ASSESSMENT AND PROGNOSIS OF ENVIRONMENTAL STATE AND DEVELOPMENT OF ENVIRONMENTALLY EFFECTIVE TECHNOLOGIES

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The oil fields of West Siberia are one of the world's greatest hydrocarbon resources. West-Siberian crude made the USSR the world's number one producer until the economy collapsed in 1988. Despite of the drop in oil production in the coming decades, Siberian oil and gas fields occupy a leading place in the balance of the hydrocarbon production in Russia.

The development of oil fields and a rapid growth of the oil industry in the West Siberia had a negative effect on the environment. This negative influence still remains, despite of the decrease in oil production.

As an example of this effect Fig. 1 shows the time history of emissions of oil-gas industry of the Tomsk oblast [1]. Since 1990 the time history of oil production in Russia has been negative, the amount of waste decreased, nevertheless, it does not linearly depend on the oil production. What are the reasons of the large waste?

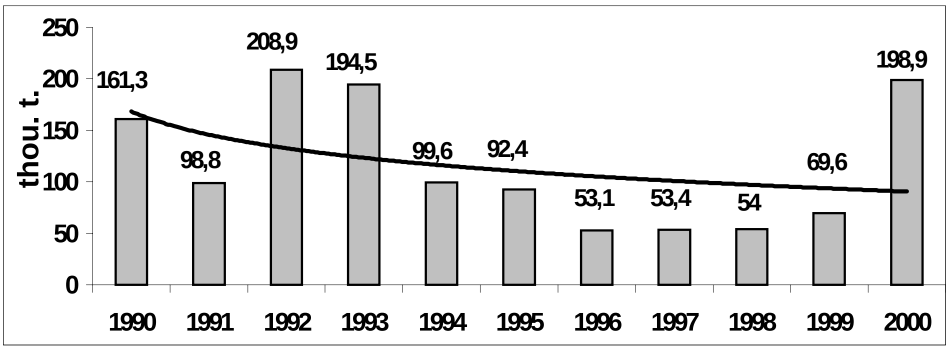

Fig. 1.Dynamics of the changein specific number of contaminant discharge per 1 mln. t. of the produced oil

The main sources of the environmental pollution are as follows:

Oil wells;

Flares for associate gas combustion;
Oil and gas pipelines;
High-pressure water conduits;
Other facilities.
The largest amounts of waste fall on carbon dioxide and hydrocarbons.

The flares give the largest amount of the emissions:

1 ton of the gas burnt forms from 50 to 70 kg of hazardous substances (carbon oxides, soot).

In the regions of oil production the contamination of surface water basins by oil products is significant. Why? The main reasons are accidents and spills at oil wells and pipelines.

The soil is also polluted by oil products and salty reservoir water. Mineralized water comes to the surface together with the oil produced.

The soils are salinized due to the spills of mineralized water at the accidents.

The ecosystems oil-gas producing and oil-refining regions are under a multiyear impact of a pollution monitored. During military operations at the bombardments there occurs a significant pollution of the natural environment as a result of the destruction of product and oil pipelines, petroleum storage depots and oil-refining facilities. The scale of such pollution may be comparable to the multiyear impact on the natural environment during oil production and refining or even surpass it.

Technogenic environmental impact is one of the permanent hazards for the world society. This impact changes the structure of the natural ecosystems, reduces the biodiversity. The consequences of the territory pollution may acquire an irreversible nature and a worldwide scale.

Therefore, topical is the development of the technologies for the selection of ecologically sound and nature-protecting technologies.

Such developments are based on the assessment and forecast of the environmental state. The analysis shows that chemical pollution of air and surface waters are the most hazardous factors of the impact on the natural environment.

We believe that the development of ecologically sound and nature-protecting technologies is the most important goal of the sustainable development and rehabilitation of the region environment.

A generalized scheme of the selection of nature-protecting technologies based on the ecological analysis and the analysis of the technologies is given in the paper of Politschiuk et al [1] and in Fig. 2.

This scheme implies to carry out a complex analysis of the environmental state to identify the main pollutants. The computer analysis of the technologies allows one to select the acceptable technologies taking into account the main pollutants.

We suggested a novel approach to the assessment of technogenic impact. It is based on the combination of sanitary-hygienic and landscape-geographic approaches.

The approach suggested requires the application of large volumes of ecological, cartographic and other data on the state of environment components. The information technology of the solution of the problems of ecological impact should be based on the application of geographic information systems (GIS). A feature of the technology suggested is including software means for simulating the technogenic impact on natural environment into GIS. By overlapping the zones of technogenic impact on the landscape map using GIS, the relative areas of the polluted landscape complexes were calculated. To operationally assess the impact on the environment, we developed a procedure based on the application of the satellites photographs to obtain data on the landscape territory structure. Fig. 3 illustrates the procedure of overlapping the pollution zones on the map of the territory studied.

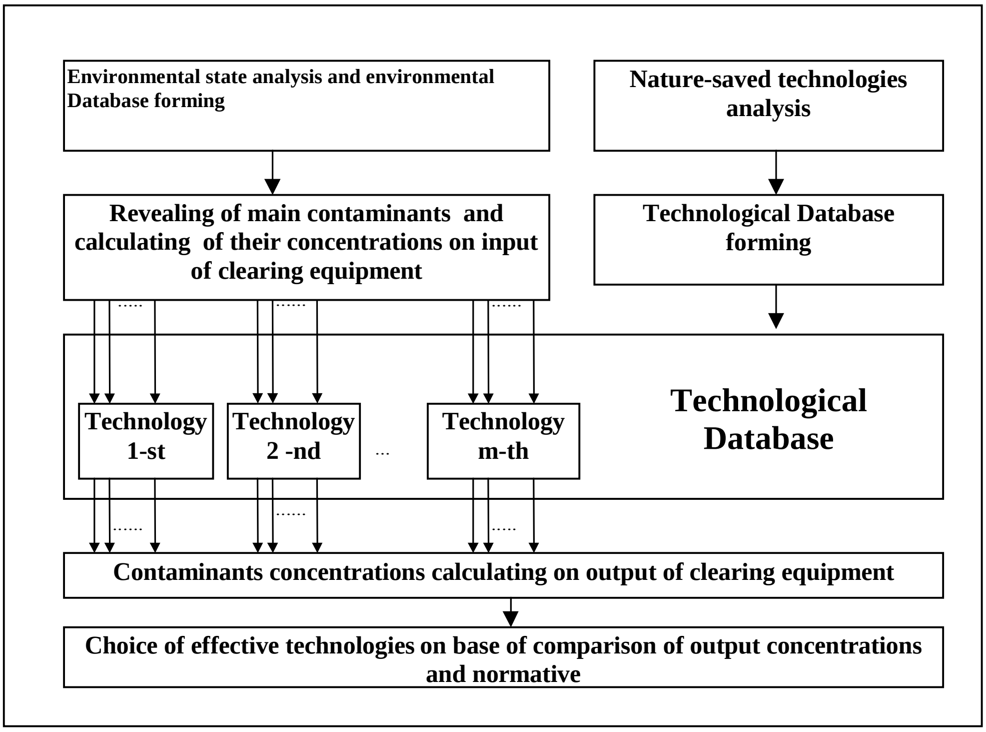

Figure 2. Generalized scheme of the technologies choice

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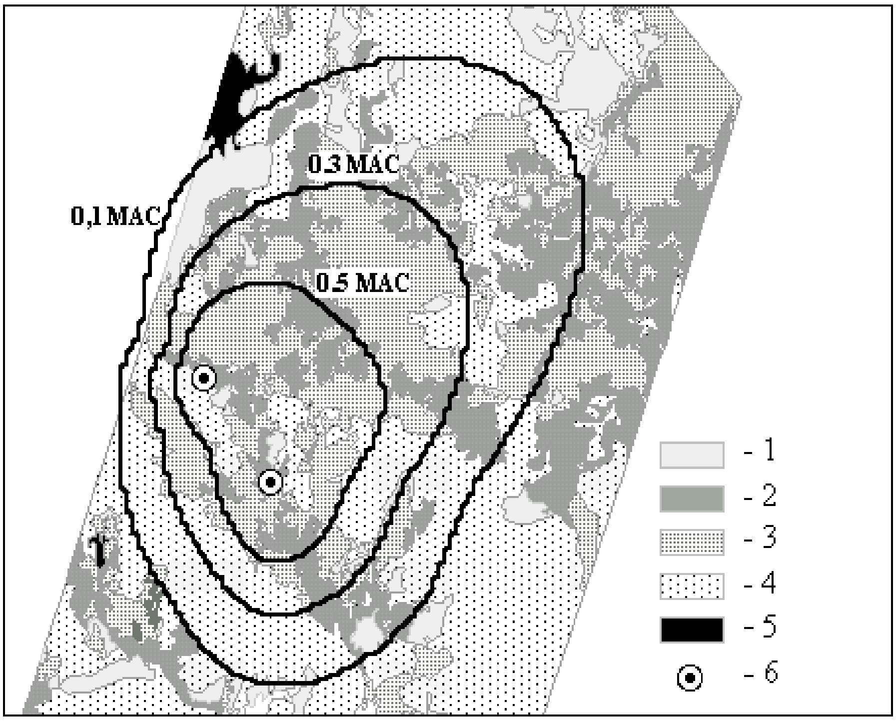

Fig.3. Overlapping the pollution zones on the satellite photograph: 1 – pine forest, 2 – dark-coniferous forest, 3 – birch forest, 4 – march, 5 – floodplain, 6 – flare, MAC - maximum allowable concenyration

The scale of the pollution of the natural environment demands for high-effective advanced technologies for their elimination.

A method for oil product containment on the water surface has been developed. For this purpose, floating booms (oil collectors) are used. The booms are manufactured as compact strong rectangular pieces. The oil-absorbing mats are based on natural and synthetic fibrous adsorbents representing non-woven fabrics. It is possible to build the spill booms and mats for collecting the oil spots of any size from individual elements. The adsorbents posses a high efficiency of oil products collection. The efficiency is reached due to the fiber treatment by special polymer additives produced on the basis of oxidized atactic polypropylene (APP) *(Fig. 4).*

These additives provide for hydrophobic properties and a high capacity for oil products. The capacity of commercial samples is somewhat lower and reaches up to 15 kg of oil per 1 kg of adsorbent. Cellulose, basalt fiber, synthetic carbon tissues, and fibrous products of the recycling of thermoplastic waste and some other materials are used as adsorbing materials.

A system for the regeneration of the mats has been developed. The regeneration provides for mat application in no less than 10 cycles. On this basis a system for rapid oil spill containment and oil product collection from water surface at the accidents was devised.

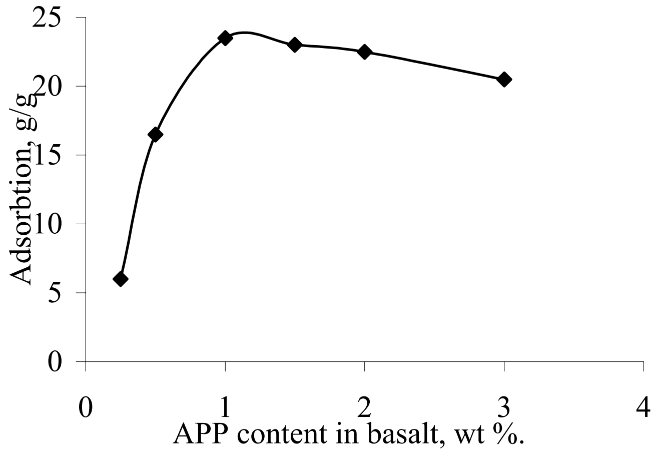

Fig. 4. Oil adsorption versus activated atactic polypropylene content in basalt fiber (contact time is 30 min)

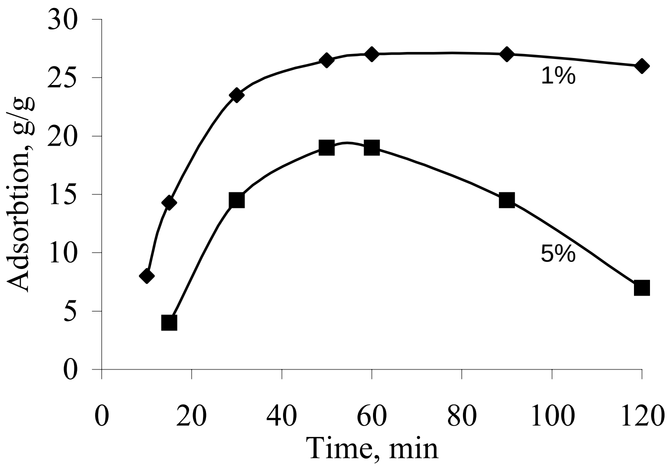

Fig. 5. Oil adsorption by basalt fiber versus contact time and atactic polypropylene content. Adsorption, g/g

A residual 'iridescent' oil film may be eliminated by special thin tissues. Their action is based on the same principles of hydrophobization and activation.

A distinctive property of the adsorbents developed is an ability to efficiently operate at low temperatures.

Nowadays novel adsorbents based on the activated basalt fiber are developed *(Fig. 5).* We expect to reach the capacity of the fibrous adsorbents up to 20-30 kg of oil per 1 kg of adsorbent. The adsorbent capacity depends on the content of the polymer additive. The additive concentration of about 1 % of an oxidized atactic polypropylene is an optimum one (Fig. 4-5).

Our study has revealed that oxide-hydroxide aluminium phases are effective adsorbents to extract oil products from water solutions and emulsions /3/. Such phases are produced via thermal hydrolysis of electroexplosion nanosized aluminium powders by water at the temperatures from 50 to 70 ^{o}C. Nanosized oxidic adsorbents create an electric potential of 100-150 mV at the phase boundary. This leads to a fast destruction and coagulation of oil microemulsions. The adsorbent particles represent complex structures with a developed surface. The particle size is less than 1 µm. The specific surface is 270-500 m^2/g. The adsorbent consists of the phases as follows: aluminium hydroxide $(Al_2OH)_3$ - 7 %, AlOOH - 47 %, γ -Al_2O_3 - 25 %, α - aluminium oxide Al_2O_3- 21 %. Such adsorbents are successfully applied to purify the wastewater of oil storage depots and wastewater of drilling and oil production.

The isotherms of adsorption of oil, diesel fuel and gasoline are given in Fig. 6. They have a form that is classic for molecular adsorption and are described by Freundlich equation:

$$\mathbf{A=A_{00}bC_0^n,}$$

where A is the adsorption observed (mg per 1 g of adsorbent), A_{00} - is the limiting adsorption, b is a factor, C_0 is the initial concentration, n is degree index (0<n<1). At a given adsorbent-solution ratio the adsorption observed is not high. At the initial concentration (C_0) equal to 20 mg/l the adsorption observed is 0.3-0.8 mg/g. From aqueous solutions the diesel fuel is adsorbed best of all. The lowest adsorption is observed for gasoline. This is connected to the differences in the oil product composition. Low-solubility hydrocarbons, complex molecules, and heteroatomic compounds are best adsorbed from aqueous solutions.

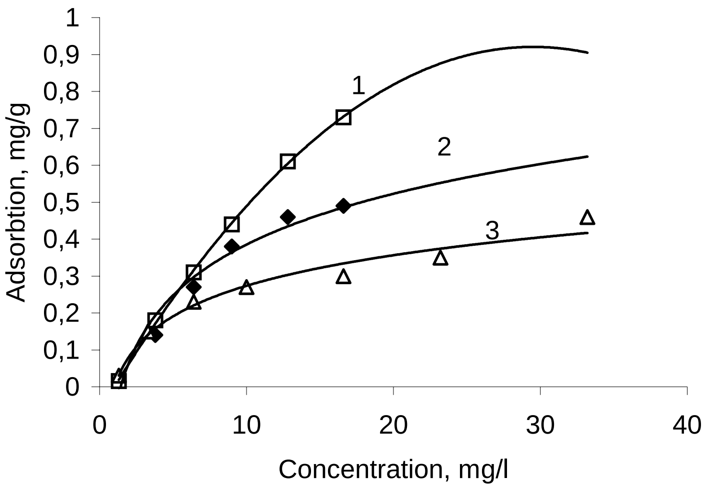

Fig.6 Isoterms of oil products adsorbtion from aqueors solutions.
1 - oil; 2 - disel fuel; 3 - gasoline.

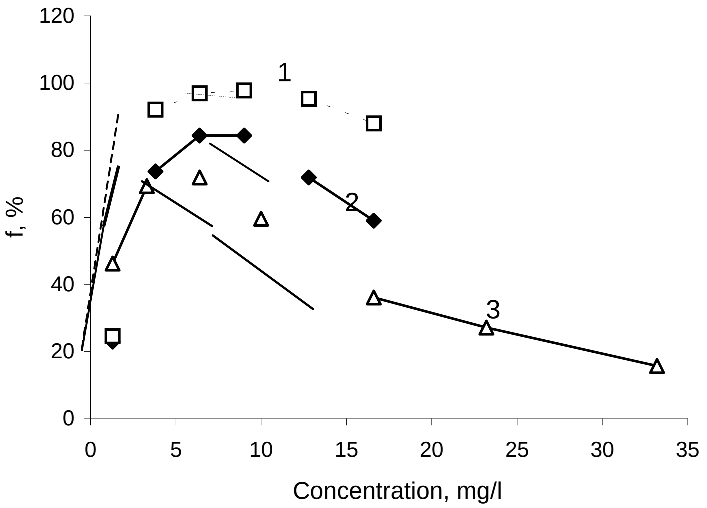

Fig.7. Degree of purification from dissolved oil products versus their initial concentration. 1 – oil; 2 – disel fuel; 3 – gfsoline.

The efficiency of water purification from the oil products are determined by the formula $f=(C_0-C_k)/C_0$. This value reaches 98 % for the solutions of diesel fuel. As seen from Fig. 7, the maximum efficiency for oil and gasoline is 85 and 73 % respectively. The relationship between the purification and the initial concentration for all the oil products has an extreme nature. The maximum is at the concentration of 6-10 g/l. At the concentration of more than 10 g/l the efficiency decreases. This *efficiency* decrease is conditioned by a high residual concentration of soluble compounds. Such compounds form hydrate structures with water. Their content in gasoline is higher than in other oil products.

Fig. 8 shows that the adsorption of oil products from the microemulsions is significantly higher. It reaches 20 mg/g of adsorbent. The concentration of oil products in the micro-emulsions is higher than in the solutions. The adsorption efficiency is comparable for all the types of oil products. The adsorption isotherm from the microemulsions has a linear nature. The difference between the isotherms of adsorption from the solutions and the microemul-sions is connected to the difference in the adsorption mechanisms. Adsorption from the solutions occurs at the molecular level. The microemulsions coagulate under the action of the electric potential of the adsorbent. Due to this fact, the microemulsions are adsorbed on the particle surface in the form of the films (macroadsorption). The *efficiency* of the microemulsions purification is apparently higher than that of the solutions. It less depends on the initial concentration of the oil product in the microemulsions. The highest purification degree (99%) is reached for less soluble motor oil.

The values of the oil product adsorption from the microemulsions strongly depend on the adsorbent-solution ratio (m/V, g/l of the emulsion). With increasing ratio, the value of oil adsorption decreases, and the purification *degree* increases. Nevertheless, the increase in the purification degree has a non-linear extreme nature. This is determined by the interac-tion of 2 factors: the increase in m/V ratio and decrease in adsorption value with increasing m/V ratio. At the m/V value (adsorbent-solution ratio) of 5-6 g/l the purification degree reaches almost 100 %.

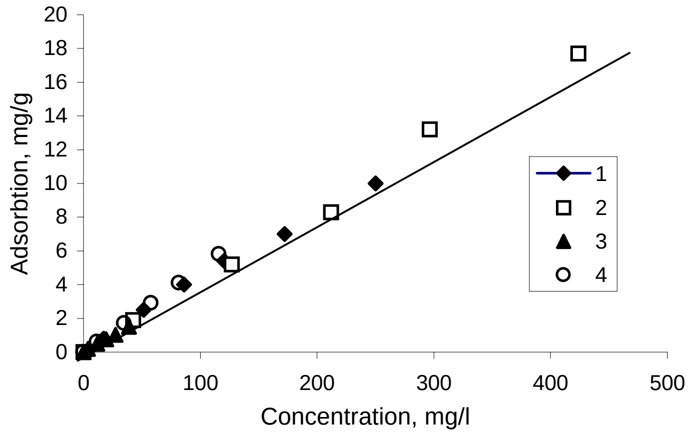

Fig. 8. Generalized isoterm of adsorbtion of oil products from aqueous solutions. 1 – oil; 2 – disel fuel; 3 – gasoline; 4 – industrial oil.

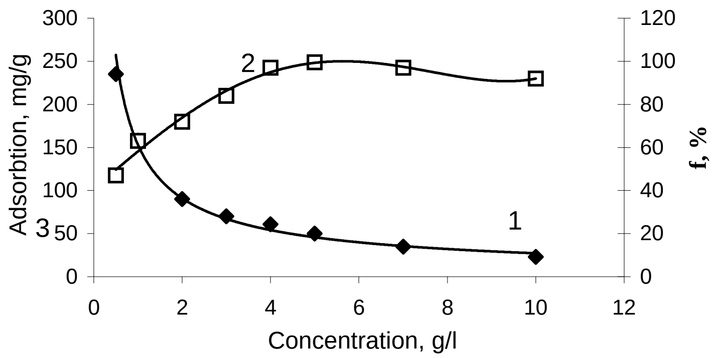

Fig. 9. Influence of adsorbent-solution ratio (m/V) on the adsorbtion rate (1) and degree of water purification (2) 3-calculated adsorbtion value.

The further increase in adsorbent content leads to the decrease in purification degree. The real dependence between the adsorption and the ratio is above the calculated curve (dotted line on Fig. 9). This is explained by a stronger influence of the electric potential of the adsorbent particles with their increasing concentration in the emulsion volume, which provides for a drastic increase in the purification degree at the adsorbent-solution ratios less than 6 g/l. The data of Fig. 9 show that the increase in the adsorbent content from 4 to 10 g/l provides for the purification degree of more than 90%. In general, with increasing adsorbent-solution ratio the purification efficiency increases.

With *increasing* adsorbent-solution ratio the adsorption value decreases. The rate of oil product adsorption by an adsorbent also decreases. At the same time the rate of changes in the concentration of the oil products (purification rate) increases. This is connected to the increase in difference between the initial and the final concentrations. At the adsorbent-solution ratio more than 5 g/l the degree of emulsion purification decreases and the purification rate increases more slowly.
Novel adsorbents based on nanosized powders of oxide-hydroxide phases of aluminium effectively recover solved oil products and coagulate emulsified oil products from aqueous medium. By combining fibrous and powder adsorbents, one may improve the efficiency of the purification. The adsorbents of both types are placed in accordance with 'sandwich' arrangement (Fig. 10). In this case the powder adsorbent quickly adsorbs the components solved and coagulates the emulsions. The fibrous sorbents are the collectors with a high capacity for oil products and accumulate them in the process of filtration through a multilayer column.

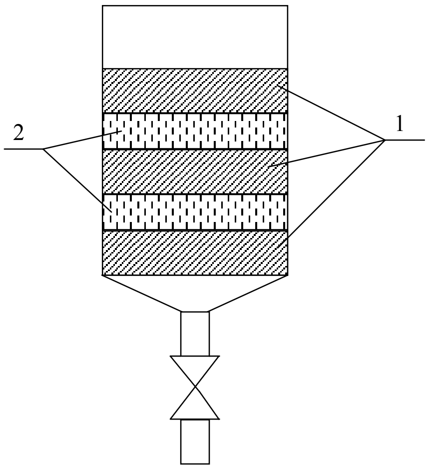

Fig. 10. Multilayer adsorption.
1-fibrous adsorbent, 2-powder adsorbent

In this process scheme it is advisable to use the basalt fiber as a fibrous sorbent. By the contrast to cellulose and other natural vegetable materials, it is not subjected to the action of the microorganisms, it has a higher capacity being significantly cheaper than the carbon fibers.
Adsorption of oil, diesel fuel, and gasoline was studied when passing them through a column containing a multilayered adsorbent made in accordance with the above arrangement.
The oil product emulsions were passed through a column at a rate of 7 l/h. Linear filtration rate was 4.8 m/h. This rate corresponds to the filtration rates applied in practice. The main results are given in Table. These data reveal the differences in the output concentration for various oil products. They are connected only to a different content and water solubility of different components. In all the cases the degree of water purification from oil products is no less than 98-99%. Such purity is reached even at the emulsion concentrations of 1.5-2 g/l. The oil product concentration at the output of the column does not surpass 0.05 mg/l for oil and diesel fuel and 5 mg/l for gasoline. The adsorption isotherm under dynamic

conditions represents a straight line, similarly to Fig. 8. The experimental points for various oil products are located along this line. Adsorption of emulsified oil products occurs in the form of the generation of surface coagulated films of oil products.

Table. Oil products adsorption on multilayered adsorbents

Crude oil		**Diesel fuel**		**High-octane gasoline**	
Oil products concentration, mg/l					
Initial	**Final**	**Initial**	**Final**	**Initial**	**Final**
29	0,05	77	0,05	60	2,92
58	0,05	154	0,05	119	4,21
116	0,05	308	0,05	238	4,93
231	0,05	616	0,08	474	23,44
374	1,01	926	0,73	715	16,11
463	7,30	1233	6,29	953	20,96
694	9,24	1850	18,45	1430	23,45

This principle became a basis for the developed cascade process schemes of the purification of oily sewage. The output concentration of one filter is the initial concentration for the next one. The efficiency of such a purification system may be evaluated using the data of the Table.

The present technology has been commercially applied. At Tomsk oil storage depot a station for sewage purification was built, which has operates successfully. The station consists of 6 units containing a multilayered adsorbent. As the adsorbents are saturated, they are regenerated by steam. The waste formed is used as boiler fuel.

A simulation of the application of this technology for the purification of surface water was carried out. The results evidence that a single water pass via a multilayered column provides for a satisfactory purification degree.

The authors hope that the represented results will be useful at the elimination of the pollution by oil products of the natural environment of Yugoslavia.

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