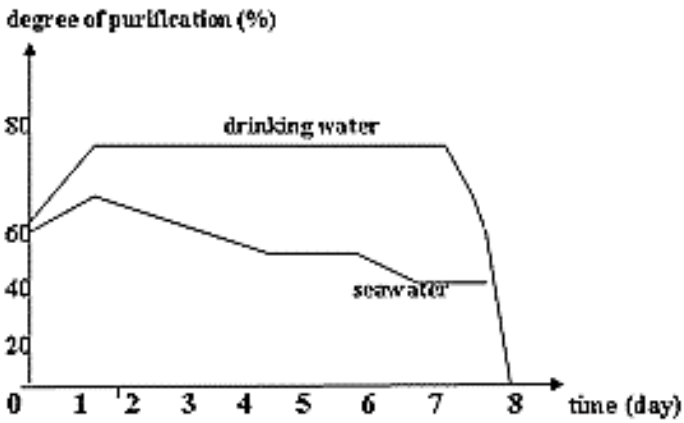

Figure 4. Time dependence of oil absorption

After studying the absorption of both oil samples (Oil Rocks and 28 May) with oils of natural origin in laboratory conditions, it was found that the absorption of both crude oils occurs differently in drinking water and sea water (table 2). Thus, absorption in sea water occurs in different ways at different time intervals, which can be explained by its multi-component composition. As can be seen from Table 2, the value of the aggregation constant (K) is smaller in seawater than in drinking water. This is explained by the fact that the reagent has a more effective effect in drinking water. Thus, as the numerical value of K increases, oil globules have a smaller area, in other words, effective collection occurs (figure 4).

CONCLUSION

Thus, environmental monitoring was conducted in the areas of Oil Rocks and 28 May, and representatives of 15 polycyclic aromatic hydrocarbons and 11 phenolic organic compounds were analyzed based on mass spectroscopy in seawater. The physico-chemical properties of sea waters were also studied. Many of the PAHs and phenolic organic compounds exceeded the permissible concentration limit as the examined seawater samples were exposed to petrogenic pollution. Later, in laboratory conditions, the crude oil taken from these two areas was used for the sorption of bio-oils of natural origin to purify drinking and sea water, and it was determined that the accumulation of oil on sea water and drinking water in hexane or heptane environment, at room temperature for three hours, soybean and castor bean performed better with oils.

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None.

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