RESEARCH ARTICLE

Study of phenol adsorption by modified birch leaves: Preparation and adsorption characteristics

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Abstract

Aim and Scope: One of the priority areas of chemistry and ecology is the receipt of highly effective, cheap, and accessible sorption materials. The waste from industrial and agricultural production is considered as the sources of such sorption materials. In connection with the foregoing, modified sorption materials based on birch leaves (Betula pendula) were prepared by surface treatment with the solutions of sulfuric acid at the concentrations of 1–5% and their sorption properties were studied with respect to phenol in the static adsorption regime.[1] **Material and Methods:** The study of the sorption properties of materials was carried out in the static adsorption regime on model systems. **Result and Discussion:** Sulfuric acid-modified birch leaves were obtained by the processing of material surface with the solutions of sulfuric acid at the concentrations of 1, 2, 3, 4, and 5%. Sorption properties of native and modified sorption materials were studied with respect to phenol in the static adsorption regime. They created the isotherms of phenol sorption by studied materials. It was found that the process of phenol sorption by native birch leaves at the temperature of 25°C is best described by the Dubinin-Radushkevich equation, and at 35°C and 45°C by Langmuir's equations, while the process of phenol sorption by modified birch leaves at all three temperatures is best described by Temkin's equations.**Conclusion:** Thermodynamic constants of the phenol sorption process by native and modified birch leaves have been calculated. It has been established that the processes of phenol sorption by native and modified birch leaves refer to physical processes (according to modulus: $E < 8$ kJ/mol, $\Delta H < 100$ kJ/mol, $\Delta G < 20$ kJ/mol) with maximum sorption capacities of 0.06 mmol/g and 0.128 mmol/g, respectively, at 25°C.

Key words: Adsorption, birch leaves, phenol, sorption isotherms, sulfuric acid treatment

INTRODUCTION

A renewed biomass of wood foliage occupies a separate position. The latter is formed annually in huge quantities and can be used as a sorption material to remove various pollutants from aqueous media such as heavy metal ions,[2] dyes,[3,4] oil, and petroleum products.[5,6]

One of the most toxic pollutants falling into surface waters with chemical, petrochemical, pharmaceutical, steelmaking, and other industries is phenol (PDKr.x = 0.001 mg/dm^3).[7]

Earlier, the sorption properties of cellulose-containing sorption materials with respect to phenol were studied in Bhatnagar and Sillanpää[8] and Soto *et al.*[9] To increase the sorption properties of cellulose-containing materials, it is proposed to use chemical surface modification using acid solutions in Kondalenko *et al.*[10] and O'Connell and O'Dwyer[11] and Bhatnagar and Sillanpää.[8]

In connection with the foregoing, modified sorption materials based on birch leaves (*Betula pendula*) were prepared by surface treatment with the solutions of sulfuric acid at the concentrations of 1–5% and their sorption properties were studied with respect to phenol in the static adsorption regime.

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MATERIALS AND METHODS

Preliminary preparation and modification of sorption materials. A preliminary preparation of native materials consisted in thorough washing of the initial sorption materials with distilled water to remove dust and other unwanted impurities from the sorbent surface and dry the materials in a drying cabinet at the temperature of 110°C until the constant mass of the sorbent is gained.

The chemical modification consisted in sorbent surface treatment for 24 h with the solutions of sulfuric acid at the concentrations of 1–5%. The resulting modified sorption materials were washed with distilled water to a neutral pH of the wash water and dried at the temperature of 110°C to constant weight.

The study of the sorption properties of materials in the static adsorption mode. The determination of material sorption properties was carried out in the static adsorption regime on model systems - the aqueous solutions of phenol with initial concentrations (Cs): 0 mg/dm^3, 1 mg/dm^3, 3 mg/dm^3, 5 mg/dm^3, 10 mg/dm^3, 20 mg/dm^3, 30 mg/dm^3, 50 mg/dm^3, and 100 mg/dm^3, with the sorbent dosage of 10 g/dm^3, the sorption time of 5 h, the temperatures of 25, 35, and 45°C. The stirring of the phenol solution with the sorption material was carried out by a magnetic stirrer with heating. The initial and equilibrium concentration of phenol was determined by the fluorimetric method on the analyzer of "Fluorate 02-2M" brand. The mass concentration of phenol in the resulting solution was measured 5 times and the arithmetic mean was determined.[12]

RESULTS AND DISCUSSION

At the first stage of the study, the main characteristics of the birch leaves are set using the standard techniques [Table 1].

The Study of the Sorption Properties of Materials with Respect to Phenol

Based on the phenol adsorption data obtained by native and modified birch leaves in the static adsorption regime, the sorption capacity of materials (A) was calculated from formula 1, and the isotherms of phenol sorption were constructed by native and modified materials [Figure 1].

$$A = \frac{C_s - C_e}{m} V \quad (1)$$

Where A is the sorption capacity (mmol/g), C_s is the initial concentration of adsorbate (mmol/dm^3), C_e is the concentration of adsorbate after sorption (mmol/dm^3), V is the volume of solution (dm^3), and m is the mass of sorption material (g).

The isotherms of phenol sorption by native and modified birch leaves belong to the 1st type of sorption isotherm, according to Brunauer Deming-Deming-Teller classification,[8] and to L type, according to the classification of the Gils sorption isotherms,[13] and describe the monomolecular adsorption of phenol on the sorbent surface (typical Langmuir sorption isotherm). It is clear from the sorption isotherm that as the concentration of the acid-modified increases, the sorption properties of materials increase with respect to phenol.

The effect of temperature on the course of phenol sorption processes by native and modified birch leaves is shown in Figure 2.

It can be seen from Figure 2 that the sorption properties of the materials increase as the temperature increases.

For the purpose of the mathematical description of monomolecular adsorption isotherms, Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin equations are usually used.[14] The results of phenol adsorption isotherm calculation by the studied materials are presented in Table 2.

According to Table 2 data it is established that the process of phenol sorption by native birch leaves at the temperature

Table 1: Characteristics of birch leaves

Characteristic	Value
Bulk density, kg/m^3	110
Water absorption, g/g	8.2
Moisture content, %	6.5
Buoyancy, %	57.5
Ash content, %	0.84
Specific surface, m^2/kg	84.0

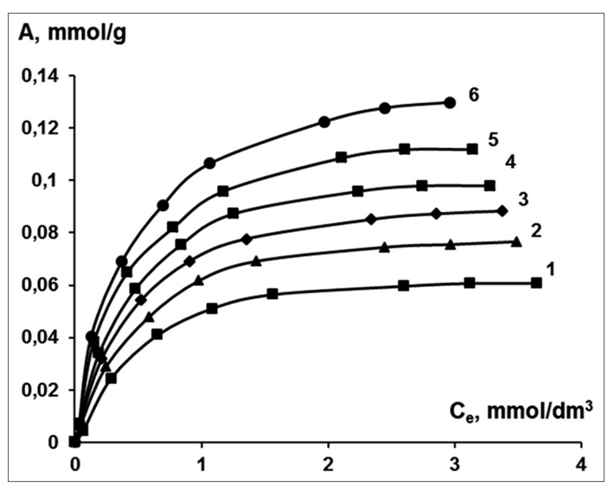

Figure 1: Isotherms for adsorption of phenol by birch leaves, modified with solutions of sulfuric acid with concentrations: (1) 0%, (2) 1%, (3) 2%, (4) 3%, (5) 4%, and (6) 5%

Table 2: Results of calculations of phenol adsorption isotherms by raw and modified birch leaves

Adsorption material	T, °C	Adsorption model	Adsorption equation	Coefficient of approximation
Raw birch leaves	25	Langmuir	y=14.336x+6.8148	R^2=0.9909
		Freundlich	y=0.6196x-1.4292	R^2=0.8771
		Dubinin-Radushkevich	y=−2E-08x-1.8507	R^2=0.9937
		Temkin	y=0.0147x+0.0457	R^2=0.9778
	35	Langmuir	y=10.68x+8.8013	R^2=0.9962
		Freundlich	y=0.5924x-1.3864	R^2=0.8953
		Dubinin-Radushkevich	y=−2E-08x-1.7943	R^2=0.9933
		Temkin	y=0.0155x+0.0495	R^2=0.9794
	45	Langmuir	y=9.1277x+7.1623	R^2=0.9948
		Freundlich	y=0.5979x-1.3148	R^2=0.8964
		Dubinin-Radushkevich	y=−2E-08x-1.7208	R^2=0.9921
		Temkin	y=0.0179x+0.0579	R^2=0.9844
Modified by 5% sulfuric acid solution birch leaves	25	Langmuir	y=4.2693x+3.7114	R^2=0.9865
		Freundlich	y=0.587x-1.0438	R^2=0.8952
		Dubinin-Radushkevich	y=−2E-08x-1.4583	R^2=0.9864
		Temkin	y=0.0283x+0.1012	R^2=0.9963
	35	Langmuir	y=3.9456x+1.461	R^2=0.9417
		Freundlich	y=0.5793x-0.9737	R^2=0.8598
		Dubinin-Radushkevich	y=−2E-08x-1.4039	R^2=0.9843
		Temkin	y=0.0323x+0.113	R^2=0.9947
	45	Langmuir	y=3.5777x+0.0244	R^2=0.8834
		Freundlich	y=0.5872x-0.9	R^2=0.8393
		Dubinin-Radushkevich	y=−2E-08x-1.3445	R^2=0.9815
		Temkin	y=0.0359x+0.1351	R^2=0.9902

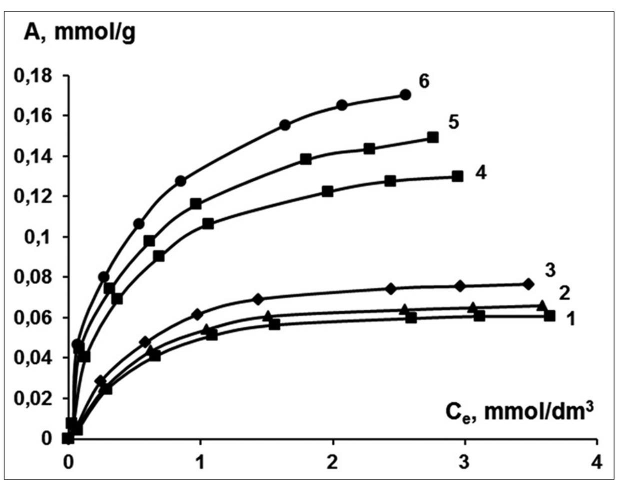

Figure 2: Isotherms for adsorption of phenol by raw birch leaves at temperatures: (1) 25°C, (2) 35°C, and (3) 45°C, and modified by 5% sulfuric acid solution birch leaves at temperatures: (4) 25°C, (5) 35°C, and (6) 45°C

of 25°C is best described by the Dubinin-Radushkevich equation, and at 35°C and 45°C by Langmuir's equations, while the process of phenol sorption by modified birch leaves for all three temperatures are best described by Temkin's equations. Thus, it can be concluded that the chemical modification of the surface of birch leaves with a 5% solution of sulfuric acid not only increases the sorption properties of birch leaves with respect to phenol but also affects the mechanism of the process.

The Calculation of Thermodynamic Values of Phenol Sorption by Native and Modified Cellulose-containing Sorption Materials

The thermodynamic constants are determined by equations 2–5 using Langmuir and Dubinin-Radushkevich constants and are presented in Table 3.

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

$$\Delta G^\circ=-RT\ln K_L \quad (3)$$

$$\Delta H^\circ=R\frac{T_2T_1}{T_2-T_1}\ln\frac{K_{L2}}{K_{L1}} \quad (4)$$

$$\Delta S^\circ=\frac{\Delta H^\circ-\Delta G^\circ}{T} \quad (5)$$

Table 3: Thermodynamic constants of phenol adsorption processes by raw and modified birch leaves

Sorbent	T, °C	E, kJ/mol	ΔH, kJ/mol	ΔS, J/mol•K	ΔG, kJ/mol	Adsorption mechanism
Raw birch leaves	25	5.000	−3.991	−11.401	−1.842	Physical adsorption
	35	5.000			−0.479	Physical adsorption
	45	5.000			−0.601	Physical adsorption
Modified birch leaves	25	5.000	−65.125	−217.38	−0.347	Physical adsorption
	35	5.000			−2.461	Physical adsorption
	45	5.000			−12.358	Physical adsorption

According to the sources,[15-17] the physical adsorption proceeds are represented by the following values (modulus): The adsorption energy is <8 kJ/mol, the adsorption enthalpy is <100 kJ/mol, and the Gibbs energy is <20 kJ/mol.

CONCLUSIONS

The chemical modification of birch leaves with the solutions of sulfuric acid increases the sorption properties of the material in relation to phenol by more than 2 times. The obtained isotherms of phenol adsorption by native and modified birch leaves describe the monomolecular adsorption of phenol on the materials under study. The isotherms of phenol adsorption by native birch leaves at the temperature of 25°C can be described by the Dubinin-Radushkevich equation (R^2 = 0.9937), at 35°C and 45°C by the Langmuir equation (R^2 = 0.9962 and R^2 = 0.9948, respectively), and phenol adsorption isotherms modified with birch leaves at the temperatures of 25°C, 35°C, and 45°C are best described by Temkin's equations (R^2 = 0.9963, R^2 = 0.9947, and R^2 = 0.9902, respectively). It is revealed by the values of the thermodynamic values of phenol adsorption processes and by native and modified birch leaves that the processes under study are related to the processes of physical adsorption.

SUMMARY

Sulfuric acid-modified cellulose-containing sorption materials based on birch leaves were obtained. Sorption properties of native and modified birch leaves were studied under the conditions of static adsorption at the temperatures of 25, 35, and 45°C. It has been revealed that the sorption properties of modified birch leaves are more than 2 times higher than the native form of the sorbent with respect to phenol. The isotherms of phenol sorption by native and modified birch leaves are referred to the 1st type of international union of pure and applied chemistry and L-type isotherms according to Gils classification and describe monomolecular sorption of phenol on the surface of materials. The treatment of isotherms in the framework of Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models revealed that the process of phenol sorption by native birch leaves at the temperature of 25°C is best described by Dubinin-Radushkevich equation, and at 35°C and 45°C by Langmuir equations, while the sorption process of phenol with modified birch leaves at all three temperatures is best described by Temkin equations. The thermodynamics of phenol sorption by native and modified materials was studied at the temperatures of 25°C, 35°C, and 45°C. According to the calculated energy of sorption, enthalpy, and Gibbs energy, it is noted that both sorption processes pertain to physical processes.

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