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## Adsorption of industrial wastewater from oil products with application of mathematical modeling

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**Abstract.** The granulated hydrophobic sorption material created on the basis of the chemical water treatment sludge of thermal power plants "SM-5" is studied. The information basis obtained in the experiments on the kinetics of adsorption makes it possible to model the dynamics of adsorption in a fixed bed of "SM-5" granules.

Nowadays one of the leading branches of the industrial sector of the Republic of Tatarstan is the chemical and petrochemical industry, where a significant amount of wastewater is formed. The more efficient and environmentally friendly methods of wastewater treatment are required because of the increasing the requirements for the permissible discharge of wastewater.

Different methods of wastewater treatment are used to reduce the anthropogenic impact on water resources. One of the methods of the dissolved oil wastewater treatment is adsorption on activated carbons of different types. Industrial-produced sorbents are expensive (several hundred thousand rubles per ton). Therefore, developments of finding the new cheap sorption materials based on waste production and modeling these processes are of great scientific and practical importance.

In the early works [1, 2], granulated hydrophobic sorption material "SM-5" was obtained. This material was create on the basis of the chemical water treatment sludge of thermal power plants and was used for the oily wastewater treatment at the enterprises of the chemical and petrochemical complex. The creation of granules was consisted of the following stages: heat treatment at 700 ° C for 60 minutes, granulation of material to optimal particle size of 0.5-2.5 mm, impregnation with 5% aqueous emulsion "GKZh-94M" at a ratio of 1: 2 with a binder, drying at 150 ° C for 60 minutes. The bulk density of resulting material was a 536 kg / m<sup>3</sup>, a total pore volume of 0.57 cm<sup>3</sup> / g, an average granule size of 0.5 to 2.5 mm, an abrasion resistance of 68% (mass), a moisture capacity of 0,9% (mass), buoyancy - 99% (mass) / 96 h.

The mechanism and kinetic of dissolved oil adsorption onto the "SM-5" granules under static and dynamic conditions are studied. The adsorption isotherm under static conditions is obtained. The efficiency of oily wastewater treatment under dynamic conditions simulating an industrial adsorption filter is determined.

The model case of isothermal adsorption without temperature effects is considered. A model solution with an oil product concentration (OP) of 1.35 mg / dm<sup>3</sup> is passed through the adsorbent layer of length x. This concentration is the average at the inlet to the adsorption filters in wastewater treatment systems from the OP. The height of the "SM-5" layer is 20 cm, the weight is 54.38 g, the filtering speed is 3.5 m / h. Inadequate cleaning efficiency of OP is fixed at a concentration of 0.1 mg / dm<sup>3</sup>. The initial concentration is denoted by C<sub>0</sub>, the specific water velocity per unit section of the



adsorbent is denoted by  $w$ . These parameters are kept constant. In addition, we assume that the concentration of OP in the adsorbent before the start of the experiment is zero.

The basic system of assumptions is formulated. The change of the flow density of wastewater due to the loss of OP can be neglected. Flow in the filter has the same direction at a constant speed. The flow of wastewater through the filter will be considered as a pseudobinary mixture consisting of water and OP. The sorption layer is considered to be a continuous porous body. The presence of only OP in wastewater leads to a decrease of sorption of other components. Components with a less than 0.1% are not considered.

In this case, the dynamics of adsorption can be described by the equation of the material balance between the solid and liquid phases, the kinetics of the impurity transfer process from the liquid to the adsorbent grains and the adsorption isotherm.

The total material balance describing the adsorption process in the form of a nonlinear partial differential equation is considered (1) [3]:

$$\rho_b \frac{\partial a}{\partial \tau} + w \frac{\partial c}{\partial x} + \varepsilon \frac{\partial c}{\partial \tau} - \varepsilon D^* \frac{\partial^2 c}{\partial x^2} = 0, \quad (1)$$

$a$  – adsorption, kg / kg;  $c$  – current concentration of OP in the flow, kg / m<sup>3</sup>;  $\tau$  – time, s;  $w$  – velocity of the liquid flow, m/s;  $x$  – coordinate depending on the height of the adsorbent bed, m;  $\varepsilon$  – porosity of the sorbent;  $D^*$  – the longitudinal diffusion coefficient with molecular diffusion and convective mixing along the layer, m<sup>2</sup> / s;  $\rho_b$  – bulk density, kg / m<sup>3</sup>.

The equation of the kinetic of the adsorption process is written in the form (2):

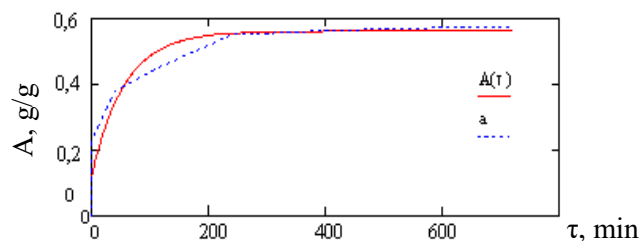
$$\rho_b \frac{\partial a}{\partial \tau} = \beta_i (c - c^*), \quad (2)$$

$\beta_i$  – mass-transfer coefficient, s<sup>-1</sup>;  $c^*$  – equilibrium OP concentration, kg / m<sup>3</sup>. The equation of the adsorption isotherm is in the form (7):

$$a = f(c^*). \quad (3)$$

Differential equations of mass transfer in a granular layer are solved with initial and boundary conditions:  $\tau = 0$ ;  $0 \leq x \leq L$ ;  $c = 0$ ;  $a = 0$ ;  $T = T_0 = \text{const}$ . The boundary conditions for  $x = 0$  are written in the form:  $\tau > 0$ ;  $x = L$ ;  $c = c_0 = \text{const}$ ;  $a = a(\tau)$ ;  $T = \text{const}$ .

The obtained data on the adsorption capacity were used to construct the kinetic curve of adsorption (Fig. 1).

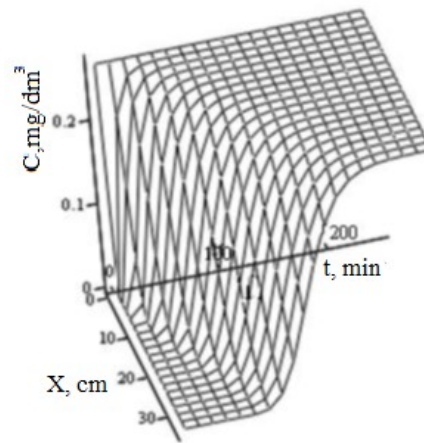


**Figure 1** – Kinetic curve of OP adsorption on SM-5 material:  $a$  - experimental data,  $A(\tau)$  - approximation by exponential dependence

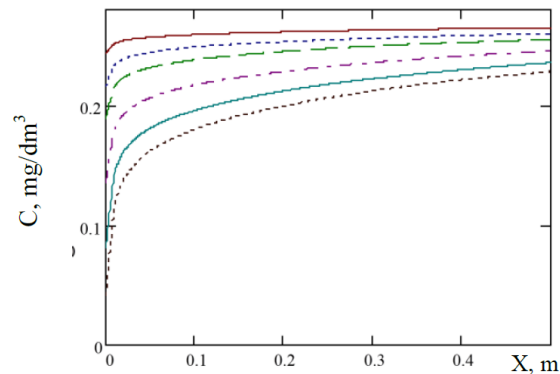
The mathematical model equations were solved by the iterative method.

The solution of the system of differential equations (1) - (3) is the determination of the OP concentration in the flow.

In each differential element of the SM-5 layer a surface that reflect the change in concentration both in the layer and in time is formed during the calculation of material balance of the adsorption process. In calculations absorption kinetic of the OP from the wastewater is considered (Fig. 2). The concentration dependences of the adsorbed OP in the sorbent layer is identified from the particular solution of the equations system.



**Figure 2** – Concentration dependence on layer height and contact time



**Figure 3** – Concentration distribution of the OP in the sorbent layer

The adsorption isotherm has a convex form (the L-type isotherm). The convex isothermal line is of type I according to the BET classification and indicates the presence of micropores in the adsorbent.

In the case of longitudinal diffusion two factors have a place simultaneously. The first factor causes dilution of the adsorption front. The second factor is related to the type of isotherm. The coefficient  $D^*$  is found experimentally.

The convex adsorption isotherm shows the adsorption of OP on the surface of the sludge granules. Let's consider the motion of two points of the adsorption front  $C_1$  and  $C_2$ , with  $C_2 > C_1$ . The derivative of the isotherm is  $f'(C_1) > f'(C_2)$ , so the point with the concentration of  $C_2$  should move faster than the point with the concentration  $C_1$ . But the saturation of the layer at the  $C_2$  concentration should be preceded by the saturation of the layer  $C_1 > C_2$ . As a result, the front along the layer should become stronger.

But these simulations refer to the model situation in the reactor of ideal displacement without the front blurring. In practice, the final adsorption rate and the inhomogeneity of the layer, inevitably leads to a smearing of the adsorption front. In this case the adsorption kinetics is defined by the equations:

$$\rho_b \frac{da}{d\tau} = \beta_{\text{liq}}(c - c^*), \quad (4)$$

$$\rho_b \frac{da}{d\tau} = \beta_{\text{sol}}(a^* - a). \quad (5)$$

$\beta_{\text{liq}}$ ,  $\beta_{\text{sol}}$  – coefficients of external and internal mass transfer;  $c$  – is the concentration in the flow outside the grain;  $c^*$  – the concentration at the external surface, which is in equilibrium with the amount of adsorption in the grain volume;  $a$  – adsorption;  $a^*$  – equilibrium adsorption in the flow.

When the process is limited by external diffusion formula (4) and when the process is limited by internal diffusion formula (5) are used.

The information basis obtained in the experiments on the kinetics of adsorption makes it possible to model the dynamics of adsorption in a fixed bed of "SM-5" granules. It is implemented on the basis of the material balance equations in partial derivatives and the subsequent approximation using the built-in functions of various computational programs.

## Reference

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