THE USE OF OIL-CAKE (SUNFLOWER) IN THE DEPOLLUTION OF PETROLEUM INFESTED WATER

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ABSTRACT

Oil pollution of surface and groundwater is an undesirable phenomenon but it is possible to happen. The pollutant can appear as a result of leaks from the transport pipelines, the damage of the oil extraction and processing installations, and the distribution states of the petroleum products.

In the vast majority of interventions to combat pollution, polymeric sorbents are used which are spread over the pollutant and then washed with warm water.

This technology does not completely clean the pollutants, and the polymeric sorbents are difficult to remove.

Oil-cake (sunflower) is a grated residue after oil extraction and contains the amino acid lysine and high content of fiber and methionine. At a quantity of 100 kg of sunflower seeds, a processor obtains a quantity of 35 kg of residual mass consisting of a sunflower meal.

This product can be used as a sorbent for petroleum products, being then used to produce green energy.

The physical properties of two sorbent substances (sunflower oil and peat) are presented.

Also, their adsorption capacities for four pollutants specific to the oil industry (gasoline, diesel, paraffin oil and sulfur oil) are analyzed, as well as the adsorption kinetics.

The adsorption equations of the pollutants are also described.

Keywords: *Oil-cake (sunflower),sorbent, oil products, water, pollution*

INTRODUCTION

Oil pollution of surface waters can be removed by:

- crowding (dispersion) of the film to favour its spread under the action of natural factors, with the help of dispersants.
- chemical neutralization of toxic hydrocarbon products, by "binding" them in various less active combinations.

- adsorption of hydrocarbons on the surface of special materials, easier to control and recover.
- oil film burning (not indicated).
- biodegradation of the oil film with the help of microorganisms.

The use of biodegradable adsorbents on the surface of the water, in extreme cases, must be accompanied by their immediate recovery and removal from the environment. These adsorbents are 100% biodegradable are oleophilic, but only partially hydrophobic.

These adsorbents can adsorb an amount of pollutant 3 to 15 times larger than their mass, but some of them have the disadvantage that they also absorb an amount of water which causes them to sink faster and greatly prevents their collection.

Failure to recover from water causes the maintenance of oil pollution in the polluted area or, worse, causes the occurrence of secondary pollution, in the same place or in different places, much more harmful and dangerous than the initial pollution.

The aggregates of 100% natural biodegradable adsorbent product.

biodegradable adsorbents can form agglomerations of petroleum product and adsorbent, which are heavier than water density and transfer to its bottom [1].

The phenomenon is much more complex, the agglomerates of adsorbent / petroleum product deposited on the bottom of the water basin enter the degradation process only after a time of 90 - 120 days and are not completely realized after 120 days [2].

The reality is that the 100% natural biodegradable adsorbent product degrades first and long before the oil product, the degradation of the last component (oil product) being less intense.

After degradation of the 100% natural biodegradable adsorbent, the amount of petroleum product left undegraded on the bottom of the water basin slowly rises to the surface of the water. Most of the organic materials can only be used on land and are not recommended to be used on water to eliminate oil spills.

The grated residue (oil-cake) after oil extraction contains the amino acid lysine and high content of fiber and methionine.

At a quantity of 100 kg of sunflower seeds, a processor obtains a quantity of 35 kg of residual mass consisting of sunflower meal.

40 kg of oil are produced from 100 kg of sunflower seeds and 25 kg are oily residues.

This product can be used as a sorbent for petroleum products, being then used for energy production in power plants (its use as fuel).

PREVIOUS STUDIES

The recovery of crude oil, petroleum products, mineral oils (Table 1) and their waste accidentally discharged into surface waters, when they are in the form of very thin films, is achieved in the final phase by using sorbents [3], [4], [5].

Adsorbents are those solids or liquids that have the property of absorbing vapors or dissolved substances.

Ad / absorbents (sorbents) are divided into three main categories of materials :

- natural organics: peat (peat moss), sawdust, cut hammers, straw, carbon-based products;
- natural inorganics: clay, perlite, vermiculite, glass wool, sand or volcanic ash (Table 2 and 3);
- synthetic: polyurethane, polyethylene, polypropylene, etc.

Of these three categories of sorbents, only natural organic materials are biodegradable, while natural and synthetic inorganic materials are non-biodegradable adsorbent materials.

Biodegradation refers strictly to the decomposition of sorbents after the recovery of petroleum products from the polluted area. The largest amounts of adsorbents used in Romania on the water were and are 100% natural organic adsorbent materials, biodegradable, floating on the surface of the water. In over 90% of cases, imported peat sorbents. More 10 % of sorbents are synthetic [6].

PRESENT STUDY

In order to ensure adequate scientific support, in conducting the study, research methods and means were used, both general and specific, namely:

- The method of analysis and synthesis - consisted in consulting bibliographic sources to obtain general data;
- Observation method - was used for laboratory research in order to make observations, measurements;
- Comparative method - was used to evaluate the absorption capacity of the 2 natural adsorbents analyzed;

Tests were performed with sorbents such as peat and sunflower oil.

Also used were 4 pollutants specific to the oil industry (the most persistent pollutants in accidental pollution with petroleum products), namely Romanian Oil, Russian Export Blend Crude Oil, Diesel and gasoline (Table 1).

Table 1. *Properties of polluants using in analysis*

Polluants	Diesel	Gasoline	Romanian Oil	Russian Oil
Density, kg/dm^3 at 20°C,	0.823	0.736	0.838	0.8615
Viscosity, cst,	2.45 at 40°C	18.41 at °C	21.21 at °C	20,58 at °C
Freezing point, °C	-23	-20	+8	-8

Table 2. *Density of sorbents using in analysis*

Polluants	peat	sunflower oil
kg/dm^3 at 20°C	0.157	0.228

Table 3. *Properties of sunflower oil*

Properties	Value
Ca, %	0,3
P, %	0.98
Gross fat, %	1,34
Crude cellulose, %	16
Lysine, %	1,25
Methionine, %	1,34
Crude protein , %	33

To determine the properties of sorbents we using regulation developed by ASTM (American Society for Testing and Materials named Standard Test Methods for Sorbent Performance of Adsorbents (F716-09 and ASTM F726 – 12).

The first experiment was performed between the petroleum products and the sorbents used:

a) Addition of sorbents to used petroleum products to 20ºC temperature,

b) Measurement of absorption capacity at 15 minutes and 24 hours to 20ºC temperature.

In Figure 1,2,3 is presented the mixtures of diesel, oil and sorbents.

Sorption capacity testing

The quality of the sorbents is to retain the hydrocarbons. The experiment consisted in observing the encapsulation capacity of the oil and determine the amount of liquid absorbed by the amount of sorbent (g petroleum product / g sorbent) (figure 4).

Capillary ascent testing

This test highlights the phenomenon of absorption by capillary action, a phenomenon that takes place the removal of petroleum products from the affected environment.

The sorbents act through both the absorption and the adsorption mechanism.

The absorbents act as sponges and collect the product by the action of capillarity or suction. They allow the liquid to enter the space of the pores of the material from which they are made, while the adsorbents attract the liquid on their surface but do not allow their penetration into the material. In some cases, sorbent materials can use both principles to recover the oil product.

We tested the kinetics of the capillary rise of different liquids in the pores of sorbents.

The REBCO type crude oil, diesel and petrol (75 ml) were introduced in a column (1.5 cm diameter and 12 mm length), filled with natural peat sorbents and sunflower stew (up to 4 cm).

The volume of oil absorbed by the sorbent was monitored.

The results obtained are represented in Figure 5,6 and Table 4 and 5.

Fig. 1. *Diesel in contact with sunflower*

Fig. 2. *Romanian Oil in contact with sunflower*

***Fig. 3**. Romanian Oil in contact with peat*

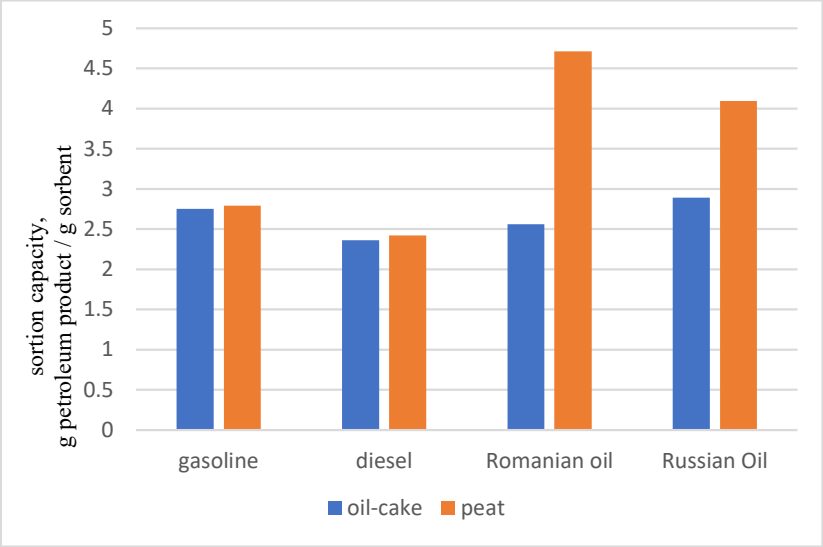

***Fig. 4**. Sortion capacity of oil-cake and peat*

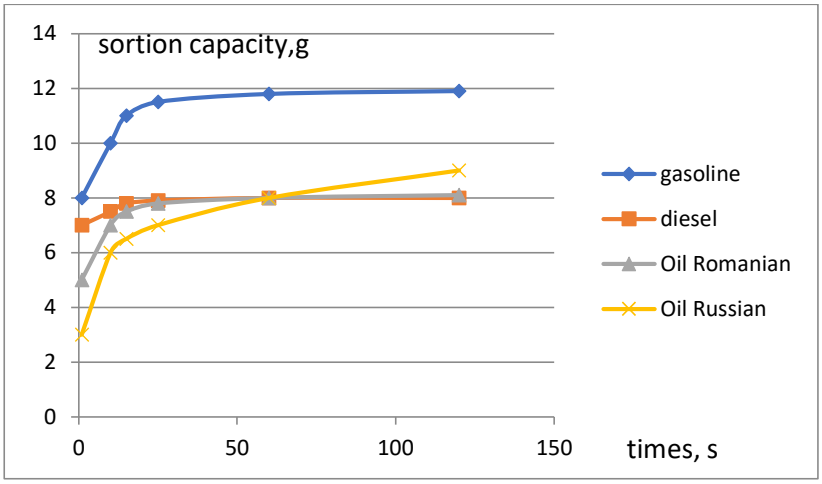

Fig. 5. *Kinetics of fluid retention in peat pores*

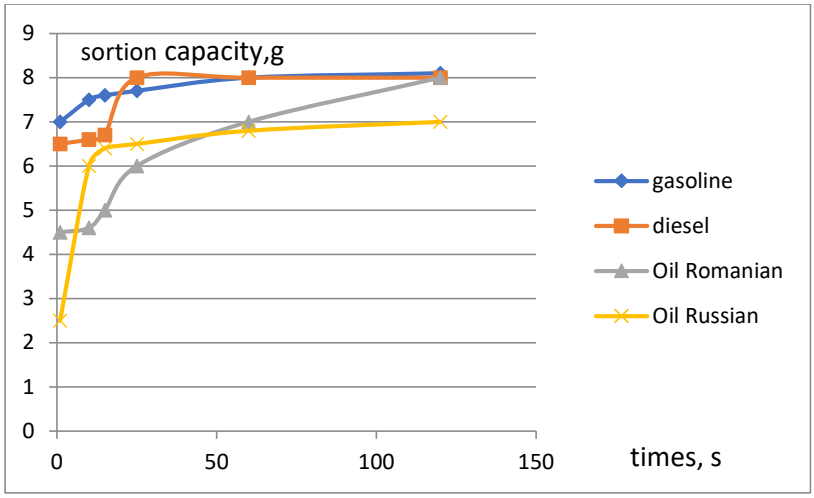

Fig. 6*. Kinetics of fluid retention in oil-cake*

Table 4*. Equation of kinetics retention in peat pores*

Poluants	Equation y is sortion capacity x is times to sortion	R^2
Gasoline	y = 0.8663ln(x) + 8.2295	0,9324
Russian oil	y = 1.235ln(x) + 3.0613	0.9982
Romanian oil	y = 0.6698ln(x) + 5.3232	0.9193
Diesel	y= 0.2247ln(x) + 7.0593	0.9219

Table 5. *Equation of kinetics retention in oil cake*

Poluants	Equation y is sortion capacity x is times to sortion	R^2
Gasoline	y = 0.2354ln(x) + 6.9787	0.9925
Russian oil	y = 0.7424ln(x) + 3.7329	0.7593
Romanian oil	y = 0.7424ln(x) + 3.7329	0.7593
Diesel	y = 0.7424ln(x) + 3.7329	0.7593

CONCLUSION

In the article, we presented the effects of oil pollution on two natural sorbents (easy to find in nature). The first sorbent (peat) is widely used in the oil-polluted environment recovery industry. The second adsorbent is proposed by us for use, having important adsorption capacities and being a residual product.

At this time, the sunflower meal is burned in ovens, having a low caloric capacity.

By using it as an adsorbent you can increase the caloric capacity and especially by refining you can recover the oil product.

Based on the studies carried out in the previous chapters of the paper, the following conclusions were obtained:

- the peat retains the oil production in the first 20 seconds, followed by a period of filling the pores,
- sunflower meal is useful for retaining heavy products (high density),
- the output capacity is 2.5-4 times greater than the weight of the sorbent,
- sunflower meal is a good and useful sorbent, is then used for the production of electricity or heat.

In this paper we wrote the logarithmic equation of determination is sortion capacity function by times to sortion.

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