

## ИССЛЕДОВАНИЕ ПРОЦЕССА СОРБЦИИ НЕФТИ И НЕФТЕПРОДУКТОВ ПЕНОПОЛИМЕРНЫМИ СОРБЕНТАМИ НА ОСНОВЕ УДАРОПРОЧНОГО ПОЛИСТИРОЛА

Н.Т. Кахраманов, Ю.Н. Кахраманлы, Р.В. Курбанова, Р.С. Гаджиева

Наджаф Тофик оглы Кахраманов \*

Лаборатория механохимической модификации и переработки полимеров, Институт полимерных материалов НАН Азербайджана, ул. С. Вургуна, 124, Сумгайыт, Азербайджан, AZ5004

E-mail: najaf1946@rambler.ru \*

Юнис Наджаф оглы Кахраманлы, Рена Вагиф гызы Курбанова, Рейхан Шахмардан гызы Гаджиева

Кафедра химии и технологии неорганической химии, Азербайджанский государственный университет нефти и промышленности, просп. Азадлыг, 20, Баку, Азербайджан, AZ1010

E-mail: yunis1m@yahoo.com, rena0.72@yandex.ru, reyhan.haciyeva@gmail.com

*Приводятся результаты исследования влияния объемной массы шитых и вспененных сорбентов на основе композиций вторичного ударопрочного полистирола с битумом и стеаратом цинка на их сорбционную емкость по нефти и нефтепродуктам. Механохимический синтез пенополимерных сорбентов проводили на экструдере с 3-х зонным материальным цилиндром. В качестве пенообразователя использовали азодикарбонамид, а сшивающего агента перекись дикумила. Пенополимерные сорбенты обладают высокой плавучестью и гидрофобностью, что в совокупности способствует повышению селективности процесса сорбции нефти и нефтепродуктов с водной поверхности. Сорбционную емкость определяли весовым методом по разности массы сорбента до и после сорбции. Показано, что нефть лучше всего сорбируется на пенополимерных сорбентах с низкой объемной массой и большим диаметром закрытоячеистых структур. В то же время, дизельное топливо хорошо сорбируется на сорбентах с относительно высокой объемной массой и соответственно меньшим диаметром пор и ячеек. Нефтяные масла наиболее эффективно сорбируются на пенополимерных сорбентах, объемная масса и диаметр ячеек которых занимает промежуточное положение в сравнении с сорбентами, предназначенными для сорбции нефти и дизельного топлива. Установлено также, что независимо от диаметра пор и ячеек скорость сорбционных процессов возрастает с повышением температуры водной среды. В этом случае, в зависимости от типа сорбата, объемной массы сорбента и температуры среды изменение сорбционной емкости происходит по определенной закономерности. Показано, что полученные сорбенты характеризуются способностью к многократной регенерации при сохранении высокой плавучести, гидрофобности и сорбционной емкости по нефти и нефтепродуктам.*

**Ключевые слова:** сорбция, пенополимеры, объемная плотность, диаметр ячеек, сорбционная емкость, сорбенты, нефтепродукты, водная поверхность, изотерма, диффузия, плавучесть, гидрофобность, экстракция

## STUDY OF SORPTION PROCESS OF OIL AND OIL PRODUCTS WITH FOAM POLYMER SORBENTS BASED ON HIGH-IMPACT POLYSTYRENE

N.T. Kakhramanov, J.N. Gahramanly, R.V. Kurbanova, R.Sh. Gadzhiyeva

Nadzgaf T. Kakhramanov \*

Laboratory of Mechanochemical Modification and Processing of Polymers, Institute of Polymer Materials of Azerbaijan NAS, S.Vurgun st., 124, Sumgait, Azerbaijan, AZ5004  
E-mail: najaf1946@rambler.ru \*

Junis N. Gahramanly, Rena V. Kurbanova, Reyhan S. Gadzhiyeva

Department of Chemistry and Chemical Technology of Inorganic Chemistry, Azerbaijan State Oil and Industrial University, Azadliq ave., 20, Baku, Azerbaijan, AZ1010  
E-mail: yunis1m@yahoo.com, rena0.72@yandex.ru, reyhan.haciyeva@gmail.com

*Research results of influence of volume mass of crosslinked and foamed sorbents on the basis of secondary high-impact polystyrene with bitumen and zinc stearate upon their sorption capacity are represented. The mechano-chemical synthesis of foamed polymeric sorbents was carried out on the extruder with a three zone material cylinder. Azodicarbonamide was used as foaming agent and dicumyl peroxide was used as crosslinking agent. Foam polymer sorbents have a high buoyancy and hydrophobicity. This circumstance contributes to increasing the selectivity of sorption process of oil and oil products from water surface. The sorption capacity was determined by gravimetric method according to difference between sorbent weights before and after sorption. It was shown that petroleum are better sorbed on foamed polymeric sorbents with low volume weight and greater diameter of closed-celled structures. In the same time the diesel fuel sorbed well on sorbents with relatively high volume weight and accordingly lesser diameter of pores and cells. Petroleum oils are most effectively sorbed on foamed polymeric sorbents which volume weight and cells diameter are interim in comparison with sorbents for sorption of petroleum and diesel fuel. It was determined that rate of sorption processes increases with rising of temperature of aqueous medium independently on pores and cells diameter. In this case changing in sorption capacity occurs according to certain regularity depending on sorbate type, volume weight of sorbent and medium temperature. It was shown that obtained sorbents are characterized by capability to multiple regeneration at keeping of high buoyancy, hydrophobicity and sorption capacity on petroleum and oil products.*

**Key words:** sorption, foam polymers, bulk density, cells diameter, sorption capacity, sorbents, oil products, water surface, isotherm, diffusion, buoyancy, hydrophobicity, extrusion

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## INTRODUCTION

With increasing production and transportation of oil, respectively, increases the number and scale of environmental disasters related to the accidental oil spills, polluting the land and water area of seas and

oceans. The increased environmental footprint contributes to a gradual decrease in the compensatory capacity of the natural environment, as a result of which the ecological situation grows into a global human problem. Pollution of the seas in the process of oil extraction

from the seabed and its transportation by tankers and underwater main pipes always carry the danger of an ecological catastrophe [1, 2].

In recent years, more and more attention is paid to the development of effective methods of eliminating emergency spills, one of which is the use of various types of organic and inorganic sorbents. From an economic point of view, preference is given to the use of sorbents based on waste derived from the industrial processing of agricultural products or secondary technological polymer waste [2, 3].

The article describes the process of sorption of oil and petroleum products using polymeric sorbents based on polymer foams secondary impact polystyrene (PSIPS).

#### EXPERIMENTAL PART

Foam-polymer sorbents were prepared by extrusion in the mixing process of the secondary high-impact polystyrene (HIPS) having an average melt flow rate of 2.3 g/10 min, blowing agent – azodicarbonamide (ACA) in an amount of 5-6, crosslinker – dicumyl peroxide – 1.0, zinc stearate – 0.5 and petroleum bitumen – 5% wt. The whole mixture was mixed in extrusion machine in the melt of HIPS at 403-468 K [4]. As a result of the thermomechanical action of the extruder on the polymer melt was occurred the decomposition of the ACA with the evolution of nitrogen promoting the foaming of the polymer matrix. Cross-linking of the polymer sorbent is a desperate measure that facilitates not only the process of its foaming, but also improves the physicomachanical properties of the foam polymers. However, this measure allows simultaneously extending the range of the technological parameters of its processing by extrusion.

It is possible to obtain crosslinked, foamed and bitumen filled polymer sorbents with closed-cell macrostructure and high degree of buoyancy by regulating the temperature regime and extrusion pressure, and also by selecting the mixture components ratio [4, 5]. The introduction of petroleum bitumen into the composition of the polymer composite makes it possible to obtain hydrophobic sorbents, by means of which high selectivity of the process of sorption of oil and oil products from the water surface is achieved. The cross-linked structure of the sorbents was provided high strength and sufficient resistance to swelling in oil medium. In the process of extrusion, continuous foamed polymer strands were obtained, which were then cut into crumbs of 5-7 mm in size.

The average diameter of the cells in the macrostructure of the sorbent was determined using an optical microscope, and bulk density (apparent density) of

PSIPS was determined from the ratio of the mass of the sample to its geometric volume.

The content of the gel fraction in the PSIPS formed as a result of crosslinking the polymer matrix with dicumyl peroxide was determined by extracting the sorbent in a Soxhlet extractor with toluene.

Some physico-chemical characteristics of Binagadi oil have been given below:

Density,  $\text{kg/m}^3$  – 902

Kinematic viscosity,  $\text{mm}^2/\text{s}$  – 14.6

Hardening temperature, K – 223

Coking capacity, % mass – 2.81

Sulphur content, % mass – 0.28

In determining the average cell diameter, apparent density and sorption capacity for oil and oil products relative measurement error is respectively: 5%, 8%, and 7%.

The sorption capacity for oil and oil products was determined by the weight method. A suspended amount of a polymer sorbent in the form of a crumb was dumped onto the water surface containing the oil. After holding the sorbents for a certain time on a water surface with an oil layer of 1.0 mm, the samples were dried and weighed on an analytical scale. The amount of absorbed oil or oil products was determined from the difference in mass of the sample before and after sorption. The ratio of the amount of sorbed oil to the initial mass of the sorbent characterizes the sorption capacity for oil. During centrifugation the oil was pressed from the polymer sorbent, and the sorbent was sent for reuse. In this way polymer sorbents were exposed to multiple regeneration. Similarly, the sorption capacity of sorbents for fuel oil and diesel fuel was determined.

#### RESULTS AND DISCUSSION

Before proceeding to establish the relationship between the sorption process of oil and oil products with the sorbent macrostructure, it was necessary to dwell on some of the fundamental points that characterize the sorption capacity of the sorbent. In this case the sorbent is a foamed polymer with the closed-cell macrostructure in which the cells are isolated from each other. The cells located in the depth of the sorbent are isolated and filled with nitrogen gas. Therefore, we can agree with the concept of Scheidegger that the cells will be correctly called the gas-structural element (GSE), meaning by this statistically averaged model of not only the cell of the foam plastic, but also the walls of its closure [3].

Previously, with the example of polyethylene foam, it was shown that the bulk density of the foam polymer sorbent and the diameter of the GSE have significant influence on the regularity of sorption from the

water and earth surfaces [5, 6]. It was necessary to find out how to change the regularity of sorption when used as a sorbent PSIPS.

In Table 1 presents the results of research of the influence of exposure time and the bulk density of sorbents based on PSIPS on their sorption capacity for oil and oil products on the water surface. Comparing the data of Table 1, it can be established that, with decrease in the bulk density of the sorbent, the oil absorption of the latter at an exposure time of 96 hours increases by 10.2 kg/kg. It is characteristic that at low values of the bulk density of the sorbent, most of the oil was sorbed in the first 2-3 h. All this is explained by the fact that the volume mass is inversely proportional to the diameter of the cells and varies according to the known regularity given in [4].

It was also found that with a decrease in the volumetric mass of sorbents in the series 535 → 310 → 190 → 80 kg/m<sup>3</sup>, the diameter of their cells increases, respectively, in the following sequence 0.04 → 0.09 → 0.45 → 1.0 mm. Proceeding from this, it was believed that the oil would diffuse into larger diameter cells at a higher rate, i.e. in sorbents with a smaller bulk density.

**Table 1**

**The influence of exposition time and volume weight of PSIPS upon its sorption capacity on petroleum and oil products**

**Таблица 1. Влияние времени выдержки и объемного веса PSIPS на его сорбционную емкость по нефти и нефтепродуктам**

Apparent density kg/m <sup>3</sup>	Exposure time, h	Sorption capacity of PSISP, kg/kg		
		Oil	Fuel oil	Diesel fuel
80	3	18.0	6.3	2.6
	10	19.5	21.0	4.0
	24	20.8	26.5	4.1
	48	21.3	27.3	4.5
	72	21.5	27.5	4.5
	96	22.0	28.0	4.5
190	3	14.0	3.0	6.0
	10	15.8	3.5	7.2
	24	17.1	4.0	8.0
	48	18.0	4.8	8.8
	72	19.3	5.0	9.3
	96	20.0	5.0	10.0
310	3	12.5	3.0	9.0
	10	14.0	3.5	10.0
	24	14.3	4.0	10.7
	48	14.8	4.8	11.4
	72	15.5	5.0	12.0
	96	16.3	5.0	13.0
535	3	6.5	2.0	10.0
	10	9.0	3.0	11.8
	24	9.3	3.5	13.0
	48	10.8	4.0	14.0
	72	11.0	4.2	14.0
	96	11.8	4.2	14.8

In this connection, it seemed interesting to study the selective effect of certain petroleum products – fuel oil and diesel fuel, which are part of the Binagadi oil, on the sorption characteristics of the concerned sorbents.

Analyzing the data given in Table 1, it can be seen that with an increase in the bulk density of the sorbent, the sorption capacity of the sorbent sharply decreases for fuel oil. And in this case, a high sorption rate is established in the first 2-4 h, and then the sorption rate for fuel oil has sorbents with bulk density of 535 kg/m<sup>3</sup>.

By identifying the data (see Table 1), it can be established that, unlike oil and fuel oil, the sorption of diesel fuel is most efficiently carried out on sorbents with a bulk density of 310-535 kg/m<sup>3</sup> and cell diameter of 0.1-0.04 mm. It was found that further increase in bulk density of the sorbent already leads to decrease in the sorption capacity. The latter circumstance is important, since it allows us to assume that for each type of oil product there are certain types of sorbents with an optimal combination of bulk density and cell diameter, at which the maximum effect is achieved by their sorption capacity. At lower bulk density values with a cell diameter of 0.8-1.0 mm, the diffusion of diesel fuel is sharply slowed down due to the fact that it flows out of the sorbent with a large diameter of the cells during weighing. This is explained by the fact that the reduction in the sorption of diesel fuel on coarse-celled structures is possibly connected with the difficulty of retaining a low-viscosity component in cells of large size (0.8-1.0 mm), i.e. in this case there is a situation where the forces of attraction between sorbent and sorbate molecules are lower than the forces of attraction between sorbate molecules.

It is important to note that when collecting oil and oil products from the water surface, the ambient temperature has a significant effect on the diffusion of sorbate in the foam polymer sorbent. In table 2 is shown the results of research of the influence of the temperature of aqueous medium and bulk density of sorbents on the sorption capacity for oil and oil products. In this case, the PSIPS sorbents with cell diameter of 0.8-1.0 and 0.1-0.2 mm are considered, with an exposure time of 48 h. As can be seen from Table 2, with an increase in temperature, there is a general tendency to increase the sorption capacity for oil and fuel oil and, conversely, a decrease in the sorption capacity for diesel fuel. It can be assumed that an increase in the tem-

perature of the medium contributes to a certain decrease in the viscosity of oil and fuel oil and, accordingly, to an increase in the rate of diffusion of the sorbate into deeper layers of the sorbent. As a result, there is a general tendency to increase the sorption capacity. It should also be noted that in the regularity of change of sorption capacity of sorbent (535 kg/m<sup>3</sup>) for oil and fuel oil, there is some abnormal change in the value of this index from temperature.

Table 2

The influence of water medium temperature and volume weight of sorbents on basis of PSIPS upon their sorption capacity on petroleum and oil products

Таблица 2. Влияние температуры водной среды и объемного веса сорбентов на основе PSIPS на их сорбционную емкость по нефти и нефтепродуктам

Apparent density kg/m <sup>3</sup>	Temperature of aqueous medium, K	Sorption capacity of PSISP, kg/kg		
		Oil	Fuel oil	Diesel fuel
80	283	10.0	7.0	1.5
	288	16.3	13.6	3.0
	293	21.2	27.7	4.0
	303	23.5	27.8	4.1
	313	25.4	29.5	3.5
	323	28.8	30.4	2.0
535	283	5.5	1.5	9.0
	288	8.0	2.8	13.5
	293	10.7	4.0	14.0
	303	10.8	4.2	15.2
	313	10.8	5.7	16.7
	323	13.0	6.0	19.3

For example, in the temperature range of 293-313 K the sorption capacity for oil practically does not change. Exactly the same situation occurs with fuel oil at temperature of 293-303 K. It is possible that definite sorption equilibrium is achieved in this temperature range. At a higher temperature (323 K), sorption equilibrium is disturbed toward an increase in the sorption capacity. Apparently, to fill small cells requires a relatively higher temperature and exposure time, at which the sorption equilibrium shifts toward an increase in the sorption capacity. One cannot exclude the fact that under the influence of temperature certain increase in the

volume of the sample and diameter of its cells can occur in the polymer sorbent with bulk density of 535 kg/m<sup>3</sup>, which, in the final, can also lead to an increase in the sorption capacity of oil and oil products.

Sorbents with low bulk density and correspondingly with a relatively large diameter of the cells (0.8-1.0 mm) are characterized by small values of the sorption capacity for diesel fuel. An increase in the temperature of the experiment from 303 to 323 K for sorbents with a bulk density of 80 kg/m<sup>3</sup> leads, on the contrary, to an increase in the desorption of diesel fuel, as evidenced by a decrease in the sorption capacity from 4.1 to 2.0 kg/kg. Perhaps this is due to the fact that an increase in temperature leads to an even greater reduction in the forces of attraction between sorbent and sorbate molecules and, as a consequence, a decrease in the sorption capacity.

One of the important characteristics of polymer sorbents is the ability for multiple regeneration. This important feature of the foam polymer sorbent contributes not only to increasing the efficiency of their use, but also to a substantial reduction in the cost of material. In the course of the studies, it was found that even after 5-fold regeneration, the sorbents retain sufficiently high values of the sorption capacity. So, for example, in sorbents based on the PSIPS with a bulk density of 80 kg/m<sup>3</sup>, the sorption capacity for oil relatively to its initial value (before regeneration) after the first regeneration was 95%, the second – 93%, the third 87%, the fourth 82%, the fifth – 70%.

Thus, it can be concluded that foam polymer sorbents on the basis of PSIPS are among the universal sorbents possessing sufficiently high values of the sorption capacity for oil and oil products, buoyancy, hydrophobicity and the ability for multiple regeneration. It becomes obvious that in order to correct choice of polymer sorbent for collecting spilled oil or oil products in emergency situations, it is necessary to have sufficiently complete data on the bulk density and macrostructure of the sorbent. Only a comprehensive analysis of the morphological features of the macrostructure of sorbents that predetermine the efficiency of the sorption process opens up a promising opportunity for their rational use in performing operational cleaning of the water surface from spilled oil products.

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