International Journal of Innovations in Engineering and Technology (IJIET)
http://dx.doi.org/10.21172/ijiet.182.03

Mathematical Modeling of Polimeric Sorbents Adsortion

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Abstract- Oil pollution (crude oil and petroleum products) of water is an undesirable phenomenon, but it occurs due to deficiencies in its transport and in the exploitation of offshore deposits. This paper analyzes polymeric sorbents and their sorption equations. In first part I presenting evolution of sorbent materials and application of this sorbents. A special analysis is dedicated to analised absortions of crude oil mixed to sea water by polyethylene and polypropylene. Conclusion of this paper is dedicated to analysis of polymeric sorbents. The marine pollution states that 35% of oil spills come from shipping and 45% are due to spills from surface waters (marine tributaries), from water from drilling operations and especially from atmospheric precipitation. Also, the counting of the number of pollutions depending on the marine transport, shows us that their number has decreased, due to the high penalties and especially the integrated control of the world environment (pollutant control). Over the years, studies of the restoration of the marine environment have focused on reducing the effects of pollution and analyzing the effects of pollutants on the marine environment.

Keywords –Oil Pollution, Polimeric Sorbents, Mathematical Modeling, Environment.

I. INTRODUCTION

Oil pollution reduces the possibilities of using the marine environment as a health factor and seawater as a mineral raw material, prevents fishing and navigation, creates the possibility of fires, destroys vegetation and infests coastal beaches [1,2,3].
Oil pollution has a detrimental influence on the flora and fauna of water basins. It slows down the exchange of gases, moisture and heat from the water and the atmosphere, prevents the absorption of carbon dioxide, and the penetration of oxygen into the earth's atmosphere.
In oil pollution there are a number of known processes (dispersion, biodegradation, evaporation, emulsification) that will change the characteristics and behavior of the stain.
The factors that affect the behavior of the oil product spot are [4,5,6].

- physical characteristics of petroleum products: specific gravity, viscosity and volatility;
- chemical characteristics and composition of petroleum products;
- meteorological conditions (water temperature, amount of precipitation, wind speed and direction, etc.);
- characteristics of the aquatic environment (specific gravity, aquatic currents, presence of bacteria, presence of solid suspensions, etc.);
- characteristics of the polluted soil (of the shore).

Equipment needed to combat pollution and reduce the effects of oil on the marine environment includes a series of floating barriers designed to prevent the rapid dispersion of pollutants, equipment or ships specially designed for collecting pollutants (skimmers) and certain natural or synthetic absorbent materials.
These methods are used to capture and store the pollutant until it is properly disposed of. Special containers are also used for the transient storage of the pollutant [6,7,8].
Synthetic sorbents are most effective in recovering petroleum products from the water surface [9,10].
In some cases, a weight ratio of petroleum product: sorbent of 40: 1 compared to 10: 1 for organic products and 2: 1 for inorganic products can be achieved.

Despite their limited adsorption capacity, organic and inorganic sorbents can be attractive because they are abundant in nature or are waste from an industrial process and can be easily purchased at a reduced price or even for free.
This paper analyzes polymeric sorbents and their sorption equations.

II. MATERIAL AND METHOD

PP-polypropylene belongs to the category of polyolefins, thermoplastic materials with a wide distribution to the products that are made by injection.
Polypropylene is composed mainly of propylene (C_3H_6) and comes from a low pressure process, based on catalysts. The molecular formula of polypropylene is (-$CHCH_3$-CH_2-)n and is described as a linear chain polymer [10].
Polyethylene marked with the abbreviation PE (or polymethylene) is a thermoplastic polymer. It is a white or semi-transparent semi-crystalline product.It should be mentioned that it is the most wides pread plastic material being obtained through the polymerization process [10].
The sorption capacity of polyethylene and polypropylene was analyzed for two crude oils that polluted a seawater.
The experiment consisted of polluting 50 mL of sea water with 1 mL of crude oil (Table 1).
Then polyethylene and polypropylene were spread on this crude oil which was mixed with water and crude oil for 2 minutes.
Polyethylene and polypropylene were recovered and weighed.
The water was extracted by the electric centrifuge extraction process.

Table 1.Crude oil used for the experiment

Properties	Sulf oil	Non sulphur oil
density, g/cmc la 20 °C	0,8731	0,9266
viscosity cSt	11	111
sulph	1,7	2,8
asphaltene, % greutate	1,5	9

The efficiency of the sorghum was measured by weighing the weight of the absorbed crude oil relative to the crude water weight (Table 2,3).
Equation of sorption efficiency is:

100% sorption efficiency= (weight of polymer with absorbed crude oil / weight of crude water) x 100

We also analyzed under an electron microscope unpolluted and polluted polyethylene as well as unpolluted and polluted polypropylene (SEM- scanning microscope electronic -50 μm) (figure 1,2,3,4).

Table 2. The efficiency of polypropylene dust in recovering crude oil from seawater

Weight of sorbent polypropylene,g, powder compared to 1 g weight of crude oil	Efficiency,% Sulph oil	Efficiency,% Non Sulph oil
0,5	20	40
1	30	50
1,5	55	62
2	65	70
2,5	66	73
3	68	74
3,5	70	75
4	80	80

Table 3. The efficiency of polyetilene dust in recovering crude oil from seawater

Weight of sorbent polyetilene,g, powder compared to 1 g weight of crude oil	Efficiency,% Sulph oil	Efficiency,% Non Sulph oil
0,5	30	55
1	40	56

1,5	**45**	**70**
2	**59**	**72**
2,5	**62**	**80**
3	**78**	**81**
3,5	**78**	**82**
4	**84**	**84**

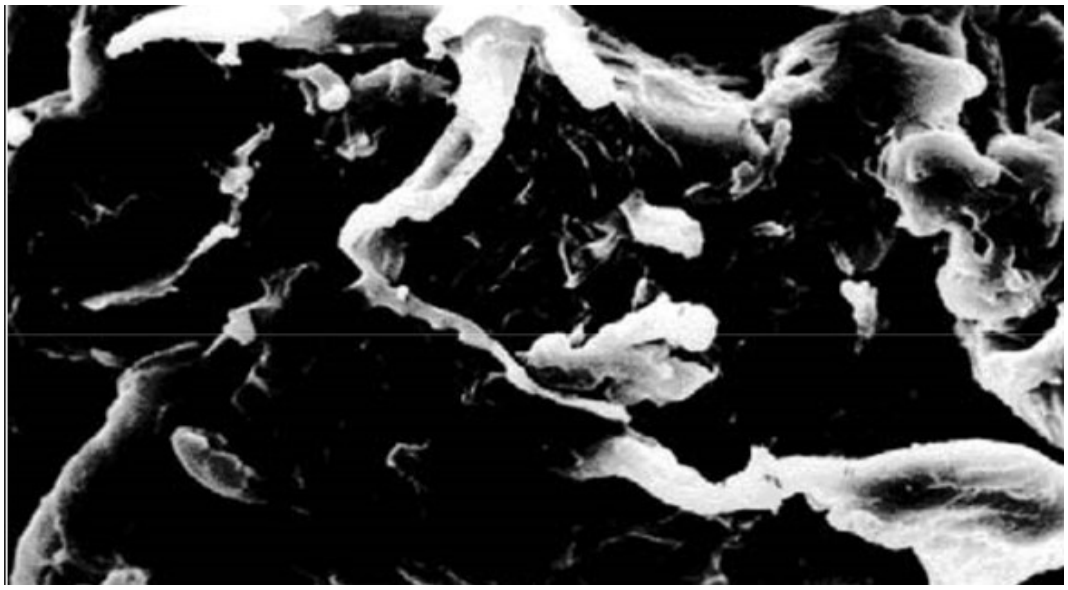

Figure 1. Unpolluted polyethylene [11]

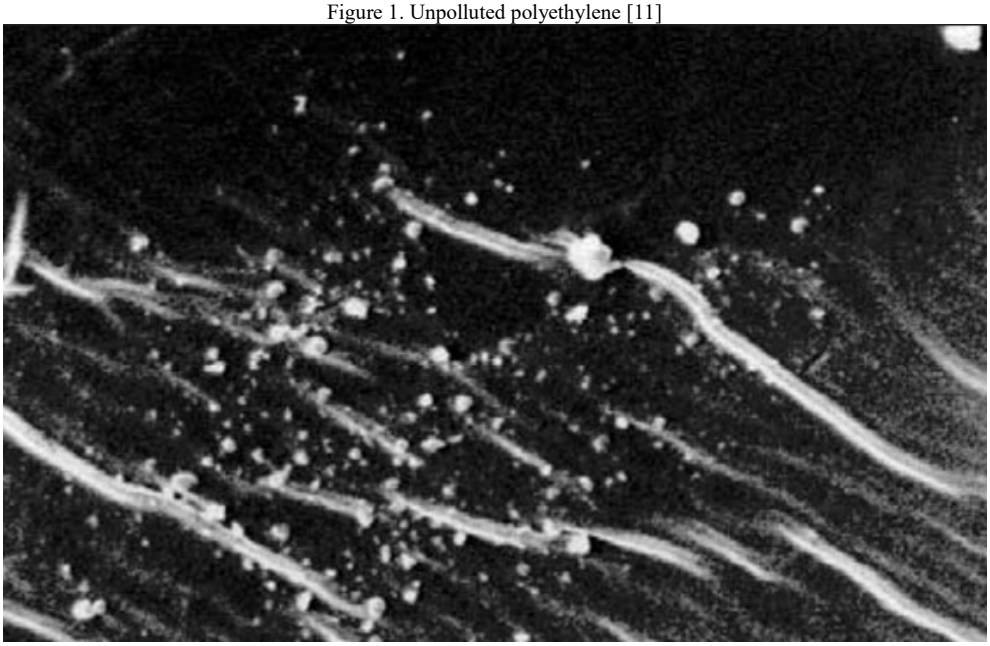

Figure 2. Polluted polyethylene [11]

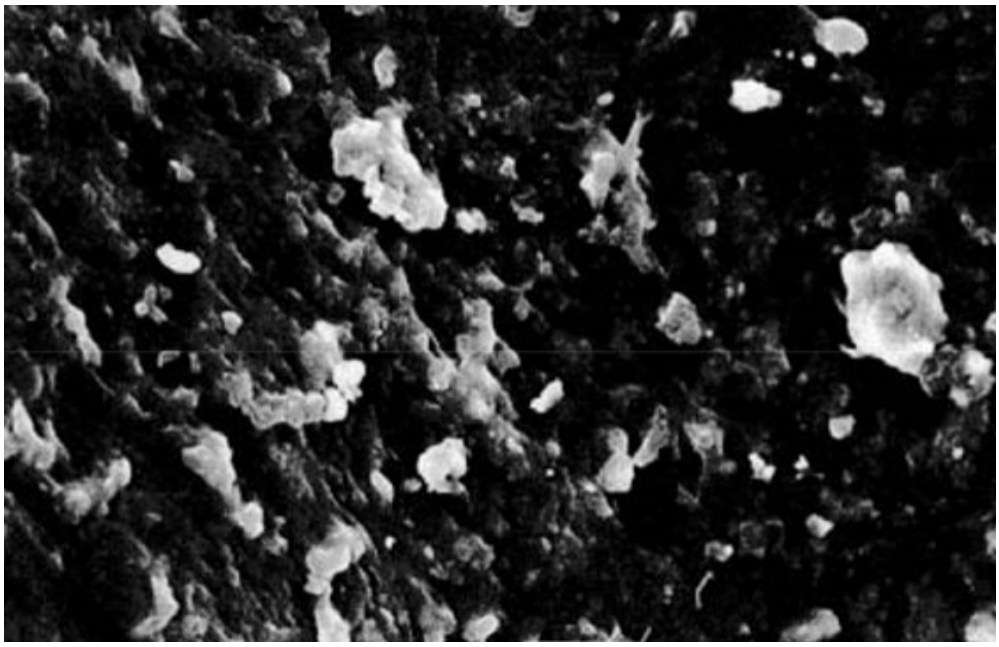

Figure 3.Polypropylene not polluted with Oil [11]

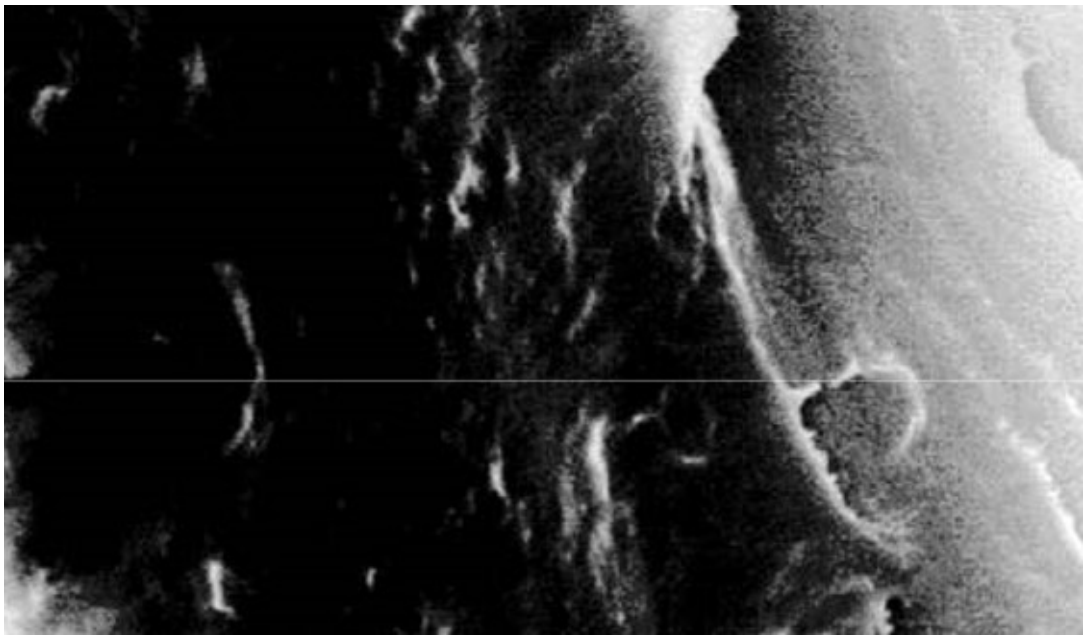

Figure 4. Polypropylene polluted with oil [11]

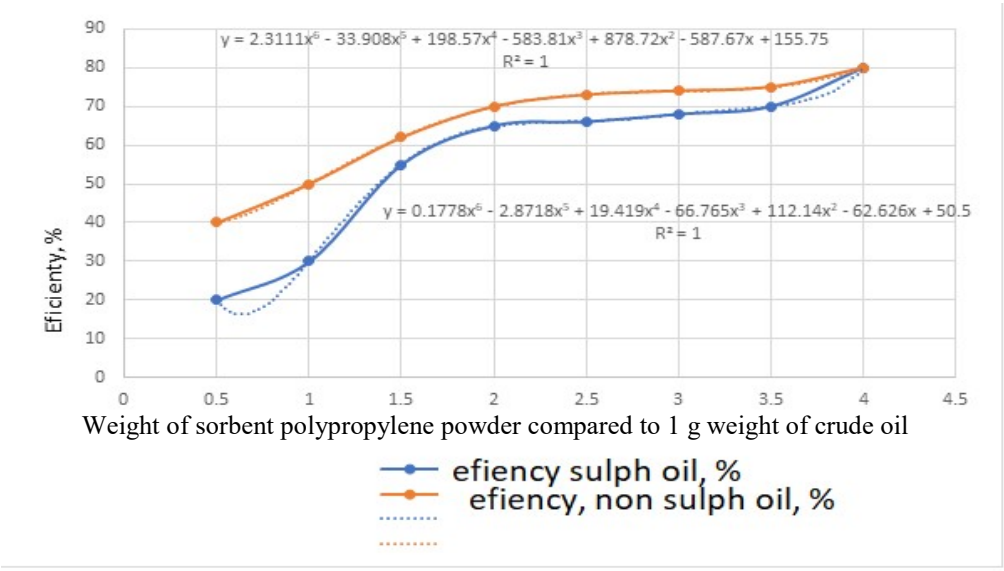

Figure 5. Efficiency of sorbent polypropylene powder

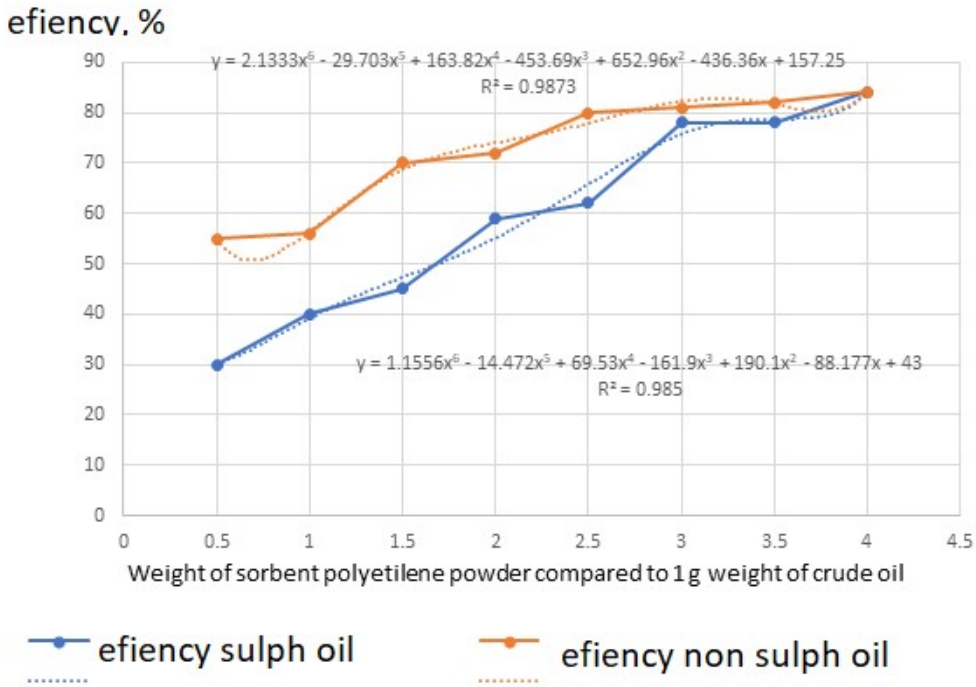

Figure 6. Efficiency of sorbent polyetilene powder

The oil adsorption equations of polypropylene and polyethylene are 6th order mathematical relations, having results close to reality (Table 4 and 5).
In this equation *x is Weight of sorbent polypropylene powder compared to 1 g weight of crude oil*, and y is efiency (%).

Table 4. Equation of adsorption of oil by polyetilene sorbents

Tipe of oil	Polyetilene
Sulph oil	$y=1.1556\ x^6-14.472\ x^5+69.53\ x^4+161.9\ x^3+190.1\ x^2-436.36\ x+157.25$ $R^2=0,9873$
Non- Sulph oil	$y=2.1333\ x^6-29.703\ x^5+163.82\ x^4-453.69\ x^3+652.96\ x^2-88.177\ x+43$ $R^2=0,985$

Table 5. Equation of adsorption of oil by polypropilene sorbents

Tipe of oil	polypropilene
Sulph oil	$y=0.1778\ x^6-2.8718\ x^5+19,419\ x^4-66.765\ x^3+112.14\ x^2-62.626\ x+50.5$ $R^2=0,985$
Non- Sulph oil	$y=2.3111\ x^6-33.908\ x^5+198.57\ x^4-583.81\ x^3+878.72\ x^2-587.67\ x+155.75$ $R^2=1$

III. MATHEMATICAL MODDELING OF OIL POLLUTION

In oil pollution of marine waters there are a number of known processes (dispersion, biodegradation, evaporation, emulsification) that will change the characteristics and behavior of the stain [10,12].

As data for mathematical modeling oil discharging are required:
-quantity discharged (tonnes) Q discharged,
-time elapsed since the date of the accident (hours),
-thickness of pollutant stain H pollutant (cm),
-volatile fractions in pollutant F (% of total quantity),
-pollutant density (gm/cc),
-kinematic viscosity of water (cP),
-kinematic viscosity of the pollutant (cP),
-water temperature °C.

Calculation example

Crude oil: density 0.875 viscosity 10 cSt.

a. The evaporated quantity is given by the formula:
Qevaporated = Q spilled * F / 100 (ton)

b. Quantity of crude oil remaining on water:
Qramas on water = Qdeversat-Qevaporat (tons)

c. Infestation area (sqm):
A = Qramas on water * 100 / H pollutant

d. The volume of crude oil left on the water (m3):
Vtitei left on water = Qramas on water * Density

e. The amount dispersed in the water is 20% of the total amount of crude oil remaining on the water.

f. The speed of the film is equal to:
Vpelicula = Vvant + Vcurent * 0,3 (coefficient of attenuation of the current).

g. Oil-in-water emulsion (depending on wind, currents and oil viscosity) (Table 7).

h. The amount of crude oil left to reach the shore
Q = The volume of crude oil left on the water-crude oil dispersed in water

i. probable date of arrival of the film on the shore:
Date (s) = distance from the shore where the accident / speed of the film took place

j. The amount of fish destroyed is considered to be the ratio between the density of fish in the polluted area and the polluted area.
It is estimated that 20% of fish die from oil asphyxiation.

k.The amount of green mass destroyed (mollusks, seagrass, oysters, etc.) is considered to be the ratio between the density of green mass in the polluted area and the polluted area.
This natural resource is considered to be 100% destroyed.

Table 6. Dispersion of oil by marine water function by time of discharge

	Time of discharge	Quantity of oil discharge 5 kg	Quantity of oil discharge 50 kg	Quantity of oil discharge 500 kg	Quantity of oil discharge 5000 kg	Quantity of oil discharge 50000 kg
Infested surface kmp	1h	0.006	0.016	0.076	0.360	1.14
	2 h	0.016	0.023	0.107	0.496	2.28
	5 h	0.065	0.065	0.69	0.784	3.64
	10 h	0.183	0.183	0.24	1.11	5.15
	24 h		0.518	0.68	1.72	7.98
	48 h			1.93	2.43	11.3
	72 h			3.54	3.54	13.8
	96 h			5.45	5.45	15.6
	500 h			64.8	64.8	64.8
Film thickness mm	1h	0.980	3.6	7.5	15.8	50.1
	2 h	0.348	2.5	5.3	11.5	25.1
	5 h	0.088	0.9	3.4	7.0	15.7
	10 h	0.031	0.3	2.4	5.1	11.1
	24 h		0.1	0.84	3.3	7.2
	48 h			0.30	2.4	5.1
	72 h			0.16	1.6	4.1
	96 h			0.105	1.05	3.6
	500 h			0.009	0.09	0.9

In figure 7 is presented a equation by evolution of the pollutant spot y, cm from the infestation area x (sqm)-3.75 tones discharge.

In this exemple I simulated a quantity of 5 tons discharged into the water, 3.75 tons will be found in a stain that will have an area of 180 square meters (2 cm thick stain).

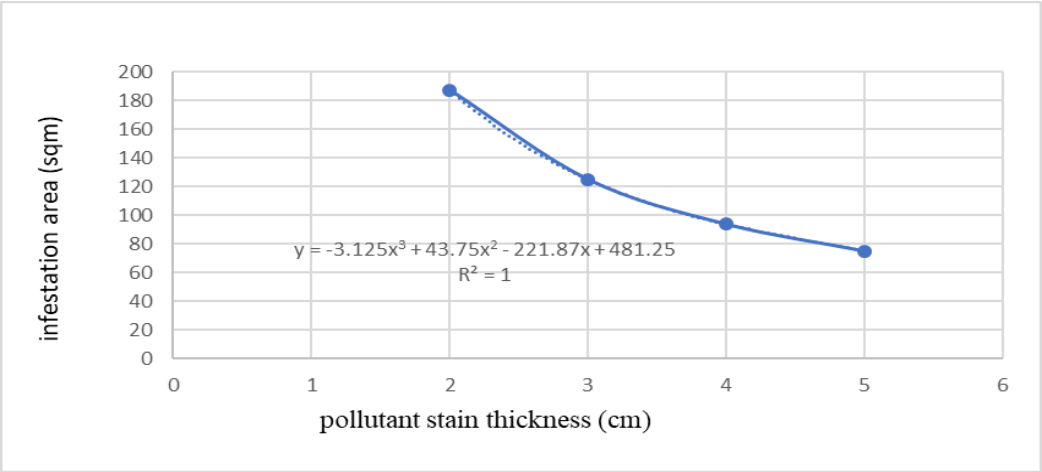

Figure 7. Evolution of the pollutant spot y, cm from the infestation area x (sqm)-3.75 tones discharge.

IV.CONCLUSION

Sulfur oil has a lower viscosity and therefore polyethylene and polypropylene have a higher efficiency.
Polypropylene is also more adsorbent in relation to crude oil.
It is very interesting the adsorption capacity of both chemical compounds, at a ratio of 4: 1 polyethylene / oil or polypropylene / oil, the efficiency is equal for both types of oil.
Oil pollution is verry impressive.
A quantity of 5 tons discharged into the water, 3.75 tons will be found in a stain that will have an area of 180 square meters (2 cm thick stain).

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