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The adsorption of phenols from model solutions by activated carbon Ecofresh carbon and NWC

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Abstract : Process of reservoirs self-purification from phenols proceeds relatively slowly, therefore before the discharge phenol-containing waste waters are subjected to additional cleaning. At present there are a lot of methods of phenol-containing waste waters purification. The variety of the systems, containing phenols, causes difficulties in selection of optimal ways of their neutralization and utilization. Many effective ways of deep phenol-containing waters purification are connected to large economic and resource expenses, use of scarce reagents with their subsequent regeneration, utilization or waste disposal. Therefore searching for the most efficient and inexpensive ways of purification of phenol-containing waste waters of small volumes is the task of an utmost importance. The adsorption of phenols was studied, by the example of resorcinol from model's solutions with activated carbon Ecofresh Carbon and NWC in static and dynamic conditions. Some theory of adsorption equations were selected to process the experimental data. They are: Langmuir monomolecular adsorption equation, BET equation of polymolecular adsorption, equation of the theory of volumetric infill of micropores with different values of degree index n. For the description of resorcinol adsorption from water solutions in static conditions the Dubinin-Astakhov equation was chosen and values of the limit adsorption and characteristic energy have been calculated. DEC, FDEC and kinetic constants of adsorption in dynamic conditions have been calculated. Protective power time and the loss of protective power time of the layer, having been computed on the base of kinetic parameters, are consistent with the experimental data for activated coconut carbon. Activated coconut carbon Ecofresh Carbon can be recommended as an optimal sorbent for purification of waste waters from phenols.
Key words : resorcinol; adsorption; adsorption theory equation; activated coconut carbon; Shilov`s equation.

Introduction

Phenols are among the most widespread pollutants, which get into surface waters with sewerages of plants and factories: paint and varnish, chemical, textile and other industries.

Phenol waters discharge into reservoirs and waterways sharply worsens their general sanitary state, influencing upon the living organisms not only because of their toxicity, but also by great changing of biogenic elements and dissolved gases (oxygen, carbon dioxide) regime. The concentration of phenols in water, equivalent to 300 mg/dm^3, causes the death of all fish during 24 hours; 15-20 mg/dm^3 – movement coordination disorder, disturbed motor activity and death of 20% of fish; 2 mg/dm^3 – death of water fleas; at 1 mg/dm^3 – the development of saprophytic mycobiota and BOD in reservoirs is disrupted, meanwhile this concentration is threshold, concerning its influence on natural self-purification of reservoirs [1]. Maximum permissible concentration (MPC) of phenols in reservoirs in Russia – is 0,1 mg/dm^3 [2].

Process of reservoirs self-purification from phenols proceeds relatively slowly, therefore before the discharge phenol-containing waste waters are subjected to additional cleaning.

At present there are a lot of methods of phenol-containing waste waters purification. They are conventionally subdivided into two big groups: regenerative and destructive. The destructive methods are applied, when extraction of admixtures from waste waters is impossible or unreasonable.

Application of regenerative methods of waste waters purification allows not only purify them, but also extract phenols for their subsequent application in industries. Regenerative methods are worthwile, if concentration of phenols in waste waters is more than 2 g/l [3-5]. Methods of deep purification of waste waters, allowing to purify water from phenols to the level of MPC and below this level, are applied at finishing stages of water purification.

The variety of the systems, containing phenols, causes difficulties in selection of optimal ways of their neutralization and utilization. Firstly it is related to the technology of deep waste waters purification, which, as a rule, dictates keeping to special conditions, hardly practicable. Secondly, many effective ways of deep phenol-containing waters purification are connected to large economic and resource expenses, use of scarce reagents with their subsequent regeneration, utilization or waste disposal. Therefore searching for the most efficient and inexpensive ways of purification of phenol-containing waste waters of small volumes is the task of an utmost importance.

Object and methods of investigation

Activated granular carbon, made of coconut shell, has high sorption properties, wear resistance and is ecological. Coconut carbon has a large total pore surface. The pore area equals to more than 1000 m^2 per 1 g. Activated coconut carbon is used in different spheres of water purification. Due to the great number of micropores this coconut carbon adsorbs many desinfectant substances well, also it improves organoleptic characteristics of water.

Table 1. Characteristics of adsorbents

Producer	Sorbent	Parameters
Ecofresh Carbon	Activated granular cococnut carbon Size of fraction: 20×50 mesh (0,84-0,30 mm)	The appearance: irregular shaped black particles Bulk density: 0.48-0.52 g/sm^3 Iodine number: 1050-1300 mg/g Carbon tetrachloride (CCl_4) activity: > 55% Sorption capacity by methylene blue: > 240 mg/g Humidity: < 5% Hardness: > 95% Ash content: < 4% Sanitary certificate is available
NWC®	Activated granular cococnut carbon Size of fraction: 12×40 mesh (1,68-0,40 mm)	

The concentration of resorcinol was measured by fluorimeter «FLUORAT-02», light filters №1 (excitation) and №3 (registration) [6].

Table 2. Physicochemical characteristics of resorcinol [7]

Chemical formula	$C_6H_4(OH)_2$
Molecular size, nm	0,56×0,47
Dipole moment, D	2,071
Polarizability, cm^3	$59{,}11\cdot10^{-24}$
Molar mass, g/mmol	110,1
The appearance	solid white substance

Density, g/cm^3	1,27
Melting point, °C	110
Boiling point, °C	280,8
Solubility in water (at 20 °C), g/100 sm^3, mmol/dm^3	140 6,06
K_1^0	$5 \cdot 10^{-10}$
K_2^0	$8{,}7 \cdot 10^{-12}$

Results and discussion

The study of adsorption in static conditions was put into practice by intensive mixing (300 rpm) of model solution of volume 100 sm^3 with resorcinol concentrations in the range of 0,01 to 20,0 mmol/dm^3 and adsorbent, weighing 0,1 g, until the fixation of equilibrium concentration in the solution. For this purpose the resorcinol concentration was measured by fluorimeter in fixed periods of time. It has been experimentally established, that the fixation of equilibrium took 8-10 days. The isotherm of resorcinol adsorption by activated carbon 12×40 mesh is shown in figure 1.

Some theory of adsorption equations were selected to process the experimental data. They are: Langmuir monomolecular adsorption equation, BET equation of polymolecular adsorption, equation of the theory of volumetric infill of micropores with different values of degree index n. The linearity of adsorption isotherm in the coordinates of the equation is the necessary condition for the poof of the legitimacy of the equation application [8].

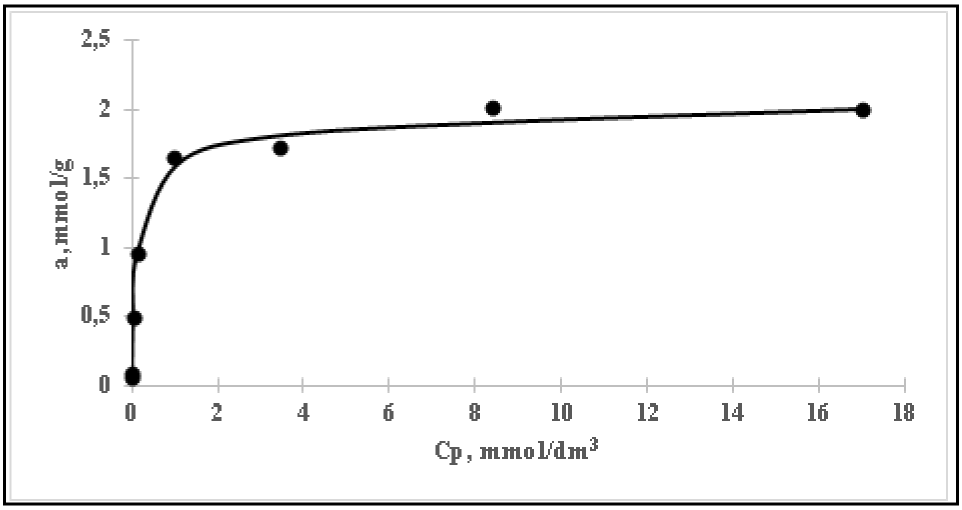

Fig: 1. The isotherm of resorcinol adsorption by activated carbon 12×40 mesh

In figures 2 and 3 the isotherm of resorcinol adsorption is represented in the coordinates of Langmuir and BET equations. The results of the approximations made have shown that Langmuir and BET equations describe the experimental data satisfactorily only in the interval of equilibrium concentrations 0,5-20 mmol/dm^3, at low concentrations the linear dependence has different parametres.

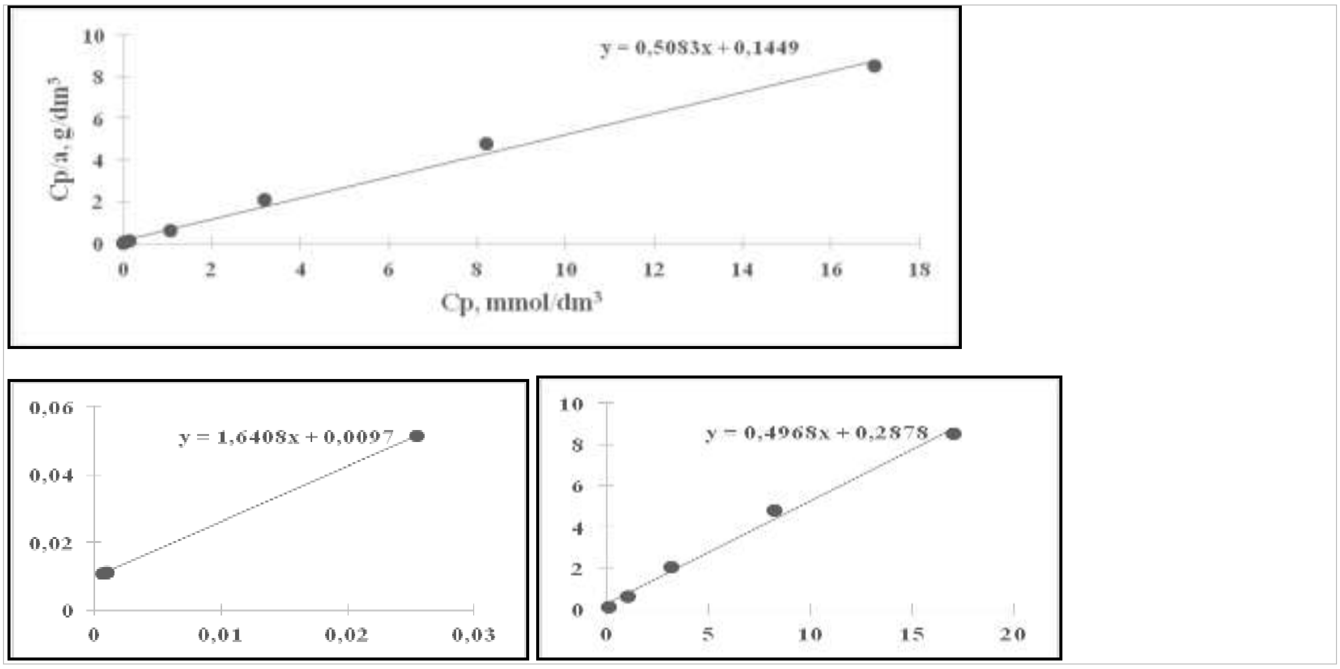

Fig: 2. The isotherm of resorcinol adsorption by activated carbon 12×40 mesh in the coordinates of Langmuir equation

The understanding of micropores as areas of space in the solid, comparable to adsorbed molecules in size, allows to state that at any character of adsorption relationship, determining physical adsorption, the adsorption field, produced by the solid, occurs in all space of micropores.

Limited nature of adsorption space of micropores determines the fact, that adsorption in micropores is characterized by the volumetric infill of adsorption space. Therefore the main geometric parameter, characterizing microporous adsorbent, is the volume of micropores, but not their «surface». The conception of volumetric infill of micropores results in clear notion of limit (maximum) adsorption value α_0, responsible for the infill of all adsorption space of micropores by adsorbed molecules [9].

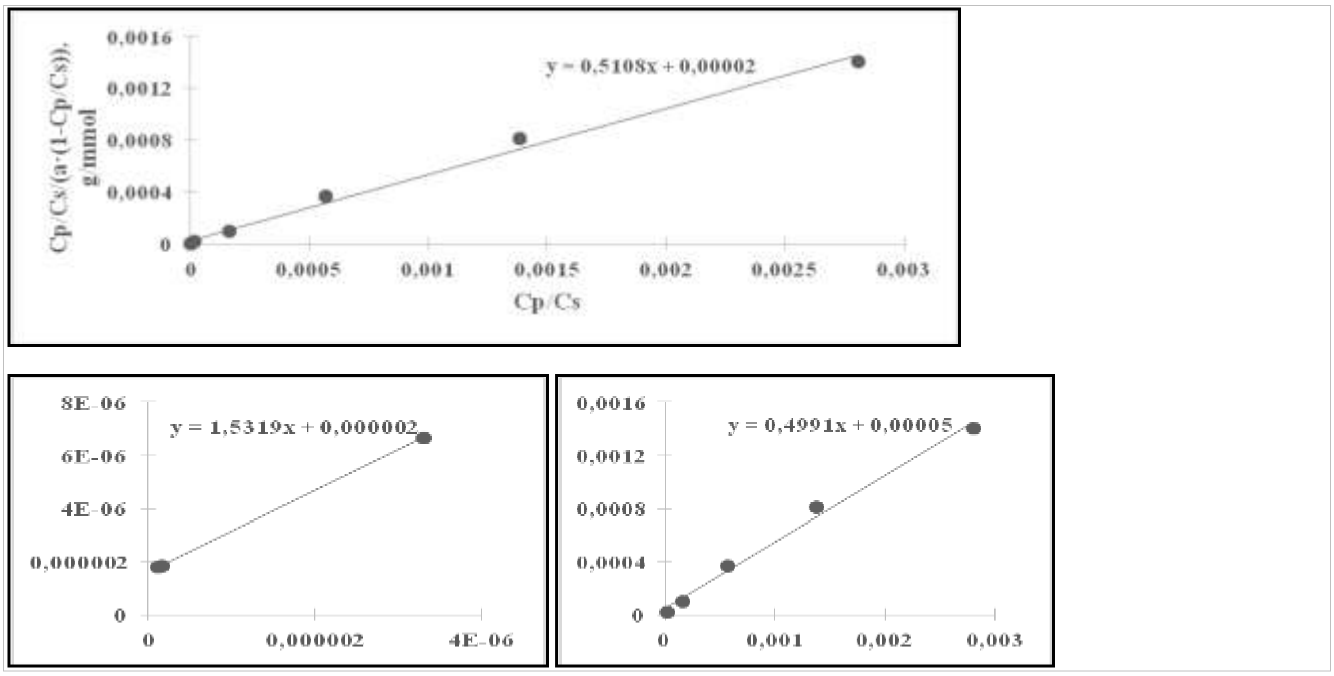

Fig: 3. The isotherm of resorcinol adsorption by activated carbon 12×40 mesh in the coordinates of BET equation.

In figures 4-5 the isotherm of resorcinol adsorption is represented in the coordinates of equations of volumetric infill of micropores theory: The Dubinin-Radushkevich equation and the Dubinin-Astakhov equation with n=4. The data were analyzed with the use of the Dubinin-Astakhov equation with diverse values of degree index n from 3 to 7. In the coordinates of the Dubinin-Astakhov equation with n=4 the isotherm has rectilinear character during the whole interval of concentration changing, the Dubinin-Radushkevich equation describes the experimental data worse.

The isotherm of resorcinol adsorption by activated carbon 20×50 mesh is analogous to the isotherm, represented in figure 1. The isotherm has rectilinear character during the whole interval of concentration changing, only in the coordinates of the Dubinin-Astakhov equation with n=4 (figure 6).

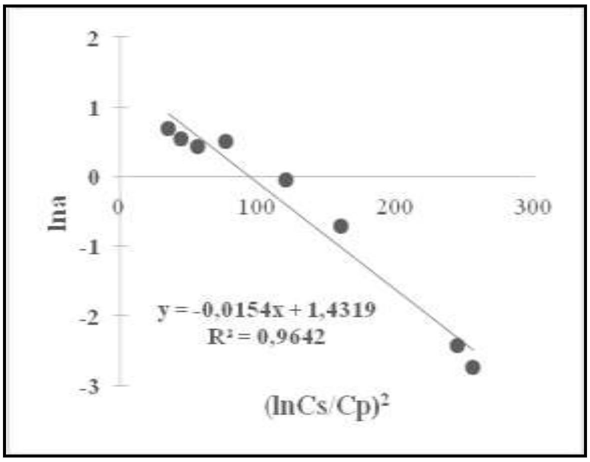

Fig: 4. The isotherm of resorcinol adsorption by activated carbon 12×40 mesh in coordinates of the Dubinin-Radushkevich equation

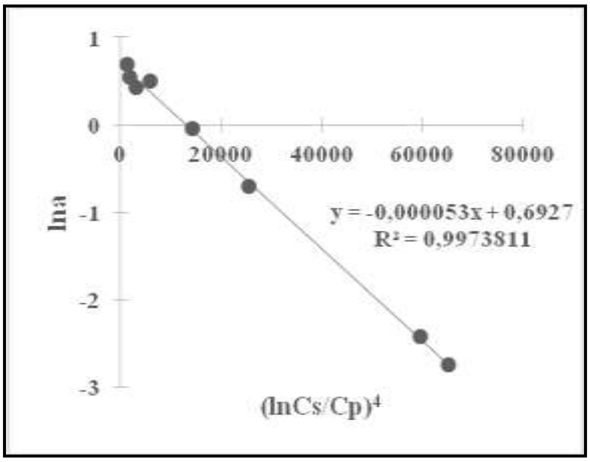

Fig: 5. The isotherm of resorcinol adsorption by activated carbon 12×40 mesh in coordinates of the Dubinin-Astakhov equation

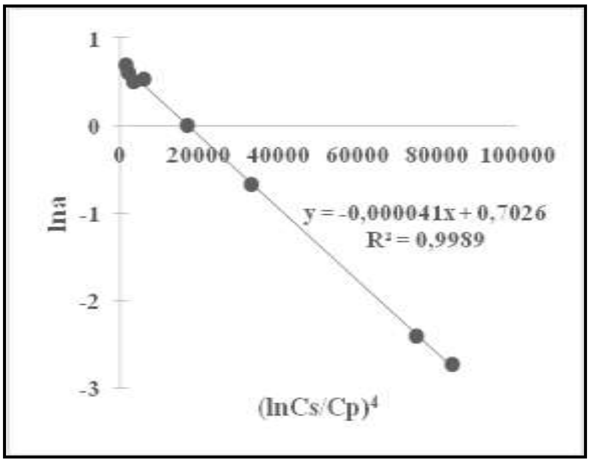

Fig: 6. The isotherm of resorcinol adsorption by activated carbon 20×50 mesh in coordinates of the Dubinin-Astakhov equation

On the basis of the data obtained during the research of resorcinol adsorption in static conditions the characteristic energy of adsorption, the limit value of adsorption and the volume of micropores for activated carbon have been calculated (Table 3). The calculations were made by the Dubinin–Astakhov equation:

$$a = a_0 \times exp[-\left({}^{A}/_{E_0}\right)^4] \quad (1)$$

$$lna = lna_0 - \left(\frac{RT}{E_0}\right)^4 \cdot ln^4\frac{Cs}{C} \quad (2)$$

$$V_0 = \frac{a_0}{\rho}, \qquad (3)$$

where $A = -\Delta G = R \cdot T \cdot \ln\left({C_s}/{C} \right)$ – molar work of adsorption, J/mol; E_0 – characteristic energy of adsorption, J/mol; a_0 – limit value of adsorption mol/g; V_0 – volume of micropores, cm^3/g; ρ – solution density, g/cm^3; C_s – concentration of saturated resorcinol solution mol/dm^3; C –equilibrium concentration of resorcinol, mmol/dm^3.

Table 3. Constants of adsorption equilibrium

Adsorbent	Characteristic energy of adsorption, kJ	The limit value of adsorption, mmol/g	Volume of micropores, cm^3/g
Act. carbon 12×40 mesh	28,55	2,00	0,23
Act. carbon 20×50 mesh	30,44	2,02	0,22

Studying of resorcinum adsorption by activated carbon in dynamic conditions was put into practice by passing model solution with resorcinol concentration 10,0 mmol/dm^3 through the layer of adsorbent until the fixation of output concentration, equal to initial. Average linear speed of transmission of resorcinol solution was 4 cm/min. Diameter of column - 1 cm. The parametres of sorbent layer are shown in table 4.

Table 4. Parametres of sorbent layer

№	Adsorbent	Mass, g	Altitude of the layer, cm
1	Activated carbon 20×50 mesh	4,46 2,23	12 6
2	Activated carbon 12×40 mesh	4,70 2,35	12 6

Received experimental data are represented in figures 7-8.

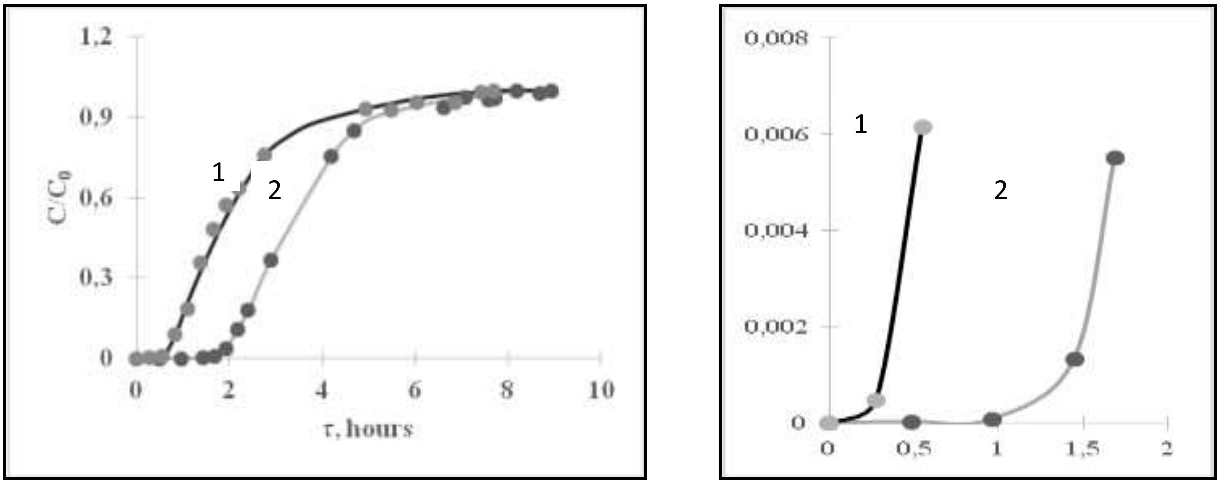

Fig: 7. Output curves of dynamics of resorcinol adsorption by activated carbon 12×40 mesh: 1- Altitude of sorbent`s layer 6 cm; 2- Altitude of sorbent`s layer 12 cm; C_0 = 10,0 mmol/dm^3

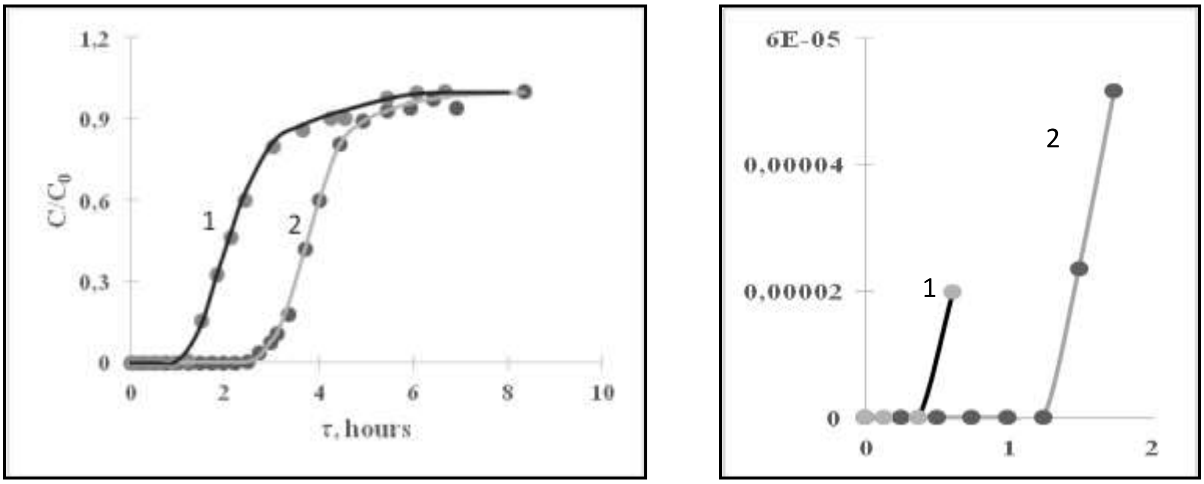

Fig: 8. Output curves of dynamics of resorcinol adsorption by activated carbon 20×50 mesh: 1- Altitude of sorbent`s layer 6 cm; 2- Altitude of sorbent`s layer 12 cm; C_0 = 10,0 mmol/dm^3.

Basing on the data, obtained during the research of resorcinol adsorption in dynamic conditions, DEC and FDEC for activated carbon have been calculated. The data obtained are represented in table 5.

Table 5. Experimental data DEC and FDEC on resorcinol

№	Adsorbent	Altitude of layer, cm	DEC, mmol/g	FDEC, mmol/g
1	Activated carbon 20×50 mesh	6	0,186	5,128
2	Activated carbon 12×40 mesh	6	0,179	5,004

As it is seen according to the represented data activated coconut carbon of two different fractions have high values of DEC and FDEC.

The process of adsorption in dynamic conditions on the whole is mixed and diffusive. General analytic solution for mixed and diffusive model of adsorption dynamics for the regime of parallel transport can be provided with Shilov`s equation [10].

$$\tau = KL - \tau_{п} \quad (4)$$

$$\tau_{п} = K_1 z_1 + K_2 z_2 \quad (5)$$

$$z_1 = \sqrt{3}\, arctg \frac{\sqrt{3}}{2p+1} + \frac{3}{2}\ln(1+p+p^2) - \frac{1}{2} - \frac{\pi}{\sqrt{3}} \quad (6)$$

$$z_2 = \ln\frac{1}{y} - 1 \quad (7)$$

$$p = (1-y)^{1/3} \quad (8)$$

$$y = \frac{C}{C_0} \quad (9)$$

$$K = \frac{\alpha_0}{\upsilon C_0} \quad (10)$$

$$K_1 = \frac{r^2 \alpha_0}{3D_e(1-\varepsilon)C_0} \quad (11)$$

$$K_2 = \frac{\alpha_0}{\beta_0 C_0}, \quad (12)$$

where τ – is the time of occurence of the certain breakthrough concentration, min; L – altitude of sorbent layer, cm; τ_l – loss of protective power time, min; C_0, α_0 – the initial concentration of adsorbate in the flow (mmol/dm^3) and equilibrium to it value of adsorption (mmol/dm^3); υ – linear velocity of the flow counting on total layer cross-section (cm/min); r – effective radius of granules, cm; D_e – diffusion coefficient in transport pores, cm/min; β_0 – outer mass transfer coefficient, cm/min; ε – layer porosity.

The computation of the constants K, K_1 and K_2 by the method of the least squares and the calculation of the sought kinetic constants of adsorption, diffusion criteria Bio and nonstationary regime duration were conducted by the means of the instrument of computer algebra MathCAD 15.0.

The obtained kinetic constants of resorcinol adsorption dynamics by activated carbon are represented in the table 6.

Table 6. Kinetic constants of resorcinol adsorption dynamics by activated carbon at linear velocity 4 cm/min, layer porosity 0,69 and resorcinol concentration 10 mmol/dm^3

Object	Parametres	Kinetic constants` values							
		Ê, min/cm	$á_0$, mmol/dm^3	$â_0$, cm^2/min	D_e, cm^2/min	Bi	$ô_l$, min	$ô_{calc}$, min	$ô_{exp}$, min
Act. carbon in fractions 20x50 mesh	L=12 ñì; r=0,025 ñì	5,512	187,395	1166	0,011	68,988	0,671	65,47	60
	L=6 ñì; r=0,025 ñì	2,913	99,051	452,848	0,0065	47,02	0,631	16,85	15
Act. carbon in fractions 12x40 mesh	L=12 ñì; r=0,05 ñì	5,408	181,699	1171	0,011	70,382	0,669	64,23	60
	L=6 ñì; r=0,05 ñì	3,017	101,375	261,084	0,0073	23,952	0,6	17,50	15

On the basis of the calcutated kinetic constants the protective power time of the layer for activated carbon has been computed. For comparison, the experimental values of the protective power time of the layer are presented. The calculated values are consistent with the experimental data. On the basis of Bio criteria values and internal diffusion coefficient for activated carbon it has been determined that the limitative stage of the process is internal diffusion.

Conclusion

1. For the description of resorcinol adsorption from water solutions in static conditions the Dubinin-Astakhov equation was chosen and values of the limit adsorption and characteristic energy have been calculated.
2. DEC, FDEC and kinetic constants of adsorption in dynamic conditions have been calculated. It has been shown that the limitative stage of adsorption process is internal diffusion. Protective power time and the loss of protective power time of the layer, having been computed on the base of kinetic parameters, are consistent with the experimental data for activated coconut carbon.
3. Activated coconut carbon Ecofresh Carbon can be recommended as an optimal sorbent for purification of waste waters from phenols.

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