Development of a Resource-Saving Technology for Utilization of Caprolactam Production Wastewaters

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Abstract

A technology for utilization of caprolactam production wastewaters has been developed. The equilibrium, kinetics, and dynamics of caprolactam adsorption from wastewaters using AG-5, BAU, AG-OV-1, and SKD-515 industrial active carbons have been studied. Optimization of the sorption filter regime was carried out by calculating the output curves based on the equilibrium adsorption layer model in the region of the linear absorption isotherm using the constants of the Dubinin - Raduszkiewicz equation, the kinetic data, and the mathematical balance equation.

Caprolactam production is accompanied by sap steam condensation, the condensate containing up to 500 mg/dm^3 of caprolactam and 2000 mg/dm^3 of ammonium sulfate. To develop a technology for utlilization of caprolactam sap condensate it is necessary first of all to solve the problem of separating the mineral and organic components, which can be realized by means of adsorption.

In the present work, we have studied the adsorption properties of commercial active carbons: AG-5, BAU, SKD-515, and AG-OV-1, which differ in the nature, structure, porosity, and specific surface.

At the first stage of this work, we examined adsorption of caprolactam from organomineral wastewaters containing 0.1-1.0 g/dm^3 of caprolactam with active carbons under static conditions.

Experimental adsorption isotherms are presented in Fig. 1. The isotherms show that the maximal adsorption capacity of carbon sorbents depends on the nature, composition, structure, specific surface, and porosity. From the experimental data it follows that the adsorption capacity changes as follows: AG-5 > BAU > SKD-515 > AG-OV-1.

For detailed characterization of carbon sorbents and calculation of adsorption parameters we employed theories of monomolecular adsorption (Freundlich and Langmuir equations), multimolecular adsorption (BET model), and micropore volume filling (Dubinin − Raduszkiewicz equation). The adsorption parameters calculated using monomolecular theory and generalized BET theory are presented in Table 1 for all active carbons.

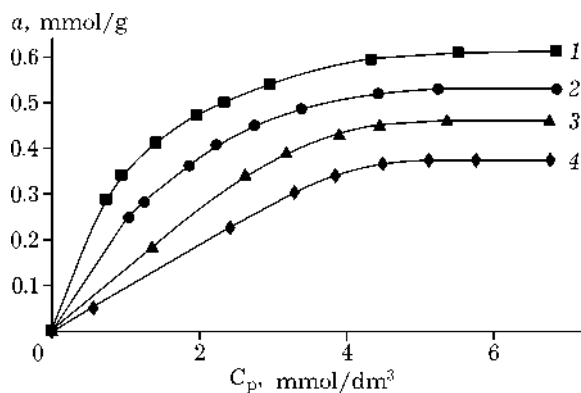The theoretical adsorption isotherms were calculated from the data obtained. A compara-

Fig. 1. Experimental isotherms of caprolactam adsorption (*a*) from organomineral wastewaters on active carbons: *1* − AG-5, *2* − BAU, *3* − SKD-515, *4* − AG-OV-1.

TABLE 1

Parameters of caprolactam adsorption by active carbons from organomineral wastewaters under static conditions

Sorbent	BET equation		Freundlich equation		Langmuir equation		
	a_m, mmol/g	K	Q, kJ/mol	$1/n$	b, mmol/g	a_m, mmol/g	K
AG-5	0.854	4.68	26.5	0.4	0.46	0.724	0.89
BAU	0.789	2.55	24.8	0.5	0.58	0.710	0.61
SKD-515	0.684	1.46	22.9	0.6	0.77	0.670	0.36
AG-OV-1	0.656	0.95	22.7	0.5	0.86	0.650	0.2

tive analysis of the experimental and theoretical adsorption isotherms demonstrated that the Freundlich equation cannot be used for describing caprolactam adsorption from technological runoff with the given active carbons. A comparison of the experimental isotherms with the isotherms calculated by the Langmuir and BET equations has revealed that the isotherms completely coincide for all sorbents in question.

To examine the applicability of the Dubinin − Raduszkiewicz equation for describing caprolactam adsorption from the technological wastewaters, we determined the exponent n in the generalized Dubinin − Raduszkiewicz equation. For all sorbents, $n \sim 2$; consequently, the Dubinin − Raduszkiewicz equation is applicable. To study the applicability of micropore space-filling theory, the adsorption isotherms of caprolactam were plotted in coordinates of the Dubinin − Raduszkiewicz equation. The experimental points fit the lines, and extrapolation of the latter gives the limiting adsorption a_0 and the limiting adsorption volume W_0. Taking into account the affinity coefficient, we determined the characteristic energies E and the half-widths of the slit-like micropores χ [1]. The results of calculations are presented in Table 2.

The calculated average half-width of a slit-like pore filled with caprolactam molecules amounts to 0.88−1.07. In view of the size of the caprolactam molecule (in projection, the maximal diameter is 0.8 nm, and the height is 0.6 nm), it is believed that caprolactam sorption occurs in the accessible micropores. The characteristic energies (15.04−18.04 kJ/mol) indicate that caprolactam sorption occurs mainly in the micro- and mesopores of the sorbents. The limiting adsorption volume is 0.24−0.31 dm^3/kg for all carbon sorbents; therefore, one can hypothesize that caprolactam adsorption follows the micropore space-filling mechanism.

The values of specific adsorption of caprolactam determined by the Dubinin − Raduszkiewicz equation coincide practically completely with the experimental values. This confirmed once again that micropore space-filling theory may be used for describing caprolactam adsorption from the technological wastewaters.

The mechanism by which the sorbate interacts with the sorbent surface can be inferred from the shape of the isotherm and from the adsorption heats. The isotherms are L-shaped. According to Gills' classification, this means that the physical nature of adsorption is determined by van der Waals forces. The adsorp-
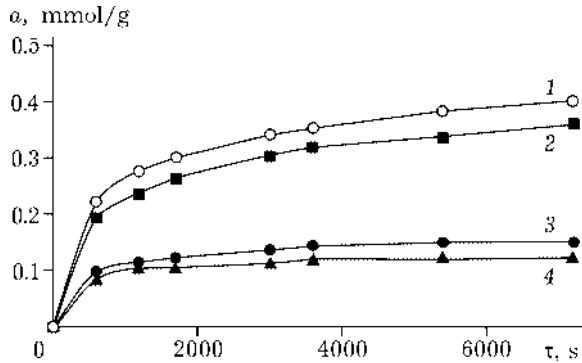
TABLE 2

Adsorption characteristics of carbon sorbents calculated by the Dubinin − Raduszkiewicz equation

Sorbent	a_0, mmol/g	W_0, cm^3/g	E, kJ/mol	E^*, kJ/mol	χ, nm	V_{mic}, cm^3/g
AG-5	2.78	0.31	18.4	13.71	0.88	0.24−0.35
BAU	2.45	0.28	17.62	13.13	0.91	0.22−0.25
SKD-515	2.24	0.25	17.23	12.84	0.93	0.28
AG-OV-1	2.09	0.24	15.04	11.21	1.07	0.32

*Calculated with allowance for the affinity coefficient.

Fig. 2. Kinetic dependences of caprolactam adsorption a by active carbons from a solution with a mass concentration of caprolactam of 500 mg/dm³: *1* – AG-5, *2* – BAU, *3* – SKD-515, *4* – AG-OV-1.

tion heats (22.7–26.5 kJ/mol) also witness the physical nature of interaction between caprolactam and carbon sorbent for all carbons under study.

The kinetic studies of caprolactam adsorption from organomineral wastewaters were carried out for a limited volume with continuous stirring. The kinetic curves were plotted using the experimental data (Fig. 2).

To determine the limiting stage of mass transfer, we used the procedure of [2]. By solving the set of equations describing the external diffusion kinetics of adsorption of a substance from a constant closed volume one can derive a theoretical equation of kinetics in the form of a dependence of the degree of adsorption equilibrium γ_τ on a dimensionless quantity T proportional to the reaction time τ:

$$\gamma_\tau = a_\tau / a_p \qquad (1)$$

where γ_τ is the dependence of relative adsorption on the phase contact time; a_τ is adsorption during the time τ; and a_{eq} is equilibrium adsorption, mmol/g.

The major kinetic parameters were calculated from the experimental data for the sorbents, and the kinetic curves of the degree of adsorption equilibrium γ versus adsorption time τ were plotted (Fig. 3, *a*).

One can assume that the dependence of γ on τ at small values of τ is linear up to $\gamma = 0.6$–0.7 for all carbons in question. Therefore, the carbon granules most probably correspond to the quasihomogeneous model, and subsequent kinetic studies can be performed using this model.

To find the mass transfer coefficient necessary for calculating dynamic adsorption, one can employ another method, namely, solving a set of equations describing the external diffusion kinetics of solute adsorption from a constant closed volume [3]. This method permits one to derive an equation that relates γ to a dimensionless quantity T proportional to the time:

$$\gamma = 1 - e^{-T} \qquad (2)$$

Using eq. (2), we calculated the dimensionless kinetic parameters T and plotted the dependences of T on τ (see Fig. 3, *b*). The presence of a linear segment on the curve $T = f(\tau)$ indicates that caprolactam adsorption from the organomineral wastewaters is limited by the external mass transfer, which occurs for 40–60 min depending on the properties of active carbon. The deviation from the linear dependence suggests that near the equilibrium the reaction rate is increasingly affected by internal diffusion. Due to the lower rate of sorption, lower rates of filtration are recommend-
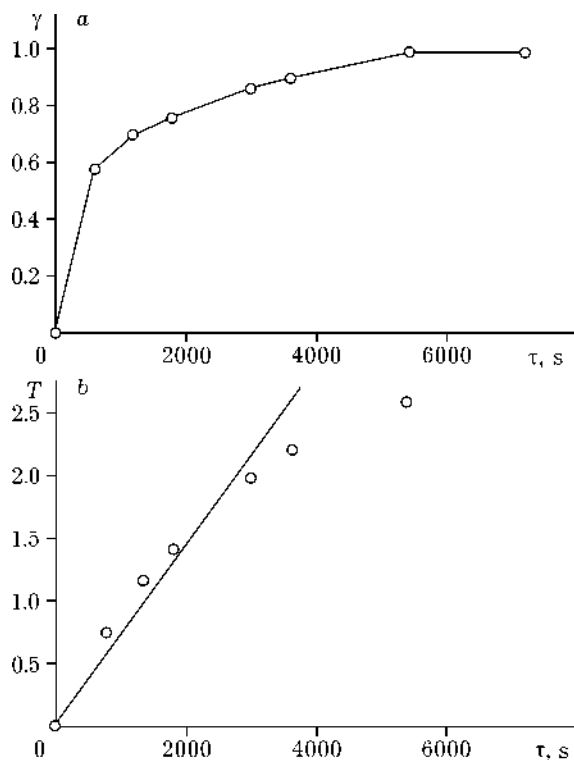

Fig. 3. Theoretical kinetic curve of caprolactam adsorption from technological wastewaters with AG-5 (*a*) and dependence of T on the caprolactam adsorption time τ (*b*).

ed toward the end of the service life of the carbon filter for maximal utilization of the sorbent layer capacity.

The coefficients of external mass transfer were estimated from the slope of the line of the dependence of the dimensionless coefficient T on τ:

Carbon brand	β, s^{-1}
AG-5	0.029
BAU	0.012
SKD-515	0.034
AG-OV-1	0.018

The similarity of these coefficients for the systems under study also indicates that at the initial moment of time adsorption is limited by external mass transfer.

Experimental study of sorption dynamics implies successive selection of parameters (type of sorbent, length of the stationary layer, flow rate, *etc.*) and plotting experimental output curves depending on one variable (*e. g.*, solution flow rate) at fixed values of others, which is a very time-consuming procedure. The experimental procedure is considerably reduced if the dynamic parameters are calculated using mathematical simulation based on the theoretical dependences describing mass transfer.

Simulation was carried out for AG-5, BAU, SKD-515, and AG-OV-1 active carbons and a

solution with 500 mg/dm^3 of caprolactam and 2000 mg/dm^3 of sulfate ammonium.

For all of these active carbons, adsorption dynamics was calculated using the equilibrium adsorption layer model with adsorption constants of the Dubinin − Raduszkiewicz equation, kinetic data, and material balance equation [4]

$$\sqrt{\tau} = \sqrt{L}\sqrt{a_0/(vC)} - b\sqrt{a_0(\beta_n C)} \qquad (3)$$

Here τ is the operation time of a sorbent layer with a length L before the overshoot concentration of the adsorbed substance C has appeared; C_0 is the initial concentration of the substance in the flow, mmol/dm^3; a_0 is the substance content of the stationary phase equilibrating with C_0, mmol/kg; v is the mean flow rate, m/h; β_n is the external mass transfer coefficient; b is the coefficient whose tabulated values for some values of C/C_0 are presented in [4].

Figure 4 presents the experimental output curves of caprolactam adsorption by AG-5 active carbon and those calculated by the equation of model (1). The equation adequately approximates the experimental output curve, validating the proposed approach to adsorption modeling.

Based on the theoretical and experimental studies, one can recommend filters loaded with
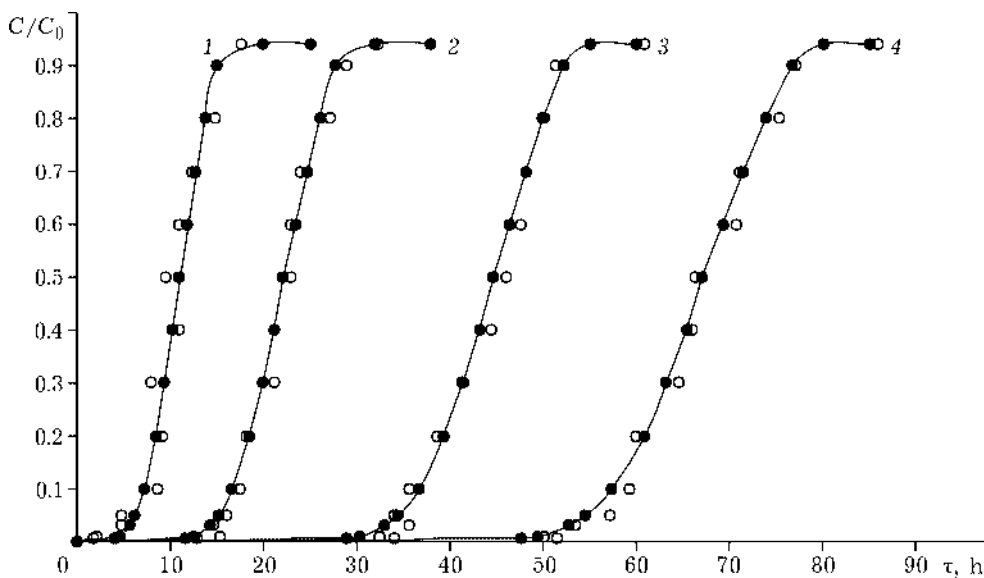

Fig. 4. Output curves of caprolactam adsorption dynamics from organomineral wastewaters for a dense layer of AG-5 for different values of flow rate v and sorbent layer height H ($C_0 = 500$ mg/dm^3):
1 − $v = 5$ m/h, $H = 1$ m; *2* − $v = 5$ m/h, $H = 2$ m; *3* − $v = 2.5$ m/h, $H = 2$ m; *4* − $v = 2.5$ m/h, $H = 3$ m;
● calculation, ○ experiment.

AG-5 or SKD-515 (diameter 3 m, loaded layer height 2.5 m, filtration rate 2.5−5 m/h) for purifying the sap steam condensate of caprolactam production.

Traditional methods employed for regeneration of active carbons are thermal and reagent methods.

The thermal methods were shown to be inefficient because at temperatures above 180 °C caprolactam polymerizes on the carbon surface.

Chemical regeneration was carried out using sodium hydroxide with $C(1/Z)NaOH = 2\ mol/dm^3$. Specimens of active carbons: AG-5 − caprolactam, SKD-515 - caprolactam, and AG-OV-1 − caprolactam were used as sorbents. To estimate the completeness of regeneration, we studied caprolactam adsorption from technological wastewaters with reduced active carbons.

The coincidence of adsorption isotherms for the starting and regenerated AC samples indicates that after regeneration activate carbons have recovered their adsorption properties almost completely.

For AG-5 active carbon, ten sorption − desorption cycles were carried out under laboratory conditions, with adsorption capacity decreased by 30 %.

Based on a comprehensive study of caprolactam adsorption and theoretical calculations of adsorption filter parameters and regime, we have developed a technology of adsorption purification of wastewaters from caprolactam and gave recommendations on the creation of ecologically safe and resource-saving production of caprolactam using a caprolactam-containing regenerating solution to prevent environmental pollution.

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