ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Study of Kinetic - Thermodynamic Aspects of Phenol Adsorption On Natural Sorption Materials.

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ABSTRACT

Phenol is one of the most toxic pollutants which get into the water ponds and streams with wastewater from chemical, petrochemical, pharmaceutical and other industries. The most effective method of wastewater treatment from phenol is its adsorption on activated carbon, but the disadvantages of this sorbent usage are its high cost, the necessity of regeneration and soot formation due to the brittleness of carbon atoms bonds. A new trend that has intensively developed in the practice of water treatment recently is the use of wastes of industrial and agricultural production as reagents for removing of pollutants from natural water and wastewater. Cellulose and keratin-containing wastes from processing of agricultural raw materials are of particular interest. The advantages of these reagents are available resource base, renewability, low cost, availability and ease of disposal. Therefore, in single-step static adsorption mode with the use of phenol solutions as the model systems the kinetics of phenol adsorption by natural materials, namely, wheat husk, rye husk, oat husk and barley husk was studied at different temperatures (25°C, 35°C and 45°C). Rye husk did not show any sorption properties in relation to phenol. For wheat, oat and barley husks the adsorption isotherms were constructed in coordinates: $1/F = f(1/C)$, $lgF = f(lgC)$, $lnF = f(\varepsilon^2)$. The equations which describe the processes of phenol sorption by wheat, oat and barley husks were calculated. It was found that processes of phenol adsorption by wheat, oats and barley husks can be better represented by the Dubinin - Radushkevich equation, although Langmuir equation can also be used to describe these processes with correlation coefficients more than 0,992. Also the thermodynamic constants and energy of phenol sorption by natural materials were determined.

Keywords: phenol adsorption, wheat husk, rye husk, oat husk, barley husk, adsorption isotherms.

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INTRODUCTION

Phenol and its derivatives are one of the priority pollutants of the environment due to their high toxicity. In particular, the maximum permissible concentration (MPC) of phenol in water reservoirs is 0,001mg/dm^3. Phenol derivatives fall into surface water bodies with wastewater of coal processing, gasoline, plastics, elastomers, disinfectants production, organic synthesis, pharmaceutical and steel industries, etc.

There is a lot of methods for removal or disposal of phenol and its derivatives from wastewater, including chemical, physicochemical and biological methods [1-10]. The most effective, as the researchers note, is the use of sorption technique by activated carbon for the phenol contaminated wastewater treatment [11-15]. Activated carbon allows almost completely removing the organic pollutants from aqueous media. The degree of purification is determined by the concentration of pollutants in the treated effluent. However, disadvantages of mentioned method are the high cost of coal and the need of its regeneration, which significantly increases the cost of purification.

The use of industrial and agricultural wastes as sorption materials for water treatment has become widely spread and relevant recently. Cellulose and keratin-containing agricultural wastes, in particular, are a great concern of environmental scientists and technologists. The advantages of these reagents are available resource base, renewability, low cost, availability and ease of disposal. Therefore, phenol sorption by various agricultural wastes was investigated earlier and described in reviews [16-19].

Cereals are the large-tonnage crops and their processing, respectively, leads to the formation of significant amounts of wastes, including straw, husks, bran, etc. Disposal of these wastes presents a specific problem. This problem is especially important for the grain processing in elevators, where husks during storage can cause an inflammation.

Therefore, in the present study the possibility of sorption removal of phenol from model aqueous media by crop husks was investigated. The kinetic and thermodynamic aspects of phenol adsorption process by agricultural wastes, namely, wheat husk (*Triticum aestivum L*), rye husk (*Secále cereále*), oat husk (*Avena sativa*) and barley husk (*Hordeum vulgare*), were investigated.

METHODS

At the initial stage of the research the pretreatment of sorption materials was conducted and their morphological properties, namely, specific surface area of particles, bulk density and water uptake, were studied. Cereal husk was thoroughly washed and dried in an oven at 110°C to constant weight. The specific surface area of particles characterizes the overall surface area of particles per 1 kg of sorbent and is defined by the formula:

$$S = (2ab + 2ac + 2bc) \cdot n \cdot 1000 , \qquad (1)$$

where a, b and c - the height, width and length of the particles, respectively, and n is the number of particles in one gram of sorbent.

Bulk density is determined by the formula (2):

$$\rho = \frac{g_2 - g_0}{g_1 - g_0} , \qquad (2),$$

where g_o, g_1 and g_2 – the weight of empty containers, the weight of container filled with distilled water and the weight of container filled with the sorbent, respectively.

Water absorption is determined by the number of grams of water, which can be absorbed by 1 gram of sorbent, and it is calculated by the formula (3):

$$B = \frac{g_2 - g_1}{m} , \qquad (3),$$

where g_1 and g_2 are the initial and final weights of water, m is the weight of the sorbent.

At the second stage of the research in single-step static adsorption mode with the use of phenol aqueous solutions (C = 0,01-1,1 mmol/dm^3) as the model systems the kinetics of phenol adsorption by natural materials, namely, wheat husk, rye husk, oat husk and barley husk, at a dosage of 10 g/dm^3 was studied at different temperatures (25°C, 35°C and 45°C). For this purpose aqueous solutions of phenol with various concentrations were prepared (C_1 = 0,01mmol/dm^3, C_2 = 0,03 mmol/dm^3, C_3 = 0,05 mmol/dm^3, C_4 = 0,11mmol/dm^3, C_5 = 0,21 mmol/dm^3, C_6 = 0,32 mmol/dm^3, C_7 = 0,53 mmol/dm^3, C_8 = 1,10 mmol/dm^3). 1 g of studied sorption material was added into the flasks with 100 ml of the resulting solution. Stirring the solution of sorbate with the studied sorption materials had been carried out by means of the magnetic stirrer with heating for 5 hours.

The initial and equilibrium concentrations of phenol were determined by bromatometric titration based on bromating by excess of bromide – bromated mixture, preparation of iodine by reacting of potassium iodide with bromine and titration of iodine with sodium thiosulphate with starch as indicator by the standard method described in the article [20]. The average value of two parallel measurements of titration had been accepted as a resulting value. The measurement error was 10^{-5} mmol/dm^3 that was acceptable for these measurements.

RESULTS

Morphological characteristics of wheat, rye, barley and oat husks are presented in Table 1.

Table 1: Morphological characteristics of natural sorption materials

Sorption material	Characteristic		
	Specific surface area of particles, 10^6 m^2/kg	Bulk density, kg/m^3	Water absorption, g/g
Wheat husk	67	38	4,925
Rye husk	8,908	50	2,92
Oat husk	10,12	136	5,68
Barley husk	21	102	8,21

Based on the experimental data, sorption capacity for phenol by studied sorption materials (F) was calculated by the formula:

$$F = \frac{C_0 - C_1}{V \cdot m}, \qquad (4),$$

where F - sorption capacity for phenol (mmol/g), C_0 - initial concentration of phenol (mmol/dm^3), C_1 - concentration of phenol after adsorption (mmol/dm^3), V - volume of solution (dm^3), m - weight of the sorption material (g).

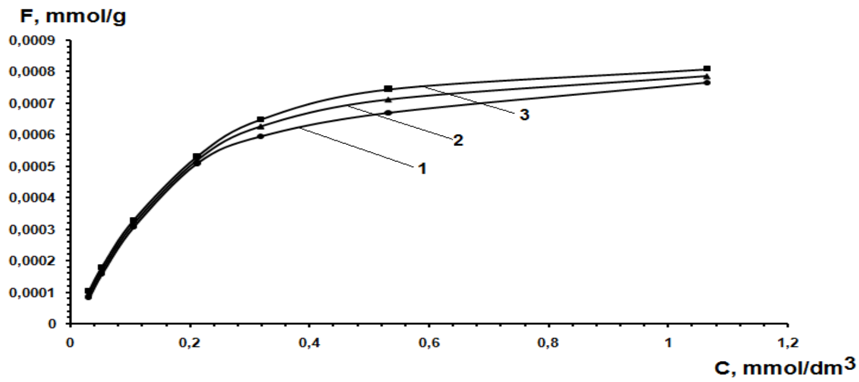

Figure 1: Sorption isotherms of phenol by wheat husk at specific temperatures: 1 - 25°C, 2 - 35°C, 3 - 45°C

According the experiments it was determined that rye husk showed no sorption properties in relation to phenol at all three temperatures. Phenol sorption isotherms on wheat, oat and barley husks are shown in Figures 1, 2 and 3, respectively.

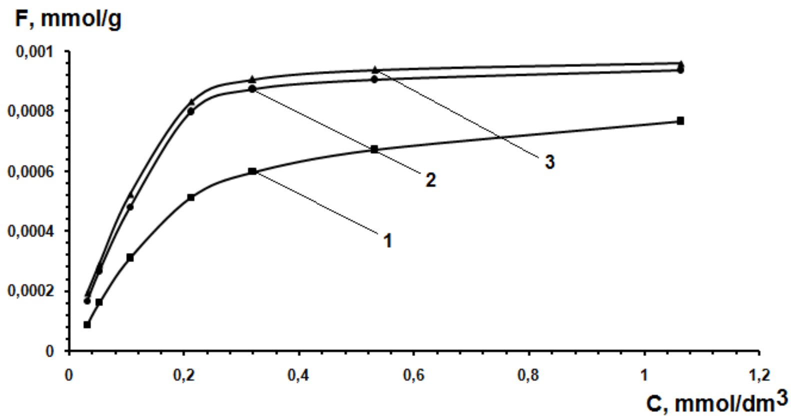

Figure 2: Sorption isotherms of phenol by oat husk at specific temperatures:
1 - 25°C, 2 - 35°C, 3 - 45°C

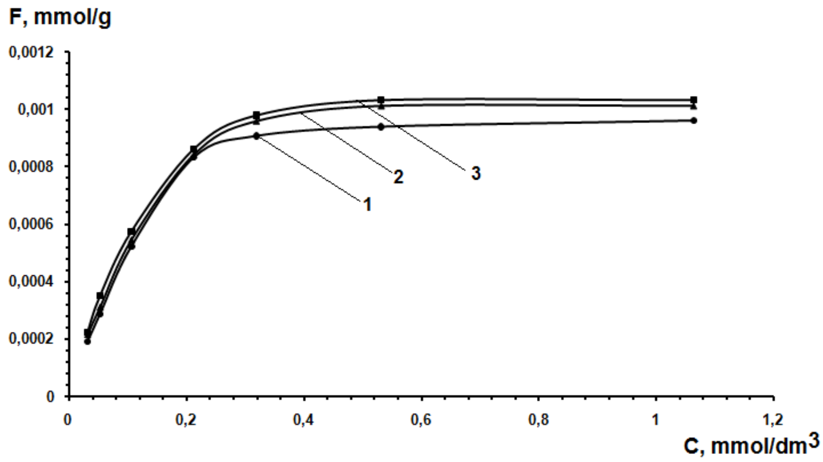

Figure 3: Sorption isotherms of phenol by barley husk at specific temperatures:
1 - 25°C, 2 - 35°C, 3 - 45°C

DISCUSSION

According the classification of BDDT (sorption isotherms classification that was proposed by Brunnauer, Deming, Deming and Teller and has been used by the recommendation of IUPAC) adsorption isotherms data correspond the type 1 of adsorption isotherms and describe monomolecular adsorption of phenol by wheat (Fig. 1), oat (Fig. 2) and barley (Fig. 3) husks. The sorption capacity for phenol in all three cases slightly increased with the increase of temperature.

For the determination of mechanism of phenol sorption by natural materials and for the mathematical description of the processes constants of the equations which describe the sorption isotherms were estimated. The most commonly used equations are Langmuir, Freundlich and Dubinin-Radushkevich models.

Langmuir sorption isotherm is described by the equation (5), Freundlich sorption isotherm by the equation (6), Dubinin - Radushkevich sorption isotherm by the equation (7).

$$1/F = 1/Q_0 + 1/(bQ_0C) \qquad (5)$$

$$\lg F = \lg K_F + 1/n \lg C \qquad (6)$$

$$\ln F = \ln X_m - \beta\varepsilon^2 \qquad (7)$$

where C - molar concentration of phenol in the solution, F - sorption capacity of phenol, Q_o and b - Langmuir constants, K_F and n - Freundlich constants, X_m - the maximum sorption capacity, β - Dubinin - Radushkevich constant or activity coefficient associated with the adsorption energy, ε - Polanyi potential, which is determined by the formula:

$$\varepsilon = RT \ln(1 + F^{-1}) \qquad (8)$$

where R - universal gas constant, T - temperature in Kelvin.

Using the method of least squares by means of «Microsoft Office Excel» software, an approximation of the kinetic sorption isotherms of phenol by natural materials, namely, wheat husk, oat husk and barley husk, was carried out in the coordinates: 1/F = f(1/C), lgF = f(lgC), and ln(f) = f (ε^2). Langmuir, Freundlich and Dubinin – Radushkevich equations shown in table 2 were obtained.

According Table 2 the sorption kinetics of phenol by of wheat, oat and barley husks at all three temperatures better fits the equation of Dubinin - Radushkevich with high correlation coefficients which reach 0.999.

Table 2: The equations of adsorption isotherms and their correlation coefficients

Sorbent	T, °C	Type of isotherm	Equation	Correlation coefficient
Wheat husk	25	Langmuir	y = 340,2x + 544,5	0,992
		Freundlich	y = 0,628x – 2,991	0,954
		Dubinin - Radushkevich	y = 0,0987·10^{-7}x + 4,085	0,999
	35	Langmuir	y = 301,4x + 640,0	0,995
		Freundlich	y = 0,612x – 2,981	0,958
		Dubinin - Radushkevich	y = 0,0996·10^{-7}x + 4,048	0,999
	45	Langmuir	y = 269,9x + 717,1	0,998
		Freundlich	y = 0,594x – 2,973	0,961
		Dubinin - Radushkevich	y = 0,105·10^{-7}x + 4,017	0,999
Oat husk	25	Langmuir	y = 168,7x + 663,3	0,996
		Freundlich	y = 0,514x – 2,893	0,932
		Dubinin - Radushkevich	y = 0,104·10^{-7}x + 3,864	0,999
	35	Langmuir	y = 157,7x + 535,5	0,998
		Freundlich	y = 0,558x – 2,803	0,950
		Dubinin - Radushkevich	y = 0,107·10^{-7}x + 3,786	0,999
	45	Langmuir	y = 155,9x + 496,6	0,998
		Freundlich	y = 0,562x – 2,786	0,945
		Dubinin - Radushkevich	y = 0,107·10^{-7}x + 3,772	0,999
Barley husk	25	Langmuir	y = 143,3x + 712,3	0,996
		Freundlich	y = 0,783x – 2,889	0,931
		Dubinin - Radushkevich	y = 0,106·10^{-7}x + 3,826	0,999

	35	Langmuir	y = 128,0x + 715,7	0,997
		Freundlich	y = 0,474x – 2,870	0,939
		Dubinin - Radushkevich	$y = 0{,}107 \cdot 10^{-7}x + 3{,}788$	0,999
	45	Langmuir	y = 118,2x + 698,9	0,997
		Freundlich	y = 0,452x – 2,866	0,936
		Dubinin - Radushkevich	$y = 0{,}107 \cdot 10^{-7}x + 3{,}770$	0,999

At the second stage of the study the thermodynamic quantities and the values of sorption energy of phenol by natural materials (Table 3) were determined using Langmuir constants and Dubinin - Radushkevich constants by formulas (9) – (12).

$$\Delta G^\circ = -RT \ln b \qquad (9)$$

$$\Delta H^\circ = R \frac{T_2 T_1}{T_2 - T_1} \ln \frac{b_2}{b_1} \qquad (10)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \qquad (11)$$

$$E = (-2\beta)^{-\frac{1}{2}} \qquad (12)$$

Table 3: Thermodynamic constants and energy of phenol sorption by natural sorption materials

Sorbent	Wheat husk	Oat husk	Barley husk
ΔH_{298}, kJ/mol	18,269	-5,230	4,627
ΔS_{298}, kJ/(mol·K)	65,216	-6,168	28,859
ΔG_{298}, kJ/mol	-1,165	-3,391	-3,973
ΔG_{308}, kJ/mol	-1,204	-3,505	-4,106
ΔG_{318}, kJ/mol	-1,243	-3,619	-4,239
E_{298}, kJ/mol	7,118	6,915	6,879
E_{308}, kJ/mol	7,083	6,849	6,843
E_{318}, kJ/mol	7,054	6,837	6,826

The values of the adsorption enthalpy have low absolute value, which is less than 100 kJ / mol, that indicated the physical adsorption of phenol on wheat, oat and barley husks.

The kinetics of adsorption processes of phenol by available and cheap natural sorption materials, namely, wheat husk, oat husk and barley husk, at 25°C, 35°C and 45°C was studied. Rye husk showed no sorption properties in relation to phenol. For wheat, oat and barley husks adsorption isotherms were constructed in coordinates 1/F = f (1/C), lgF = f(lgC), lnF = f(ε^2). The equations describing sorption processes of phenol by wheat, oat and barley husks at three temperatures were calculated. It was found that phenol adsorption process by wheat, oats and barley husks better fits Dubinin – Radushkevich equation with a correlation coefficient of 0.999. Thermodynamic sorption constants and energy sorption of phenol by natural materials were identified. The adsorption enthalpy has low absolute value, which is less than 100 kJ/mol, that indicates physical adsorption of phenol on crops husks.

ACKNOWLEDGEMENTS

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

ISSN: 0975-8585

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