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Study of phenols and petrochemicals adsorption from model solutions using various sorbents

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Abstract. The article studies petrochemicals and phenols adsorption in static and dynamic conditions from model petrochemical solutions. It was established that the adsorption of resorcinol occurs in micropores by volumetric filling, this process is best described by the Dubinin-Astakhov equation. The adsorption of petrochemicals occurs on the sorbent surface, forming a monolayer, this process is best described by the Langmuir equation. Based on the kinetic curves of petrochemicals and resorcinol adsorption, DEC (dynamic exchange capacity) and FDEC (full dynamic exchange capacity) have been calculated for activated carbons and fibrous sorption material. Using the Shilov equation, kinetic constants of the adsorption dynamics for resorcinol and petrochemicals on various sorbents are calculated. The study proved the promising use of sorbents for wastewater treatment of various industries.

1. Introduction

Phenols and petrochemicals are one of the most dangerous pollutants contained in wastewater of various industries. According to the publications [1]. For fishery reservoirs, the following maximum permissible concentrations are established: for petrochemicals – 0.05 mg/dm^3, for phenols – 0.1 mg/dm^3.

An analysis of methods used for treating wastewater from petrochemical products and phenols shows that none of them allows reaching concentrations in the treated water that correspond to the maximum permissible concentrations for fishery reservoirs [2–7]. Most of the methods used either require energy or chemical reagents, or the secondary pollution is formed. One of the most effective methods of wastewater treatment from phenols and petroleum products, in our opinion, is the adsorption method using affordable and cheap sorbents.

2. Materials and methods

As the model wastewater system containing petrochemicals, we took finely dispersed system wastewater-gasoline. The system was composed in a proportion of 1:15 (gasoline-distilled water) so that the initial concentration of petrochemicals did not exceed 250 mg/dm^3. Gasoline AI-95 was being mixed with distilled water during the day with periodic stirring. The aqueous fraction was separated from gasoline residues using a separator funnel.

An aqueous solution of resorcinol (m-dihydroxybenzene) was used as a model phenol solution. The concentration of petroleum products and resorcinol was determined by fluorimetric method.

As adsorbents, we used activated carbons of two fractions (0.30-0.84 and 0.40–1.68 mm) produced by Ecofresh Carbon and NWC and fibrous sorption material produced by JSC “VNIISV”.

In static conditions, the adsorption of petrochemicals and phenols was performed from model solutions of petrochemicals with concentrations of 20–100 mg/dm^3 and of resorcinol with concentrations of 0.01–20.0 mmol/dm^3).

In dynamic conditions, the adsorption was performed from model solutions of petrochemicals with a concentration of 200 mg/dm^3 and of resorcinol with concentration of 10 mmol/dm^3 at constant linear speed of 4 cm/min with sorbent layer height of 6 and 12 cm).

The adsorption equilibrium constants in resorcinol-sorbent solution systems have been calculated using the Dubinin-Astakhov equation and in petroleum-sorbent solution systems – using the Langmuir equation.

3. Results

The study of petrochemicals and phenols adsorption in static conditions was performed on model solutions of oil products with a concentration of 20–100 mg/dm^3 and of resorcinol with a concentration of 0.01-20.0 mmol/dm^3. The petrochemicals adsorption was studied at the ratio solution : sorbent = 100:1. The resorcinol adsorption was studied at the ratio solution : sorbent = 1000:1. The time to establish the adsorption equilibrium in the model solution-sorbent system was 48 hours (figures 1, 2).

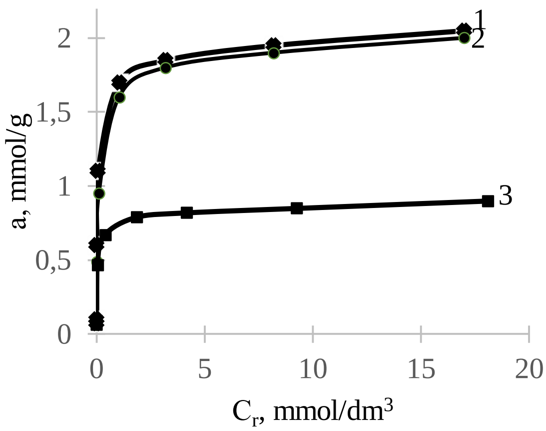

Figure 1. Adsorption isotherms of resorcinol on various sorbents.
1 – adsorption isotherm of resorcinol on activated carbon with a fraction of 0.30–0.84 mm;
2 – adsorption isotherm of resorcinol on activated carbon with a fraction of 0.40–1.68 mm;
3 – adsorption isotherm of resorcinol on carbon-filled fiber material

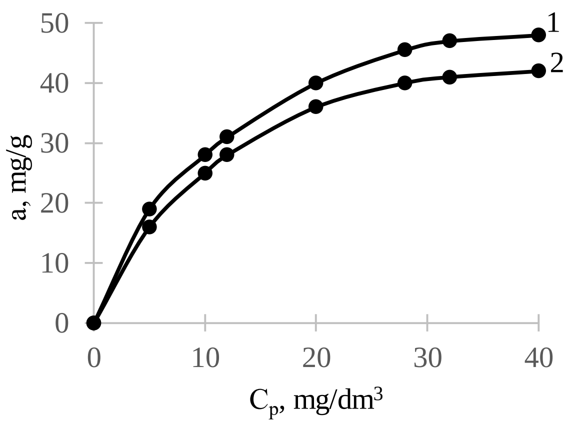

Figure 2. Adsorption isotherms of petrochemicals on various sorbents.
1 – adsorption isotherm of petrochemicals on activated carbon with a fraction of 0.30–0.84 mm;
2 – adsorption isotherm of petrochemicals on activated carbon with a fraction of 0.40–1.68 mm

There are several theories of adsorption [8], each of them is described by its own equation. The appropriateness of applying adsorption theories is determined by the linearized forms of the corresponding adsorption equations for experimental data. The experimental data approximation showed that the adsorption of resorcinol occurs in micropores by volumetric filling and the Dubinin-Astakhov equation is most suitable for describing this process (figures 3–5). The adsorption of petrochemicals occurs on the sorbent surface, forming a monolayer, and the Langmuir equation is most acceptable for describing this process (figure 6).

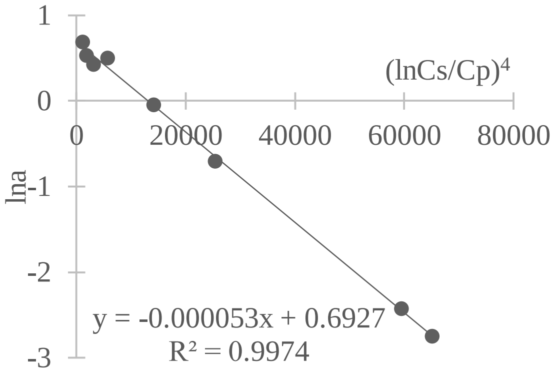

Figure 3. Dubinin-Astakhov equation in a linearized form of resorcinol adsorption on activated carbon of 0.40–1.68 mm.

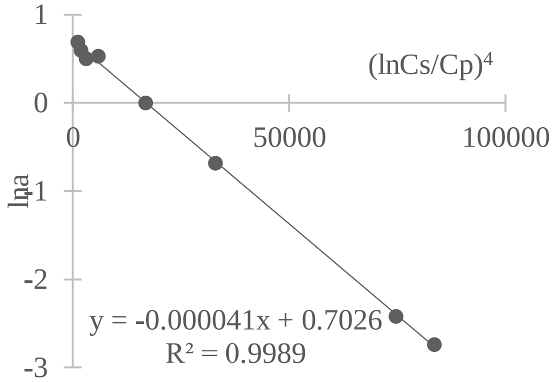

Figure 4. Dubinin-Astakhov equation in a linearized form of resorcinol adsorption on activated carbon of 0.30–0.84 mm.

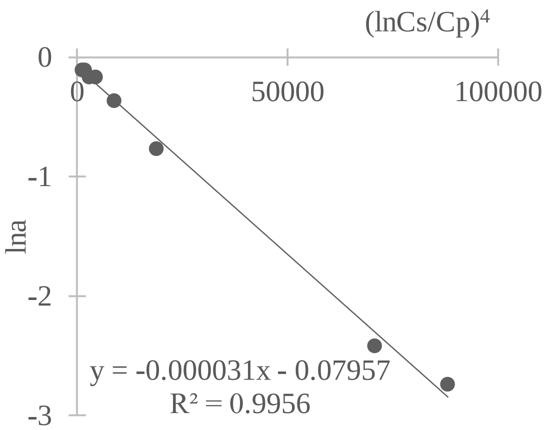

Figure 5. Dubinin-Astakhov equation in a linearized form of resorcinol adsorption on a fibrous sorption material.

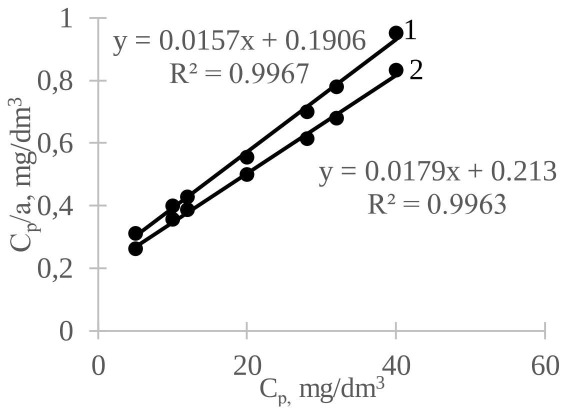

Figure 6. Dubinin-Astakhov equation in a linearized form of petrochemicals adsorption on activated carbon: 1 – fraction of 0.30–0.84 mm; 2 – fraction of 0.40–1.68 mm.

Adsorption equilibrium constants in the resorcinol-sorbent solution systems calculated according to the Dubinin-Astakhov equation, and the petrochemical-sorbent solution systems calculated according to the Langmuir equation, are shown in table 1.

Table 1. Adsorption equilibrium constants.

Adsorbent	Activated carbon 0.40–1.68 mm	Activated carbon 0.30–0.84 mm	Fibrous sorption material
Characteristic adsorption energy of resorcinol, kJ	28.55	30.44	32.64
Maximum adsorption value of resorcinol, mmol/g	2.00	2.02	0.92
Maximum adsorption value of petroleum products, mg/g	5.24	4.70	-
Adsorption equilibrium constant in the petrochemical-sorbent solution system	12.56	11.89	-
Volume of micropores, cm^3/g	0.25	0.23	0.12

The adsorption of petrochemicals and phenols under dynamic conditions was studied on model solutions of petrochemicals with a concentration of 200 mg/dm^3, and of resorcinol – with a concentration of 10 mmol/dm^3 at a constant linear speed of 4 cm/min and sorbent layer height of 6 and 12 cm (figures 7–11).

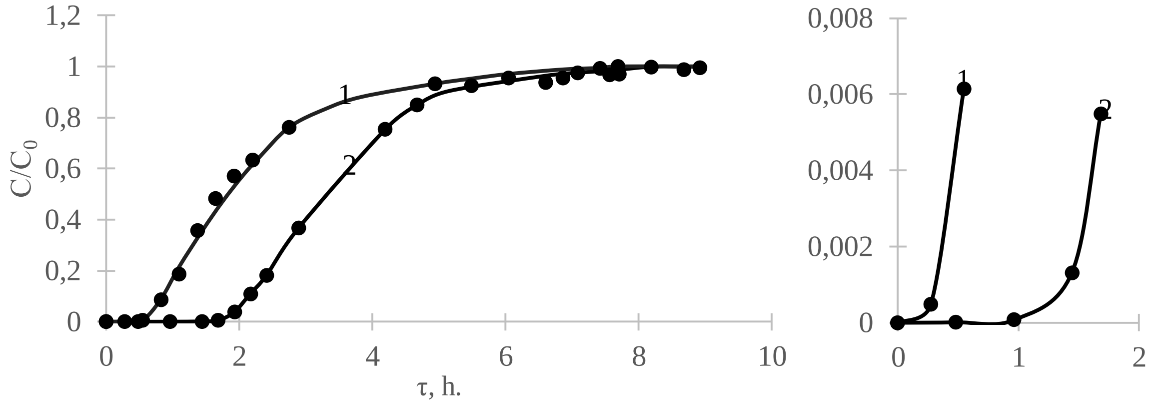

Figure 7. Kinetic curves of resorcinol adsorption on activated carbon of 0.40–1.68 mm at layer height of: 1 – 6 cm, 2 – 12 cm.

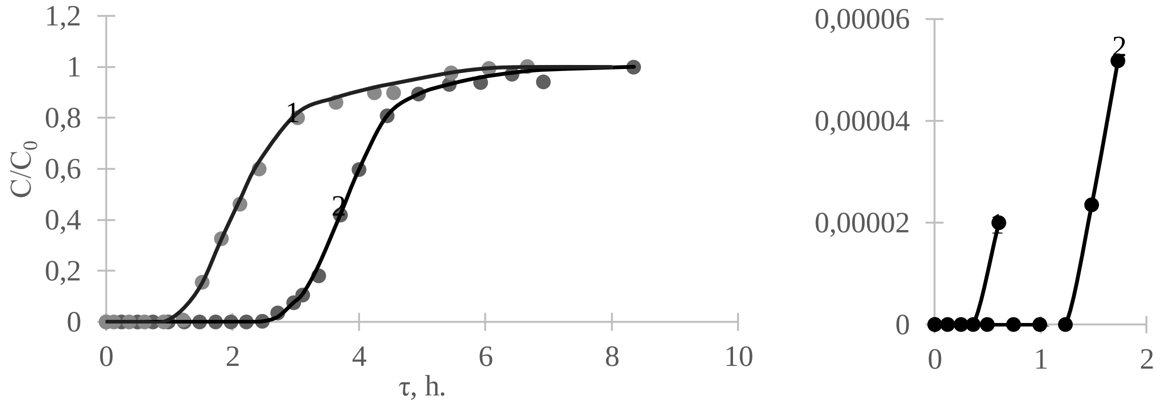

Figure 8. Kinetic curves of resorcinol adsorption on activated carbon of 0.30-0.84 mm at layer height of: 1 – 6 cm, 2 – 12 cm.

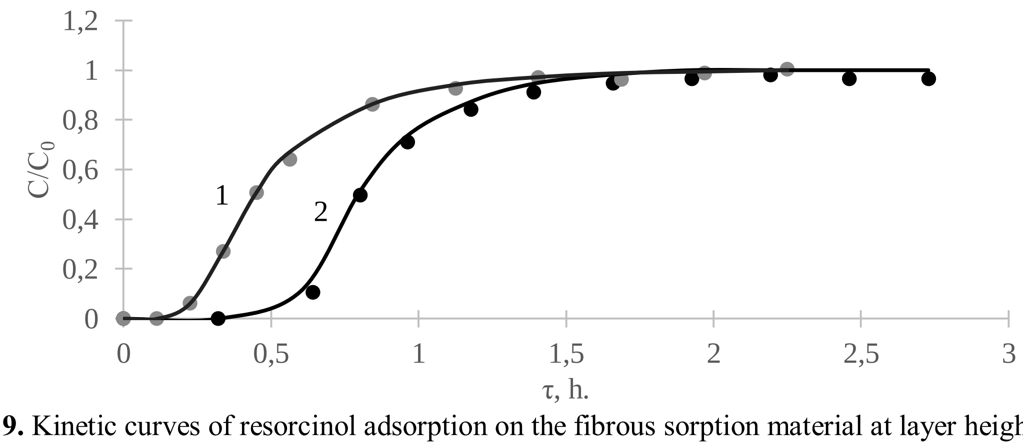

Figure 9. Kinetic curves of resorcinol adsorption on the fibrous sorption material at layer height of: 1 – 6 cm, 2 – 12 cm.

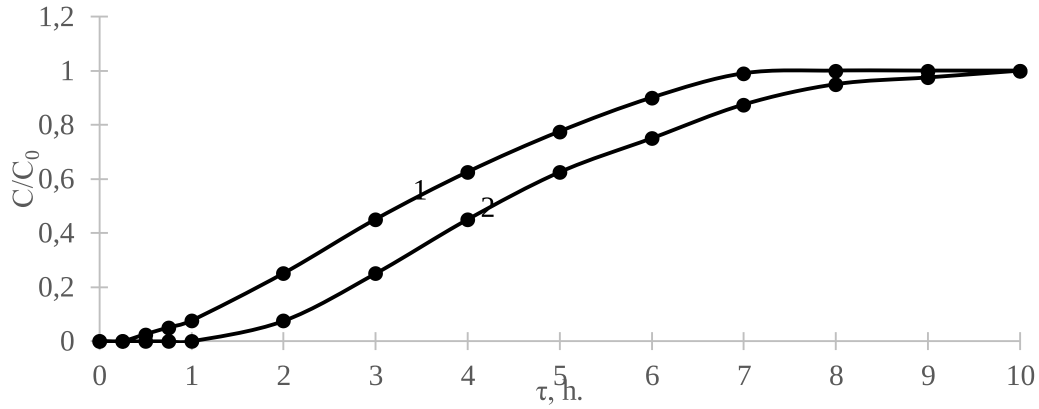

Figure 10. Kinetic curves of petrochemicals adsorption on activated carbon of 0.30–0.84 mm at layer height of: 1 – 6 cm, 2 – 12 cm.

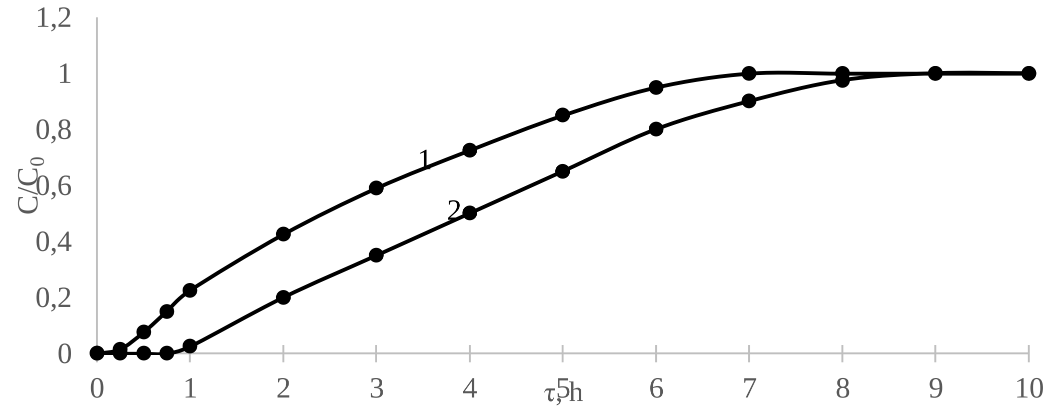

Figure 11. Kinetic curves of petrochemicals adsorption on activated carbon of 0.40 – 1.68 mm at layer height of: 1 – 6 cm, 2 – 12 cm.

Kinetic curves of the petrochemicals and resorcinol adsorption allow us to calculate the dynamic exchange capacity (capacity before the breakthrough) and the full dynamic exchange capacity for activated carbon and fibrous sorption material (table 2).

Table 2. Dynamic exchange capacity and full dynamic capacity on petrochemicals and resorcinol.

№	Adsorbent	Layer height, cm	DEC, mmol/g (mg/g)*	FDEC, mmol/g (mg/g)*
		Resorcinol		
1	Activated carbon 0.40 – 1.64 mm	6	0.19	5.13
2	Activated carbon 0.30 – 0.68 mm	6	0.18	5.00
3	Fibrous sorption material	6	0.17	3.42
		Petrochemicals*		
4	Activated carbon 0.40–1.64 mm	6	20.00	840.00
5	Activated carbon 0.30–0.68 mm	6	30.00	960.00

The kinetic curves shape corresponds to the parallel transfer mode, which allows the kinetic constants to be calculated using the Shilov equation to describe the process. Kinetic constants were calculated from the adsorption dynamics output curves by the least squares method in the computer algebra system MathCAD (table 3).

Table 3. Kinetic constants of adsorption dynamics for resorcinol and petrochemicals on various sorbents at linear speed of 4 cm/min, layer porosity of 0.69, resorcinol concentration of 10.0 mmol/dm^3, and petrochemicals concentration of 200 mg/dm^3.

Kinetic constants	Sorbents					
	Activated carbon 0.30–0.84 mm		Activated carbon 0.40–1.64 mm		Fibrous sorption material	
	h = 6 cm	h = 12 cm	h = 6 cm	h = 12 cm	h = 6 cm	h = 12 cm
K, min/cm	2.91	5.51	3.02	5.41	3.936	7.08
	1.238	1.15	0.62	1.134	-	-
α_0, mmol/dm^3	99.05	187.40	101.38	181.70	133.81	240.64
(mg/dm^3)*	684.20	1115.00	735.7	1116.00	-	-
β^0, cm^2/min	452.85	1166.00	261.08	1171.00	411.76	874.49
	137.31	260.15	143.25	316.41	-	-
D_e, cm^2/min	0.0065	0.011	0.0073	0.011	0.0015	0.0027
	0.019	0.0035	0.0078	0.013	-	-
Bi	47.02	69.00	23.95	70.38	28.94	34.61
	47.78	50.81	61.03	65.98	-	-
$\tau_п$, min	0.63	0.67	0.60	0.67	0.59	0.59
	0.61	0.64	0.63	0.67	-	-
T_{calc}, min	16.85	65.47	17.50	64.23	30.90	98.50
	15.94	62.75	12.11	49.95	-	-
T_{exp}, min	15.00	60.00	15.00	60.00	10.00	20.00
	15.00	60.00	10.00	45.00	-	-

4. Conclusion

The study on the phenols and petrochemicals adsorption on activated carbon and fibrous sorption material under static and dynamic conditions showed the promise of using sorbents for wastewater treatment in various industries from phenols and petroleum products with the aim of releasing treated wastewater into water bodies, including fishery reservoirs.

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