ФИЗИКО–ХИМИЧЕСКИЕ СВОЙСТВА СОРБЕНТОВ, ИСПОЛЬЗУЕМЫХ В ОЧИСТКЕ ВОДЫ ОТ НЕФТЕПРОДУКТОВ

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Работа посвящена изучению физико-химических и адсорбционных свойств сорбентов искусственного и природного происхождения, загрязнённых нефтепродуктами. В работе определены такие параметры, как сорбционная емкость по нефтепродуктам, водопоглощение и влагосодержание, насыпная плотность, а также параметры, характеризующие сорбционные равновесия в поверхностных слоях (коэффициенты распределения, величины предельной адсорбции, константы Генри, изменения энергии Гиббса, адсорбционные коэффициенты и степени заполнения). Изотермы адсорбции для всех сорбентов имеют практически идентичный характер с ярко выраженным линейным участком в области невысоких концентраций нефтепродуктов и соответствуют изотермам мономолекулярной адсорбции. Сорбционная емкость исследуемых сорбентов варьируется в диапазоне от 10 до 50 мг нефтепродуктов на 1 г сорбента. Максимальной сорбционной емкостью обладает Ol-Ex Hard, относящийся к сORBENT SORB и MG SORB. Выявлено, что поверхность Ol-Ex Hard практически полностью заполнена нефтепродуктом (θ→1), в то время как для шунгита поверхность будет заполнена лишь на 13 %. Показано, что наиболее эффективным для улавливания нефтепродуктов следует считать сorbent Ol-Ex Hard, для которого характерны максимально высокие значения адсорбционных параметров.

Ключевые слова: нефтепродукты, синтетические сорбенты, природные сорбенты, физико-химические свойства

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PHYSICAL AND CHEMICAL PROPERTIES OF SORBENTS USED FOR WASTEWATER PURIFICATION FROM OIL PRODUCTS

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The work is devoted to the study of the physico-chemical and adsorption properties of synthetic and natural sorbents contaminated with oil products. The parameters such as sorption capacity for petroleum products, water adsorption and moisture content, bulk density, as well as parameters characterizing the sorption equilibrium in the surface layers (distribution coefficients, maximum adsorption values, Henry constants, Gibbs energy changes, adsorption coefficients and filling degrees) were determined. Adsorption isotherms for all sorbents are almost identical in character with a pronounced linear region in the region of low concentrations of oil products and correspond to isotherms of monomolecular adsorption. The sorption capacity of the sorbents under study varies from 10 to 50 mg of oil products per 1 g of sorbent. The maximum sorption capacity among the sorbents studied the Ol-Ex Hard possesses. This sorbent belongs to the sorbents of the silicate group and Ol-Ex 82, based on polyurethane. The lowest moisture content is also characteristic for silicate sorbents and does not exceed 0.5 % of their mass. The maximum moisture adsorption is typical for sorbents of SONET Sorb and MGS Sorb. It was revealed that the surface of Ol-Ex Hard is almost completely filled with oil (θ → 1), while for shungite the surface will be filled only by 13%. The most effective for trapping oil products should be considered the sorbent Ol-Ex Hard, for which the highest values of adsorption parameters are characteristic.

Keywords: oil products, synthetic sorbents, natural sorbents, physico-chemical properties

INTRODUCTION

One of the environmental problems of our time is the problem of water pollution and deterioration of water quality, which leads to a reduction in amount of available drinking water. Problems of oil pollution aggravate more and more every year and begin to take on a global scale. Therefore, it is becoming urgent to develop technologies for liquidation of oil product (OP) spills, new technological schemes for wastewater treatment from petroleum hydrocarbons, which must meet modern requirements - to be as accessible, convenient, environmentally safe and economically feasible [1, 2].

One of the effective methods of wastewater treatment from organic compounds is the adsorption method, which allows providing a high degree of purification of industrial wastewater [3, 4]. The advantage of the method is its efficiency (up to 95 %), the possibility of treating wastewater containing several substances, as well as the recovery of adsorbed substances [5, 6].

Traditionally, natural sorbents such as zeolites [7], schungites [8], diatomites, as well as industrial wastes [9-11] and the processing of cellulose-containing agricultural products are used to remove various OP from water. A special category of sorbents is waste wood processing [11-14]. Publications related to the study of the sorption properties of individual sorbents, and also after their modification by a variety of physicochemical methods, are quite numerous [9-15]. The
possibility of modifying inorganic sorbents in a dielectric barrier discharge were demonstrated in [15]. However, there are practically no works in which a wide assortment of sorbents well be explored.

Therefore, the objectives of this work were:

Determination and comparison of the properties of sorbents of different composition;

Study of the physical and chemical properties of sorbents (sorption capacity, moisture content and water absorption, bulk density);

Evaluation of the adsorption equilibrium parameters in the surface layers of sorbents under study: distribution coefficient, maximum adsorption values, Henry's constants, changes in Gibbs energy, adsorption coefficient and degree of filling.

EXPERIMENTAL

Eleven sorbents were chosen as the objects of research, the name and chemical composition of which is presented in Table 1.

The choice of sorbent data for the study is due to their availability, as well as relatively wide application in various sectors of the economy. Model OP solution is prepared by mixing a certain volume of M-8B motor oil and distilled water.

Conditions of the experiment were: the initial concentration of oil products (C0) varied in the range of 10-700 mg/l, the volume of the solution of OP (V0) – 100 ml, the mass of the sorbent (m) was 2 g.

Table 1

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oi-Ex 82</td>
<td>Polyurethane (90 %)</td>
</tr>
<tr>
<td>SCN-Sorb</td>
<td>Cellulose (95 %)</td>
</tr>
<tr>
<td>ECOLAN</td>
<td>Pyrolysis product of wood (92-95 %)</td>
</tr>
<tr>
<td>CTR-Sorb</td>
<td>SiO2 (75-80 %), Al2O3 (13.1-15 %)</td>
</tr>
<tr>
<td>MGS-Sorb</td>
<td>SiO2 (47-50 %), Al2O3 (22.5 %), FeO3 (27 %)</td>
</tr>
<tr>
<td>SMD-Sorb</td>
<td>SiO2 (92 %), Al2O3 (6 %)</td>
</tr>
<tr>
<td>Natural zeolite</td>
<td>SiO2 (80 %), Al2O3 (13.1 %)</td>
</tr>
<tr>
<td>Natural schungite</td>
<td>C (26-30%), SiO2 (40.3 %), Al2O3 (2 %), Fe (26.9 %)</td>
</tr>
<tr>
<td>Oi-Ex Hard</td>
<td>SiO2 (80 %), Ca (1.9 %), Fe (2.42 %), Al2O3 (10.2 %), C (5 %)</td>
</tr>
<tr>
<td>VST-Sorb</td>
<td>Vermiculite (SiO2 (37.2 %), Al2O3 (6.2 %), CaO (15.3 %), FeO3 (19 %), MgO (13.1 %))</td>
</tr>
</tbody>
</table>

The concentration of oil products were determined by a fluorometric method, based on the extraction of OP from the sample by a low-polar solvent (hexane) and measuring the fluorescence intensity of the extract with the "Fluorate-02" fluorometer (Russia) [16].

Sorption capacity of sorbents was calculated by the formula:

\[ J_i = \frac{V_0 (C_0 - C_i)}{m} \text{ mg/g}, \]

where \( J_i \) – sorption capacity, mg/g; \( V_0 \) – the volume of the sample of the OP model solution, passed through the sorbent, l; \( C_0 \) and \( C \) – the initial and final concentrations of OP, respectively, mg/l; \( m \) – the mass of the sorbent sample, g.

The adsorption isotherms were constructed in the following coordinates:

\[ Q_s = f (Q_3) \]

where \( Q_s \) is the equilibrium concentration of OP after passing through the sorbent, mg/l, \( Q_3 \) is the sorption capacity of the sorbent, mg/g.

It should be noted that in the adsorption theory, the sorption capacity can be considered in terms of physical meaning as excess adsorption \( \Gamma_a \) which corresponds to the number of adsorbate moles determined by the excess concentration of the substance in the surface layer as compared to the bulk phase. In this paper, when discussing the experimental data, we used the values of the sorption capacity for OP.

For the correct determination of the thermodynamic equilibrium parameters, a transition to the total adsorption values \( \Gamma_a \) is necessary. Since the adsorption processes were realized in the region of relatively low concentrations of petroleum products, at these conditions the values of excess adsorption will not significantly differ from the total adsorption.

As additional information on the parameters of adsorption interactions, the \( K_a \) oil product distribution constants were found from the experimental data as the ratio of the excess adsorption to the equilibrium concentrations of oil in the solution. The statistical analysis carried out has showed that the average errors of excess adsorption are 6-9 % of the measured values [17].

Obviously, OPs will be sorbed on centers of a solid surface, which can be occupied by solvent molecules. Thus, adsorption will proceed along a competitive mechanism by displacing solvent components adsorbed on active sites. The interface is inert at the same time and does not enter into a chemical interaction with petroleum products. The specific surface area of the solid sorbent does not change during the process, therefore adsorption will occur in the monomolecular adsorption layer, and the monolayer capacity remains constant.

Formal processing of the obtained adsorption isotherms for all samples of sorbents was carried out within the framework of the Langmuir monomolecular adsorption model. The numerical values of the adsorption coefficients \( b \), and the limiting adsorptions \( a_m \), quantitatively characterizing the adsorption equilibria, were determined by the standard method in the linear coordinates of the Langmuir isotherm.
In addition, the values of Henry H constants were determined, which according to the physical meaning coincide with the thermodynamic coefficients of the distribution of adsorbate at low concentrations of dissolved substances [18].

Within the framework of formal processing, the maximal fillings of the surface \( \theta \) were calculated from the adsorption values \( a_i \) and the determined limiting adsorption \( a_{\text{m}} \) for every sorbent.

In addition, the known thermodynamic relationships determine the change in the Gibbs energy \( \Delta G^{\circ}(\theta) \) during the adsorption under the experimental conditions [18].

Water absorption was determined by the ratio of the mass of absorbed water to the mass of the sorbent spent on sorption.

The moisture content of the sorbents is determined by the procedure when the sample is dried in a drying box to constant weight and the product weight is determined. The mass fraction of water is expressed as a percentage [19].

DISCUSSION

The sorption process under dynamic conditions consists in filtering the sewage through the sorbent bed. This method has great technological, operational and economic advantages over sorption in static conditions. Sorption under dynamic conditions allows more complete use the capacity of the sorption material [18]. Therefore, the study of characteristics and properties of sorbents was the carried out precisely under dynamic conditions.

The results of experiments on the effect of the initial concentration of OP in the model solution on the sorption capacity of the sorbents are the shown in Fig. 1-3.

The results of the measurements show that the sorption capacity for sorbents SONET-Sorb, Ecolan, and SCN-Sorb in the range of OP concentrations under study is close and maximum value is 50 mg/g (Fig. 1).

The sorbents Ol-Ex Hard, Ol-Ex 82 and VST-Sorb do not reach the saturation limit in the investigated range of OP concentrations, in contrast to schungite, which at the initial concentration of OP in the model solution of 300 mg/l reaches the saturation limit, i.e. at OP concentration above given value, its use for purification of natural and wastewater is not advisable.

Fig. 3 shows the results of experiments on the effect of the initial concentration of OP in the solution on the sorption capacity of sorbents MGS-Sorb, CTR-Sorb,
zeolite and CMD Sorb, belonging to the group of silicate sorbents. The most effective sorbent for waste-water treatment is Sorbent CTR-Sorb, with a maximum sorption capacity of 30 mg/g.

The obtained isotherms for all sorbents have almost identical character with a pronounced linear region in the region of low concentrations and correspond to isotherms of monomolecular adsorption.

The experiments showed that the sorption capacity of the investigated sorbents varies from 10 to 50 mg/g per 1 g of sorbent. Ol-Ex Hard and Ol-Ex 82 are also the sorbents with the highest adsorption capacity of 30 mg/g.

The minimum water adsorption (0.08 g/g) has been observed for sorbent CN – Sorb and it was 10 g/g. The hydrophobic sorbents are sorbents of the silicate group. The minimal water adsorption (0.08 g/g) has been observed for schungite. Ol-Ex Hard is characterized by a high adsorption capacity and the maximum water content is also characteristic for silicate sorbents and does not exceed 0.5% of their mass. The maximum moisture adsorption is typical for SONET Sorb and MGS sorb.

The moisture content of the sorbents is presented in Table 2. The lowest moisture content is also characteristic for silicate sorbents and does not exceed 0.5% of their mass. The maximum moisture adsorption is typical for SONET Sorb and MGS sorb. It should be noted that the humidity of all the samples studied, in addition to the SONET Sorb sorbent, did not exceed 1%, which corresponds to the regulatory requirements imposed on them and allows them to be used as sorbents in water treatment and water treatment processes [19].

The bulk density of sorbents along with the sorption capacity is one of the main characteristics of sorption materials, and was also one of the criteria for choosing the further object of research. It was determined by [20], and the result is shown in (Table 2).

<table>
<thead>
<tr>
<th>Name</th>
<th>Bulk sorbent density, kg/m²</th>
<th>Moisture contents, %</th>
<th>Water adsorption, g/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SONET Sorb</td>
<td>334</td>
<td>1.04</td>
<td>0.69</td>
</tr>
<tr>
<td>Ol-Ex 82</td>
<td>150</td>
<td>0.33</td>
<td>0.57</td>
</tr>
<tr>
<td>SCN-Sorb</td>
<td>50</td>
<td>0.22</td>
<td>10</td>
</tr>
<tr>
<td>ECOLAN</td>
<td>250</td>
<td>0.35</td>
<td>0.75</td>
</tr>
<tr>
<td>CTR-Sorb</td>
<td>674</td>
<td>0.4</td>
<td>0.86</td>
</tr>
<tr>
<td>MGS-Sorb</td>
<td>1100</td>
<td>0.84</td>
<td>0.5</td>
</tr>
<tr>
<td>SMD-Sorb</td>
<td>420</td>
<td>0.06</td>
<td>1.63</td>
</tr>
<tr>
<td>Natural zeolite</td>
<td>700</td>
<td>0.39</td>
<td>0.43</td>
</tr>
<tr>
<td>Natural schungite</td>
<td>412.5</td>
<td>0.05</td>
<td>0.42</td>
</tr>
<tr>
<td>Ol-Ex Hard</td>
<td>1500</td>
<td>0.34</td>
<td>0.08</td>
</tr>
<tr>
<td>VST-Sorb</td>
<td>112</td>
<td>0.52</td>
<td>5.61</td>
</tr>
</tbody>
</table>

The results of formal processing of the obtained adsorption isotherms for all sorbent samples are presented in Table 2.

The results of calculations show that the distribution coefficients for most sorbents are in the range of 0.1-0.7. In the sorbent Ol-Ex Hard, the $K_d$ value is maximal and exceeds the other sorbents. In schungite sorbents and SONET Sorb, the $K_d$ value is minimal.

It is also interesting that a similar regularity can be traced in analyzing the maximum degree of filling of the surface of sorbents. So, the surface of Ol-Ex Hard is almost completely filled with oil product ($\theta \to 1$), while for shungite the surface will be filled only by 13%.

It should be noted that for all sorbents, certain values of $\theta$ are consistent with the stated assumption about the monolayer nature of adsorption.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Coefficient of distribution $K_d$</th>
<th>Maximum adsorption $a_{\text{max}}$, mg/g</th>
<th>Adsorption coefficient $b$</th>
<th>Henry's $H$ constant</th>
<th>Gibbs energy change $\Delta G$, kJ/mol</th>
<th>Maximum degree of filling $\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural zeolite</td>
<td>0.23</td>
<td>8.87</td>
<td>0.005</td>
<td>0.04</td>
<td>13.38</td>
<td>0.58</td>
</tr>
<tr>
<td>Natural schungite</td>
<td>0.033</td>
<td>14.68</td>
<td>0.0037</td>
<td>0.054</td>
<td>13.87</td>
<td>0.39</td>
</tr>
<tr>
<td>SMD-Sorb</td>
<td>0.56</td>
<td>20.49</td>
<td>0.006</td>
<td>0.123</td>
<td>12.67</td>
<td>0.7</td>
</tr>
<tr>
<td>SCN-Sorb</td>
<td>0.44</td>
<td>68.03</td>
<td>0.0091</td>
<td>0.621</td>
<td>11.64</td>
<td>0.52</td>
</tr>
<tr>
<td>Ol-Ex 82</td>
<td>0.12</td>
<td>5.72</td>
<td>0.0469</td>
<td>0.269</td>
<td>7.57</td>
<td>0.66</td>
</tr>
<tr>
<td>ECOLAN</td>
<td>0.28</td>
<td>13.3</td>
<td>0.0365</td>
<td>0.486</td>
<td>8.2</td>
<td>0.75</td>
</tr>
<tr>
<td>SONET Sorb</td>
<td>0.06</td>
<td>23.7</td>
<td>0.003</td>
<td>0.066</td>
<td>14.53</td>
<td>0.13</td>
</tr>
<tr>
<td>MGS-Sorb</td>
<td>0.14</td>
<td>20.62</td>
<td>0.0105</td>
<td>0.2165</td>
<td>11.28</td>
<td>0.8</td>
</tr>
<tr>
<td>CTR-Sorb</td>
<td>0.31</td>
<td>8.79</td>
<td>0.2065</td>
<td>1.815</td>
<td>3.91</td>
<td>0.87</td>
</tr>
<tr>
<td>Ol-Ex Hard</td>
<td>33.27</td>
<td>55.25</td>
<td>0.588</td>
<td>32.47</td>
<td>1.315</td>
<td>0.99</td>
</tr>
<tr>
<td>VST-Sorb</td>
<td>0.68</td>
<td>22.37</td>
<td>0.06</td>
<td>1.34</td>
<td>6.98</td>
<td>0.7</td>
</tr>
</tbody>
</table>
The values of the limiting adsorption, calculated from the linear coordinates of the Langmuir isotherm, range from ~6 to ~70 mg/g of the sorbent. The values obtained agree with the experimental data on sorption capacity of sorbents. The maximum value of the limiting adsorption is observed for the SCN-Sorb and is 68 mg/g. But, a high value of am combined with the relatively low value of the adsorption coefficient and the average value of the degree of surface filling do not allow us to consider the SCN-Sorb as the most preferred sorbent for extracting petroleum products.

Adsorption coefficients, which are the meaning of the adsorption equilibrium constants, for most sorbents have relatively low values. The maximum value of the sorbent is 0.59 belongs to the sorbent OI-Ex Hard. The changes in the Gibbs energies calculated in terms of the magnitude of the coefficients b have positive values during adsorption. The nature of the change in Henry's constants is similar to that for adsorption coefficients.

The reason for this is probably related to the influence of the different degree of dispersion of the sorbents studied on the corresponding parameters of adsorption equilibrium.

CONCLUSION

Thus, by analyzing exclusively the adsorption characteristics of the samples studied, it can be concluded that most of the sorbents can be used to extract petroleum products. However, in our opinion, the most suitable is the sorbent OI-Ex Hard, for which the highest values of adsorption parameters are observed.

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REFERENCES


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