TECHNOLOGY OF WASTEWATER PURIFICATION FROM DIMETHYLFORMAMIDE

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Abstract: The following research observes the peculiarities, rules and mechanisms of dimethylformamide adsorption from water solutions with the help of activated carbons of different nature and industrial techniques for producing. To receive activated carbon characteristics, the author analyses pore volume and chemical state of carbon surface and applies porosity measurement and potentiometric titration methods. The research helped to reveal cellular structure of the given adsorbents were calculated in isotherms of nitrogen adsorption-desorbtion. Potentiometric titration method was used for the evaluation of oxigen-containing surface acid functional groups (OFG). The analysis of balance, kinetics and dynamics of DMF adsorption from water solutions was carried out. The author found out equilibrium adsorption characteristics, rate-determining step and mass transfer ratio, calculates the parameters of adsorption column and the mode of continuous cleaning process. Mathematical model method helped to receive the following dynamic characteristics of the adsorption process: dynamic capacity, travel rate of operating space, fixed bed operational capacity, bed length, the quantity of water cleared before slip. All these characteristics can be used on practice on real homeland equipment. The author conducted the optimization of the parameters of adsorption column filled with adsorbent AG-OV-1 and the mode of continuous cleaning process. The basis of theoretical calculation is fundamental equation of outer diffusive adsorption dynamics in case of linear isotherm with the use of absorption Dubinin-Radushkevich equation constants and the experimental data on kinetics of DMF absorption from process effluent on carbon adsorbents. The result of the following article is the development of technology of wastewater adsorption cleaning from the organic component, which can help to improve environmental safety and resource conservation by means of prevention of wastewater disposal.

Keywords: activated carbon, dimethylformamide water solutions, adsorption

INTRODUCTION

The production of dimethylformamide is a kind of large-tonnage production with a great volume of low-concentration organo-mineral wastewaters. In addition, plants of organic synthesis widely use dimethyl-formamide as a solvent in the process of polyacrylonitrile fiber (nitrone, orlon) making, in the process of ethine release from gas mixture and for dye dissolution in leather, paper, viscose rayon and wood dyeing, all of which lead to the formation of effluents containing dimethylformamide. It should be noted that dimethylformamide is cancerogenic, highly toxic and the most difficult-to-remove effluent component of some chemical industries.

The most promising methods of low organic effluent treatment are sorption methods.

Activated carbon ranks first among adsorbents because of its strong cellular structure and particular qualities of the surface chemical state [1]. In industry, the process of adsorption is held in dynamic conditions.

The aim of the present research is to develop the continuous process technology of adsorptive wastewater purification from dimethylformamide.

MATERIALS AND METHODS

The targets of the research are DMF water solutions and local salable activated carbons AG-OV-1, SKD-515 and AG-5 (JSC "Sorbent", Perm) that differ in raw materials and methods for producing.

The analysis of balance, kinetics and dynamics of DMF adsorption from water solutions are to be carried out for developing an adsorption technology.

The process of adsorption was studied by the equilibrium method during 24 hours, during which the solutions were regularly stirred for 6 hours. The adsorbate was dimethylformamide water solutions with concentration 0.0025–0.25 mol/dm^3.

The methods of performing kinesthetic measurements were the following: adsorbent samples weighing 1 kg were put into flasks, 100 cm^3 by 100 cm^3 of the adsorbate solution under study were gradually being added to the substance. Kinetic measurements were conducted within the time frames from 2 to 150 minutes.

For the study of dynamic adsorption we used a column with the following parameters: H = 7 cm, d = 1.5 cm. The input concentration was $1.5 \cdot 10^{-2}$ mol/dm^3, which coincides with dimethyl-formamide content in industrial wastewaters. Adsorbate solution flowed through the adsorbent fixed bed with a steady speed during 120 minutes. The DMF concentration was measured every 5 minutes. Solution rate of transmission through the adsorbent fixed bed was 1.4 m/h.

The concentration of dimethylformamide in solutions was measured in accordance with standard methods with the help of CF-46 device.

The analysis of carbon surface pore volume and chemical state was conducted with the help of porosity measurement and potentiometric titration methods in order to get the characteristics of activated carbon.

The parameters of adsorbents cellular structure were calculated in isotherm of nitrogen adsorption-desorption fewer than 77K on ASAP-2400. All measurements were taken in accordance with the standard methods. Decontamination of the samples was performed under 3000C to vacuum of 4Pa.

Potentiometric titration was conducted for the evaluation of oxygen-containing surface acid functional groups (OFG). In order to do this we put 15 cm^3 of base (NaOH, NaHCO$_3$ or Na$_2$CO$_3$) with the amount concentration of 0.1 mol/dm^3 to the 1g sample of dry activated carbon and allowed it to stand with intermittent mixing 24 hours. Then we picked an aliquot of 5.00 cm^3 and titrated it against hydrochloric acid solution with the concentration of 0.1 mol/dm^3. The curves of potentiometric titration were recorded on potentiometer I-130. Glass electrode was used as an indicator; silver chloride electrode was used as a reference electrode. The amount of base used for neutralization of oxygen-containing functional groups was counted according to the following formula:

$$n = \frac{(V - V_{hol})C_{HCl}V_{osn}}{m\,V_{al}},$$

where n is the amount of base used for neutralization of surface carbons, mmol/g; V and V_{hol} is the equivalent volume of HCl used for base titration before and after neutralization of surface carbons, cm^3; V_{al} is the amount of base taken for titration, cm^3; C_{HCl} is the amount concentration of hydrochloric acid equivalent mol/dm^3; m is carbon weight, g.

OFG concentration was calculated on the assumption of carboxyl groups being neutralized by NaHCO$_3$,

Na$_2$CO$_3$ solution interacting with carboxyl and lactone groups and all acid OFG (carboxyl, lactone and phenic) being neutralized upon interaction with NaOH.

OFG measurments were conducted in accordance with the following formula:

$$w_{OFG} = \frac{nM_{eq}}{10}K,$$

where w is weight percent of phenic, lactone and carboxyl oxygen, %; n is the amount of phenic, lactone and carboxyl groups, mmol/g; M_{eq} is molar weight of the oxygen equivalent in accordance with OFG (15.99 g/mol for a phenic group and 31.98 g/mol for lactone and carboxyl groups); K is an organic fraction of activated carbon.

RESULTS AND DISCUSSION

The analysis of cellular structure analysis revealed that the sample of AG-5 has the highest values of overall specific surface, micropore surface (S$_{BET}$, m^2/g, S$_{micro}$, m^2/g) and also micropore volume (V$_{micro}$, cm^3/g). The sample of AG-OV-1 is characterized by relatively high rates of mesopores and low values of micropore volume and surface (Table 1).

The analysis of surface chemical state is presented in Table 2.

According to potentiometric titration data, –COOH-groups were found out on the surface According to potentiometric titration data, –COOH-groups were found out on the surface of the input carbons in the same amount. AG-5 and SKD-515 has a greater amount of –COO-groups as compared to AG-OV-1, furthermore, AG-5 sample is characterized by the lowest amount of -OH$_{phenol}$ groups. Activated carbon AG-OV-1 contains the highest amount of -OH$_{phenol}$ groups.

Experimental data of the adsorption process in equilibrium conditions are presented on Figure 1.

Table 1. Cellular structure parameters

S$_{micro}$, m^2/g	Sample	S$_{BET}$, m^2/g	V$_s$, cm^3/g	V$_{micro}$, m^3/g	V$_{meso}$, cm^3/g
369	AG-OV-1	682	0.459	0.218	0.241
554	AG-5	925	0.6	0.47	0.13
404	SKD-515	791	0.561	0.359	0.202

Table 2. Potentiometric titration data

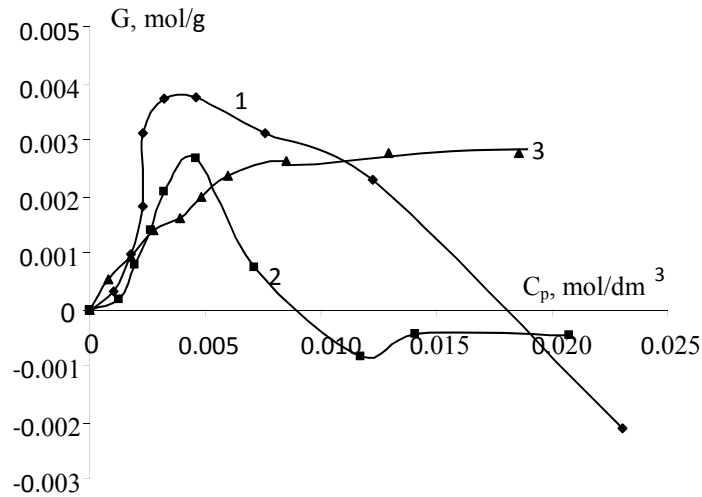| Sample	n$_{OFG}$, mol-eq/g		
	-OH$_{phenol}$	-COOH	-COO-
AG-OV-1	0.21	0.03	0.08
AG-5	0.03	0.03	0.161
SKD-515	0.181	0.03	0.16

Fig. 1. Isotherms of DMF adsorption by activated carbons: 1 – AG-5; 2 – SKD-515; 3 – AG-OV-1.

Gibbs hyper adsorption isotherms of all samples under study up to concentration value of 0.002 mol/dm^3 coincide with the isotherms of L_4 type according to Giles classification. In case of increase of DMF content in solutions, isotherm type changes to L_5 for AG-5 and SKD-515 samples. If the concentration is higher than 0.008 mol/dm^3 и 0.018 mol/dm^3, negative DMF adsorption values of the mentioned samples are registered. The isotherm form for AG-OV-1 carbon does not change during the whole concentration range under study. The picture shows that AG-5 sample has the highest adsorption activity in regard to DMF in case of concentration values up to 0.012 mol/dm^3. Within the range 0.012–0.02 mol/dm^3 AG-OV-1 has the highest adsorption activity. It may be connected to the fact that DMF belongs to the matters that influence long-range order of a polar solvent. Water medium disturbance with succeeding influence on a hydration shell in case of dimethylformamide addition is observed even at a relatively low concentration (0.01 mol/dm^3) (spectrophotometric measurement method helps to distinguish solution density when the change of system temperature is 0.1°C), when there is one DMF molecule in 5000 water molecules in average. At DMF concentration increase, the influence of DMF molecule on hydration complex become higher. As a result, big associates of water molecules are demolished and it leads to the volume increase of smaller associates with proton-donor function [2]. At the initial stage, hydration shells of DMF molecules have relatively large effective radius at low concentrations up to 0.002 mol/dm^3, and adsorption takes place generally on mesopores by means of the specific interaction between DMF associated molecules and oxigen-containing surface functional groups of activated carbon. Activated carbon AG-5 shows lower adsorption activity in respect of AG-OV-1 and SKD-515 samples because it is characterized by a relatively low volume of mesopores (Table 1). Significant reduction of a hydration shell takes place in

solution in case of DMF concentration increase, effective radii get smaller, DMF associated molecules are absorbed in micropores, which is proven by the correlation of given cellular structure parameters and adsorption capacity of the samples. Competitive adsorption takes place upon further concentration increase, water molecules displace DMF from micropores. In this regard, AG-5 and SKD-515 carbons show negative adsorption values despite high micropore values (Table 1), and AG-OV-1 sample shows positive values because it is characterized by high values of surface functional groups (SFG) – OH$_{phenol}$ and it uses the second adsorption mechanism – a specific interaction between DMF amides and SFG.

In sum, the analysis reveals that DMF adsorption depends on the structure and chemical state of activated carbon surface. Specific interaction in mesopores with oxygen-containing surface functional groups is typical of DMF adsorption process upon low concentrations. At higher concentrations, dispersive interaction in micropores takes place by means of Van der Waals forces. Negative adsorption values of AG-5 and SKD-515 upon further increase of DMF concentration in solution are stipulated by the fact that water molecules push DMF out from micropores under competitive adsorption.

Adsorption parameters necessary for engineering evaluation were received from equilibrium data.

For adsorption process optimization, it is essential to know rate-determining step of mass transfer, which can help to calculate mass transfer ratio [3].

The definition of rate-determining step of mass transfer was conducted on the basis of kinetic measurements data (Fig. 2). We calculated the basic parameters and plotted the curves of the balance degrees γ and adsorption time t. The measurements were taken only for AG-OV-1 sample because it has stable and fairly high adsorption capacity within the wide concentration range according to the research findings.
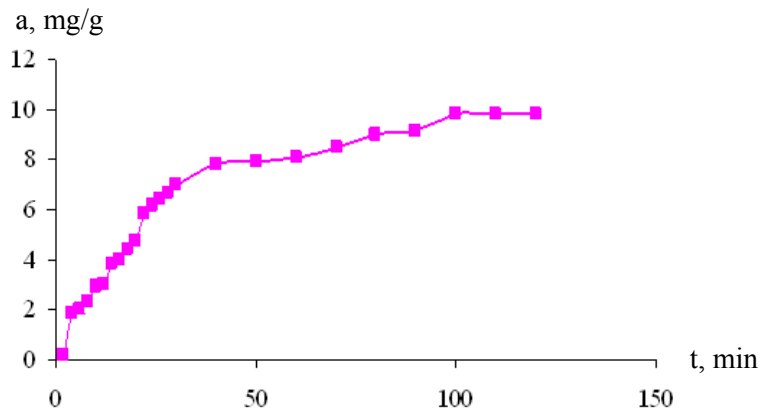
Fig. 2. Measured kinetic curve of DFM adsorbtion by AG-OV-1 sample.

Balance degrees was calculated according to the following formula:

$$\gamma = a_t / a_p,$$

where a_t is adsorption in a period of time t; a_p is a value of equilibrium adsorption.

The dependence of the balance degree on the time of adsorbtion is direct up to $\gamma = 0.3$. Consequently, we can assume that the granula of the activated carbon samples are in accordance with quasi-homogeneous model which let us keep calculations in line with this model (Fig. 3).

Nondimensional kinetic parameter T was calculated according to the formula:

$$\gamma = 1 - e^{-T}.$$

The dependence of T from γ is a theoretical kinetic curve (Fig. 4). The definition of rate-determining step comes to the comparison of theoretical and experimental curves upon the same values of γ. In addition it is known that when the external mass transfer is the rate-limiting step, graph of Tt is described by a straight line passing through the origin. According to the analytical data, the adsorption process is controlled by external mass transfer during the first 20 minutes.

External mass transfer ratio in case of adsorption from solutions can be calculated from the overall coefficient of general mass transfer, if the rate-determining step is external mass transfer [4].

External mass transfer ratio is defined according to the following formula:

$$\beta = tg\alpha / (Vo / Vs + k_G),$$

where $tg\alpha$ is a slope of the initial section of T and t dependence; Vo is the overall volume of adsorbent, cm^3; Vs is the volume of adsorbate solution coupling with adsorbent; K_G is Henry constant ($k_G = ap/Cp$).

The estimated value β is 0.011 [5].

Mass-transfer coefficient needed for engineering evaluation was calculated.

Experimental research of the process of continuous DMF extraction with the use of AG-OV-1 carbon was conducted. The results are presented on Fig. 5 (points).
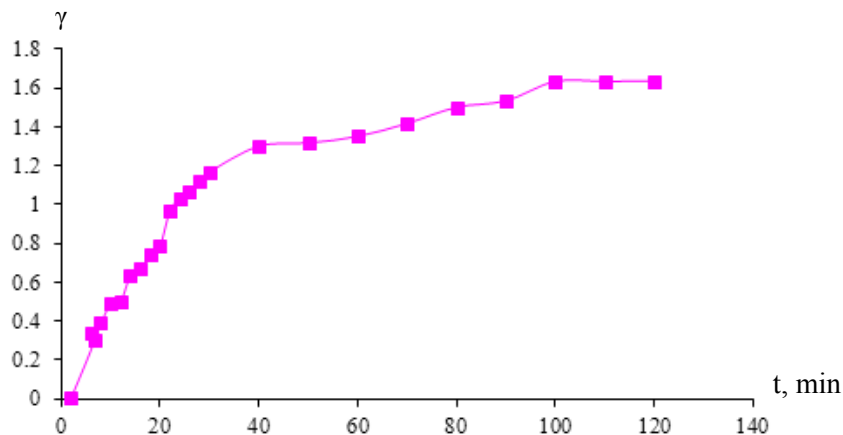

Fig. 3. Dependence of balance degree γ on the time of DMF solution contact with AG-OV-1 samples.
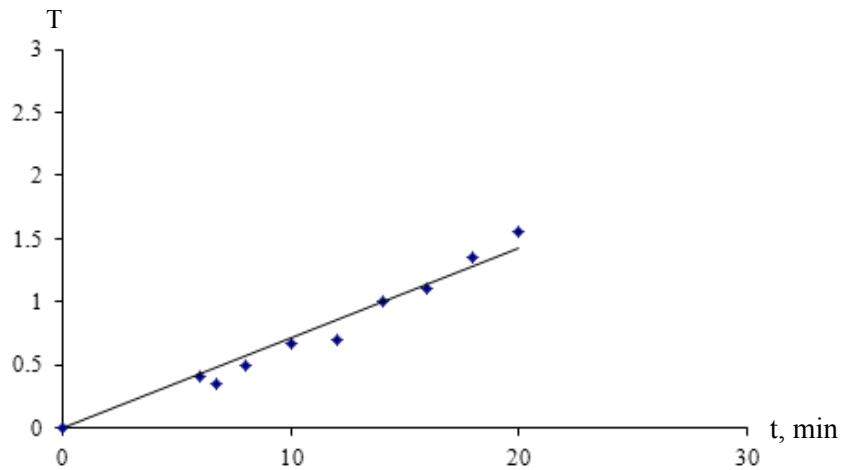
Fig. 4. Dependence of a theoretical value T on the time of DMF solution contact with adsorbent.
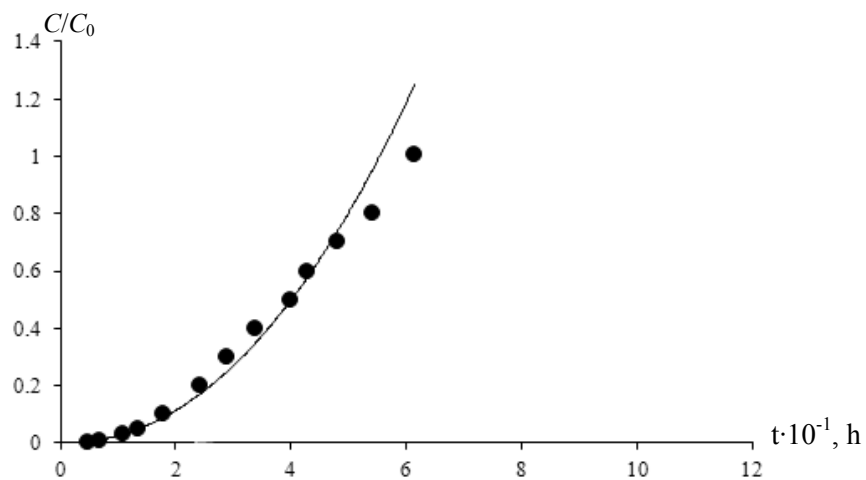

Fig. 5. Theoretical (line) and experimental (points) output of adsorption dynamics from water solution for AG-OV-1 activated carbon.

In accordance with mathematical model method we conducted the optimization of the parameters of adsorption column filled with adsorbent AG-OV-1 and the mode of continuous cleaning process. The basis of theoretical calculation is fundamental equation of outer diffusive adsorption dynamics in case of linear isotherm with the use of absorption Dubinin-Radushkevich equation constants and the experimental data on kinetics of DMF absorption from process effluent on carbon adsorbents.

$$\sqrt{\tau} = \sqrt{\frac{a_0}{w \cdot C_0}} \cdot \sqrt{H} - b \sqrt{\frac{a_0}{\beta_n \cdot C_0}},$$

where τ is the running time of an H-long bed up to breakthrough concentration of sorbing agent C; C_0 is the initial concentration in flow, mmol/dm^3; a_0 is substance content in a stationary phase in in equilibrium with C_0, mmol/kg; w is an average flow speed, m/h; β_n is an external mass transfer ratio with account of concentration difference [6]. The data are presented in Fig. 5 (line).

The overlap of theoretical and experimental values revealed that equation can be used for the calculation of adsorption column parameters.

Mathematical model method helped to receive the following dynamic characteristics of the adsorption process: dynamic capacity, travel rate of operating space, fixed bed operational capacity, bed length, the quantity of water cleared before slip. All these characteristics can be used on practice on real homeland equipment.

CONCLUSIONS

The technology of wastewater adsorption cleaning from the organic component was developed on the basis of the multicenter study of dimethyl-formamide adsorption process and theoretical calculations of the parameters and adsorption filter working pattern. This technology can help to improve environmental safety and resource conservation by means of prevention of wastewater disposal.

The developed technology of wastewater adsorption cleaning from dimethylformamide with the help of AG-OV-1 carbon can be implemented on the basis of series-produced homeland equipment and used for wastewater purification from organic compounds with slight modifications of adsorption column and mode parameters.

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