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STATICS OF ADSORPTION OF ANIONIC SURFACTANTS

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Abstract. The paper presents the results of the study of the statics of adsorption of surface-active substances from model solutions by activated carbon and zeolite. The results of photometric determination of the concentration of anionic surfactants before and after adsorption are presented. The results of adsorption capacity calculations are presented. The experimental results using the program (Langmuir 1.03) were numerically calculated. Sorption isotherms of sodium dodecyl sulfate indicate the mechanism of monomolecular physical adsorption. A good convergence of experimental data and theoretical calculations were established, the coefficient of determination $R^2>0.9$, the value of the Chebyshev criterion $9·10^{-4}$ ... $2·10^{-4,}$ and the root mean square deviation equal to 0 were established.

Keywords: adsorption, activated carbon, zeolite, wastewater, surfactant, sodium dodecyl sulfate

1. Introduction

Today, statistics show that more than 5 % of the global chemical industry is made up of manufacturers, surfactants (Liu et al., 2021). At the same time, the most significant number of surfactants used in the production of various products and materials are anionic surfactants.

They are widely used in everyday life, the textile industry, the production of polymer materials and plastic masses, pharmaceuticals, detergents, cosmetics and disinfectants. The use of surfactants in the oil refining and mining industry is associated with losses of reactants due to rock adsorption. The mass use of APAR leads to significant environmental problems primarily due to their contamination of surface and underground waters, the death of fish and aquatic fauna, and the impact of these substances on human populations. Therefore, the maximum permissible concentration of them in water samples was established – 0.1 mg/dm^3 (Liu et al., 2021; Somasundaran et al., 1964). This requires sufficiently sensitive methods that would provide fast and reliable control of the content of APAR in various samples. Surfactants are used in almost all industries as detergents, plasticizers, emulsifiers, etc. Their main function is to reduce the surface tension at the phase interface. Depending on the dissociation method, anionic surfactants (detergents), cationic surfactants, and nonionic surfactants are distinguished. The most polluted are municipal and household wastewater, the share of which is 15–20 % of all categories of wastewater (Yekeen et al., 2017; Amirianshoja et al., 2013). The main danger of the ingress of surfactants is that the content of surfactants in detergents is about 15 %, and the estimated concentration in the drains may exceed 0.6 kg/m^3. The MPC of surfactants in water is 0.025 kg/m ^{3}. Sodium dodecyl sulfate decomposes only by 80 %. Therefore, surfactants accumulate in the environment, which leads to a change in the surface tension of water and other consequences caused by the specific action of these substances.

Therefore, taking into account the above, the development of wastewater treatment technology

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for municipal and household enterprises is relevant (Yekeen et al., 2019).

Surface-active substances (surfactants) are widely used in economic activities and everyday life as detergents, anti-corrosion substances, emulsifiers and suspenders of pesticides in the production of mineral fertilizers and feed additives, components of medicines and cosmetics. Important indicators of the safety levels of surfactants in everyday life revealed the ability to absorb into fabrics, wash off dishes and cause allergic reactions. Thus, anionic and cationic surfactants, compared to nonionic surfactants, are more absorbed by tissues, but the addition of nonionic surfactants to the agent reduces the absorption of anionic surfactants by tissues by 2–3 times.

A comparative study of the washing of surfactants showed that the bulk of their mass is removed from the walls of dishes after the first rinse, but anionic and cationic surfactants are washed off worse than nonionic surfactants.

As for the ability to cause allergic reactions, the dependence of the occurrence of possible allergic reactions on the increase in the percentage of surfactant concentrations was found.

The ecological aspects of the use of surfactants extend to the cleaning of the water surface from oil and oil products, as well as cleaning the air in mines. Practically the entire planet's population comes into contact with surfactants, the number of which in the environment is increasing yearly (Sabadash et al., 2020). The intensive use of synthetic surfactants causes pollution, which can be compared with oil pollution of the World Ocean and with oil and pesticides – in soil and water. The problem of preventing environmental pollution with detergents is global (Soudejani et al., 2019; Peng et al., 2020).

The authors (Peng et al., 2020) used molecular dynamic modelling to explain the counterion effect during surfactant adsorption.

The work aimed to study the adsorption capacity of carbon and aluminosilicate materials concerning surfactants. In addition to synthetic ones, surfactants of biological nature are known, which are formed in living organisms and take an active part in their functioning. Determining the content of biosurfactants, and studying the interaction of humans and animals with synthetic and plant surfactants in the environment, has important theoretical and practical significance for modern hygiene, environmental biochemistry and physiology.

2. Experimental part

To determine the adsorption capacity of zeolite concerning surfactants, 200 cm^3 of a solution of sodium dodecyl sulfate. This solution was prepared in distilled water at different initial concentrations (C = 0.025–3.5 mg/dm^3), placed in glass flasks, and the same amount of sorbent was added (~1 d). The flasks were hermetically sealed and left with periodic stirring for two days at a temperature of +20 °C. The sorbent was separated from the solution, and the solution was analyzed for surfactant content by a photometric method (Sabadash et al., 2018) – the range of surfactant concentrations corresponded to the volume of their entry into municipal and industrial wastewater.

The adsorption method of surfactant extraction was chosen for conducting research, which allows for the extraction of trace concentrations of pollutants. Sodium dodecyl sulfate is an anionic surfactant, so the radical have surface-active properties. Activated carbon, which can absorb carbon radicals, as well as zeolites, was chosen as a sorbent.

Experimental studies of changes in surface tension during the adsorption of surfactants were carried out only on activated carbon. The surfactant molecules cause a change in the structure of the surface layer of the “solution-gas” separation boundary in comparison with the “water-gas” boundary. Furthermore, as a result, there is a decrease in the surface tension σ $E_{H_2O-\mu'''} > E_{H_2O-H_2O}$. The Duclos-Traube rule was used to estimate the surface activity of aqueous solutions of diphilic substances (alcohols, acids, amines, etc.) at 20°C. According to him, starting from the third member of the homologous series of surfactants, the surface activity increases by an average of 3.2 times when the hydrocarbon chain increases by the group ($-CH_2-$). At temperatures higher than room temperature, the coefficient of 3.2 decreases, approaching 1.

The Shyshkovsky equation well describes the adsorption isotherm.

$$\sigma = \sigma_o - B \cdot ln (1 + As),$$

where *A* and *B* are constants; *c* is surfactant concentration.

Type 3 isotherm is typical for solutions of micelle-forming surfactants. There are several ways to determine the surface tension of liquids experimentally. The stalagmometric method, the ring separation method, and the plate separation method can be named among the most common methods.

This work uses the maximum gas bubble pressure method to determine *σ*.

3. Results and Discussion

The results of experimental studies of the dependence of surface tension on the concentration of sodium dodecyl sulfate are presented in Fig. 1.

Fig. 1 clearly shows the dependence of the change in the surface tension of the solutions on the concentration in the ranges typical for municipal wastewater.

These results are consistent with the Collins law regarding the affinity of the adsorbate with water. Thus, large counterions of ionic surfactants increase surface adsorption and decrease the surface tension of solutions (Peng et al., 2020).

Dodecyl sulfate was calculated from the change in surface tension after adsorption.

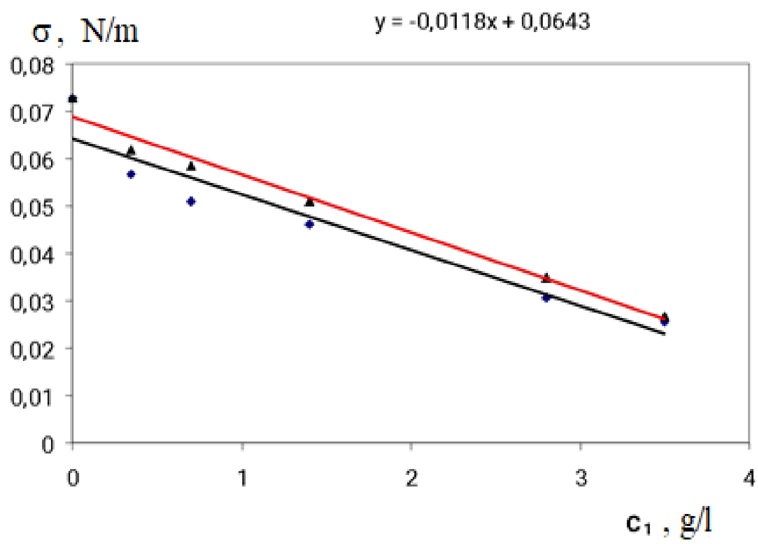

Fig. 1. Dependence of the surface tension of sodium dodecyl sulfate solution on the initial concentration of the surfactant solution, where ♦ surface tension of solutions before adsorption, ▲the surface tension of solutions after adsorption (activated carbon)

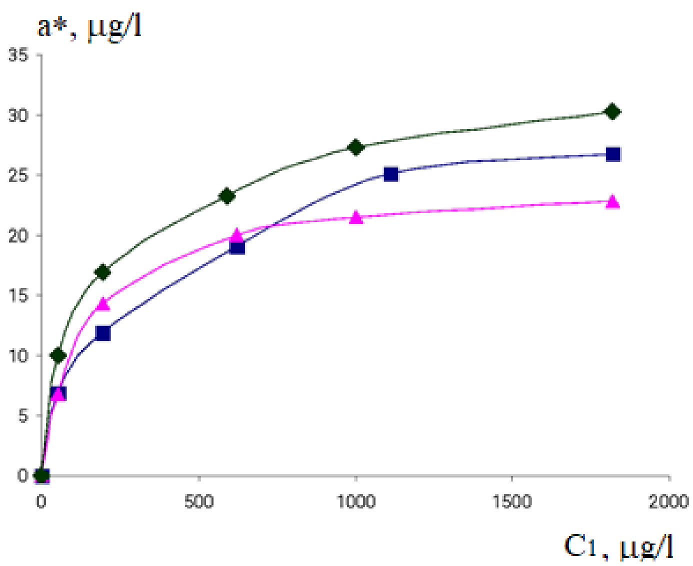

Fig. 2. Adsorption isotherm of sodium dodecyl sulfate on:
♦ – activated carbon; ■ – synthetic zeolite based on fly ash of Dobrotvirskaya CHP;
▲ – clinoptilolites of the Sokyrnytsky deposit

Analyzing Fig. 1 shows that activated carbon better absorbs sodium dodecyl sulfate. This is explained by the fact that lactic acid molecules have a carbon radical, which shows an affinity for non-polar sorbents, that is, for activated carbon (Sabadash et al., 2018). On mineral sorbents, in particular, on clinoptilolite of the Sokyrnytsky deposit, adsorption takes place with the participation of hydrophilic groups – –OH and -COOH. We assume that dodecyl sulfate is the only type of ions in the solution. The only mechanism of adsorption is valence ion bridging to the negatively charged surface areas of the zeolite.

Vanderwaal's adsorption of neutral surfactant complexes and adsorption of positively charged surface areas are not characteristic for concentrations above 1 g/dm^3 when the sorption capacity decreases, which causes by the formation of surfactant micelles. Mechanically, the adsorption process can be explained as follows. When introducing a surfactant solution at a concentration higher than the CMC, surface-active substances are present in the form of monomers and aggregate into surfactant micelles. When the solution is in contact with the surface, monomers can be adsorbed on the surface-bound by Ca^{2+}. The micelles dissociate by supplying additional monomers to the solution. According to the CMC, this mechanism maintains the same monomer concentration in the solution. The surfactant concentration falls below the CMC at the flood front, and an equilibrium establishes between monomers, available Ca^{2+} and surface sites. When the surface-active substance solution reaches the exit hole of the core, and the adsorption is completed, an equilibrium is reached between the monomers – with their concentration in the CMC, since Ca^{2+} is also present in the micelles – and the surface areas. This process was confirmed by an increase in the pH of the investigated solutions. Since the mass fraction of the hydrophobic radical is significantly higher than the functional groups, sorption is better on activated carbon.

The results of adsorption capacity calculations are presented in Table 1. The results of the experiment were numerically calculated using the program (Langmuir 1.03).

Good convergence of experimental data and theoretical calculations was established.

Table 1

The results of the numerical calculation of the Langmuir isotherm parameters for the experimental data on the adsorption of surfactants by different types of sorbents

The name of the substance	Constants of the Langmuir equation	The method of least squares	Selection according to the Chebyshev criterion	Selection by squared deviation
Natural zeolite	K	13.81	13.81	17.15
	G	0.04	0.04	0.04
	Chebyshev criterion	$9{\cdot}10^{-4}$	$7{\cdot}10^{-4}$	$7{\cdot}10^{-4}$
	Sum of squared errors	0.00	0.00	0.00
Synthetic zeolite	K	14.81	14.81	15,15
	G	0.06	0.06	0.06
	Chebyshev criterion	$9{\cdot}10^{-4}$	$7{\cdot}10^{-4}$	$7{\cdot}10^{-4}$
	Sum of squared errors	0.00	0.00	0.00
Activated coal	K	12.07	12,23	12.39
	G	0.065	0.063	0.062
	Chebyshev criterion	$2{\cdot}10^{-4}$	$2{\cdot}10^{-4}$	$2{\cdot}10^{-4}$
	Sum of squared errors	0.00	0.00	0.00

4. Conclusions

Prospects of wastewater treatment from surface-active substances were investigated. The sorption capacity of activated carbon and zeolites to sodium dodecyl sulfate under static conditions was established. The value of the surface tension of the model solutions was determined. Experimental studies showed that activated carbon is a reasonably effective sorbent, but considering its high cost, aluminosilicates – synthetic and natural zeolites - can be preferred.

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