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ADSORPTION OF DISSOLVED OIL PRODUCTS ON MAGNETIC COMPOSITE SORPTION MATERIAL

D. A. Kharlyamov, G. V. Mavrin, N. S. Scherbinin, Sharipov N. S. and Ziganshina E. A.
Department of Chemistry and Ecology, Kazan Federal University, Naberezhnye Chelny, Russia
E-Mail: kharlyamov@gmail.com

ABSTRACT

With method of chemical modification of wood fiber waste was received sample of magnetic composite sorption material. The elemental composition of materials was identified using the method of energy-dispersive X-ray spectroscopy. Sorption capacity of sorption material were researched in relation to dissolved oil products in neutral and acidic medium at temperature of 288, 298, 308 K. It was determined that with the rise of temperature appears lowering of sorption capacity, what tells about possible physical forces which are holding oil products on the surface of sorption material. In acidic medium occurs lowering of sorption capacity. Adsorption isoterms of oil products which were received describe polymolecular adsorption and are characteristic for porous SM. Adsorption capacity in neutral medium at temperature of 288 K made up 6,21mg/g, at temperature of 298 and 308 K - 6.05 and 5.83 mg/g accordingly. Adsorption isotherms worked out within Langmuire, Dubin-Radushkevich and Freundlich models. It was determined that Dubin-Radushkevich model describes adsorption process better than any other. Calculated thermodynamic constants confirmed that adsorption process of oil products on magnetic composite sorption material appears due to physical interaction. Formulated kinetic relations allowed to make a conclusion that adsorption process kinetic on considered sorption material are limited by its outer diffusion.

Keywords: oil products, waste wood fiber, magnetic composite sorption material, adsorption, sorption material.

1. INTRODUCTION

Oil and oil products (OP) are one of the top prioritized pollutions of hydrosphere, and on their own constitute special group of pollutants of water supplies. Then oil and OP gets in environmental objects it violates natural order of biochemical processes and causes changes of physical, chemical and biological characteristics of its components. Elongated interaction of oil’s hydrocarbons with environmental objects can lead to creation of more toxic chemical compounds which don’t split by microorganisms and have strong mutagenic and cancerogenic properties [1].

Now a lot of methods of cleaning OP from water mediums are offered [2-4]. For deeper cleaning of contaminated waters sorption method is used, in base of which goes using of special porous materials and ability to absorb on their surface or in volume a lot of different pollutants. [5-7].

Currently there are many known sorption materials (SM) produced from different substances and which possessing specific surface area, porosity and ion exchange properties [8-10]. Also its worth mentioning that amongst offered SM there are those possessing specific properties, for example ability to biodegrage or have magnetic properties [11-16].

Promising way nowadays is using wood waste as SM for removal of different pollutants from water mediums. In studies of a lot of authors offered studies of kinetic and thermodynamic of adsorption, written calculations about adsorption isotherms of pollutants according to different models. As SM woodworking and logging wastes are used, as in their original state, so in state after modifications with various methods [17].

In terms of this paper thermodynamic and kinetic properties of OP adsorption on magnetic composite sorption material (MCSM), obtained from chemical modification of wood fiber waste (WFW) gathered after manufactory of MDF boards are determined. During research adsorption capacity was determined in relation to dissolved OP, formulated adsorption isotherms, determined thermodynamic and kinetic parameters of adsorption processes of OP on MCSM, discussed efficiency of proposed method.

2. METHODS

MCSM were obtained from WFW out of MDF boards manufactory by treating last with water solutions of ferrum chloride and ammonia, also with ultrasound at 150 W/cm^2 and frequency of 35 kHz in water medium [18].

For research of elemental composition of SM samples was used energy-dispersive X-ray analyzer «JEOL JED-2300» (accelerating electron’s voltage 15 kW, measurement error 10%).

Research of sorption properties of SM in relation to OP were conducted in static conditions in neutral and acidic mediums. Model solutions of OP received by intense mixing of diesel fuel and distillated water using high speed mechanical mixer. After mixing solution was left for upholding and were conducted splitting of water and organic phases. Determining of OP concentration in received solution were conducted according to methodology [19].

To formulate adsorption isotherms of OP was used method of variable suspensions and constant concentrations [20]. With the aim of determining possible mechanisms of sorption process passing experiments were conducted at different temperatures (288, 298 and 308K). By received values of sorption capacity adsorption isotherms were formulated.

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To rate sorption properties of MCSM depending on the time of contact in conical flask with volume of 0,1 l 0,05 l of model solution was poured gradually and 1 g of SM was placed inside of the flask. After that flasks were put on the mixing apparat for different amounts of time (5-120 min), after which SM was removed from the solution with magnet. Value of sorption capacity was calculated using next formula:

$$A = \frac{(C_0 - C) \cdot V}{m},$$

where C_0 - initialconcentration of OP, mg/l; C - final concentration of OP, mg/l; m - mass of suspension SM, g; V - volume of model solution, l.

For the research of absorption mechanism experiments were conducted at different temperatures, made graphs of adsorption capacity in relation to time of contact.

3. RESULTS AND DISCUSSIONS

Process of obtaining MCSM based on sedimentation of magnetite (Fe_3O_4) on the surface of WFW with help of ammonia water from solution, containing mix of chlorides of tri- and divalent ferrum under ultrasonic effect. According to carried out elemental analysis (Table-1), base components as of original sample (WFW) and so of modified one (MCSM) - are oxygen, carbon and nitrogen. Presence of small amount of calcium, silicon and ferrum in original fibers is explained by usage of binding components in its manufactory, also sticking of mechanical particulates on its surface. After modification occurs noticeable rise of ferrum compounds mass fraction, which is connected to sedimentation of Fe_3O_4. Forming of Fe_3O_4 in WFW pores and on the surface confirmed by method of x-ray phase analysis [21].

Table-1. Elemental composition of sorption materials.

Sample	Elemental mass fraction, %						
	C	O	N	Fe	Ca	Mg	Si
MCSM	33,3	38,4	22,2	5,31	0,23	0,15	0,04
WFW	35,1	39,2	24,5	0,16	0,29	0,26	0,07

Research of OP adsorption was conducted in static regime. Firstly was determined equilibrium concentration of dissolved components DF after 2 h of contacting of MCSM mass equal 1g with 0,05 l of model solution with 14 mg/l concentration in neutral medium and 14,5 mg/l in acidic medium at temperatures of 288, 298 and 308 K. Measuring of mass concentration of OP was conducted on concentration meter «KN-3». Calculated values of adsorption capacity SM MCSM in relation to OP presented in Table-2.

Table-2. Adsorption capacity of MCSM in relation to oil products at different temperatures is static conditions.

T, K	Adsorption capacity			
	pH = 7,0± 0,2		pH = 4,0±0,2	
	mmol/g	mg/g	mmol/g	mg/g
288	0,032±0,005	6,21±0,93	0,031±0,005	6,11±0,92
298	0,031±0,008	6,05±0,91	0,030±0,004	5,92±0,89
308	0,030±0,000	5,83±0,87	0,029±0,004	5,64±0,85

According to data from Table-2, it is seen that rise of temperature appears lowering of sorption capacity, which testifies about possible physical nature of forces, holding OP on the surface of the SM. In acidic medium occurs lowering of sorption capacity.

By method of variable suspensions and constant concentrations adsorption isotherms of OP on SM MCSM in neutral medium at temperatures 288, 298 and 308 K (Figure-1) were formulate.

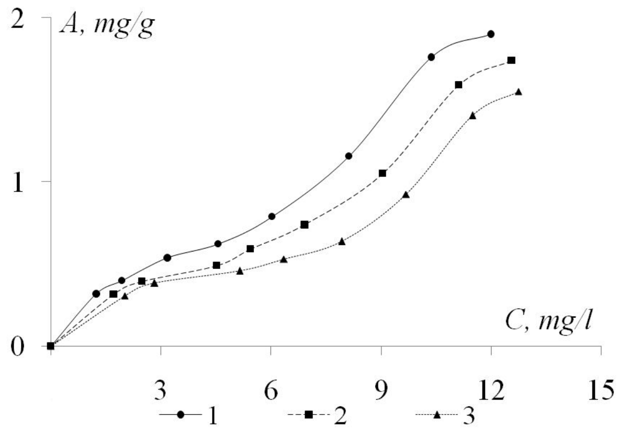

Figure-1. Adsorption isotherms of oil products in neutral medium on sorption material of MCSM at different temperatures: 1 - 288 K; 2 - 298 K; 3 - 308 K.

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According to the classification of BDDT, received isotherms relate to 4th type of adsorption isotherms and describing polymolecular adsorption, which is characteristic for porous SM. By Giles isotherms relate to L class (Langmuir class) [22]. On the beginning stage isotherms characterize by concave line relatively to concentration axis, as contents of OP in solution rises adsorption reaches saturation and leads to formation of plateau and starts process flow of polymolecular adsorption until it reaches second plateau.

Table-3. Results of processing adsorption isotherms of oil products in neutral medium on adsorption material of MCSM at different temperatures according to Langmuire, Dubin-Radushkevich and Freundlich models.

T, K	Langmuire model	Dubin-Radushkevich model	Freundlich model
288	y=3,5812x + 101,32 R^2=0,9814	y=-0,2814x - 5,0595 R^2=0,9934	y=0,7948x + 1,1119 R^2=0,9462
298	y=4,9787x + 98,612 R^2=0,985	y=-0,3353x - 5,1782 R^2 = 0,9962	y=0,8554x + 1,1092 R^2=0,9513
308	y=5,8061x + 117,94 R^2=0,9793	y=-0,3549x - 5,3343 R^2=0,9945	y=0,8378x + 1,2139 R^2=0,9687

Adsorption isotherms worked out within Langmuire, Dubin-Radushkevich and Freundlich models. By presented calculations it was determined that Dubin-Radushkevich model describes adsorption process better than any other in every situation (Table-3).

For calculating thermodynamic constants of adsorption processes of OP on SM MCSM processing of adsorption isotherms were conducted at different temperatures. Adsorption energy (E, kJ/mol) was determined by processing isotherms according to Dubin-Radushkevich model.

Gibbs energy (ΔG^o, J/mol) was calculated using constants of Langmuir equation (K_L) according to formula:

$$\Delta G^o = -R \cdot T \cdot \ln K_L ,$$

where R - universal gas constant J/(mol·K); T - temperature, K.

Enthalpy (ΔH^o, J/mol) was determined by data of two measurements at different temperatures (T_1 and T_2 accordingly), and by constants of Langmuir equations of adsorption isotherms at given temperatures (K_{L1} andK_{L2}), accordingly, by equation:

$$\Delta H^o = R \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \ln \frac{K_{L2}}{K_{L1}}$$

Entropy (ΔS^o,J/(mol·K)) was determined by formula:

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T}$$

Values of thermodynamic quantities for the studied processes presented in Table-4.

Table-4. Values of thermodynamic quantities of the adsorption processes of OP on SM MCSM.

T, K	ΔG^o	E	ΔH^o	ΔS^o (J/(mol·K))
	(kJ/mol)			
288	-8,012	4,687	23,68	110,1
298	-7,208	4,283		103,9
308	-7,404	4,191		100,8

From the received data comes that adsorption processes of OP on SM MCSM relate to process of physical adsorption.

Kinetic dependence of adsorption processes of OP on SM MCSM, obtained in static conditions on model systems presented on a Figure-2 (initial concentration of OP in solution - 1,39 mg/l, dosage of SM - 1 g/l, time of contact - 120 min, temperature - 25 °C).

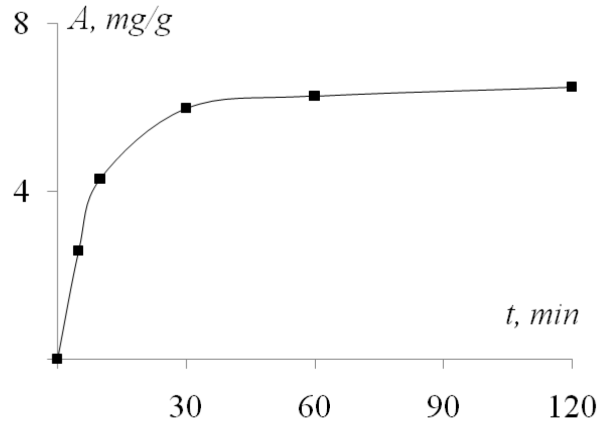

Figure-2. Kinetic dependence of adsorption processes of oil products in neutral medium on sorption material MCSM at temperature of 298 K.

To determine the limiting stage of kinetic processes of physical adsorption Boyd diffusion model

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was used. According to given model adsorption processes consist of two stages:

- external diffusion - diffusion of sorbate on the surface of SM in solution;
- internal diffusion - diffusion of sorbate in SM pores [23].

To identify the limiting stage following dependencies were formulated:

$-lg(1-F) = f(t)$, $A = f(t^{1/2})$ и $B_t = f(t)$,

where F - degree of equilibrium in the system, defined as $F=A/A_\infty$, B_t - non-dimensional Boyd's parameter, was determined by table data (as a function from F) [24].

To describe contribution of external diffusion in the adsorption process was used equation:

$$\gamma = \frac{3 \cdot D_e}{r_0 \cdot \delta \cdot K_p},$$

where D_e - external diffusion coefficient; r_0 -SM particulate radius, cm; δ - thickness of solution film around the SM granules (value of δ usually taken equal to $5 \cdot 10^{-3}$ cm, determined by expression: $\delta = 1/u$, where u - volumetric speed of the flow); K_p - coefficient of distribution ($K_p=A/C_e$); C_e - equilibrium concentration.

External diffusion coefficient (D_e) was calculated from tangent of straight line with a slope of -ln(1-F) - t by formula:

$$D_e = \frac{r_0 \cdot \delta \cdot \gamma \cdot A}{3 \cdot C_e}$$

To rate contribution of internal diffusion was used equation:

$$A = k_d \cdot t^{\frac{1}{2}} + L,$$

where L - section, cut by straight line on an ordinate axil which characterizing thickness of boundary layer; K_d - constant of the internal diffusion speed.

For calculating non-dimensional Boyd's parameter (B_t) was used classic equation of internal diffusion.

$$F = 1 - \frac{6}{\pi^2} \exp\left(-\frac{D_i \cdot \pi^2 \cdot t}{r^2}\right),$$

where D_i - internal diffusion coefficient, cm^2/s; r - radius of SM seed, cm; t - time, min.

Internal diffusion coefficient (D_i) was determined by tangent of straight line with a slope of B_t- t.

$$B_t = \frac{D_i \cdot \pi^2 \cdot t}{r^2}$$

Determining of external and internal diffusion constants were conducted by linearization of graphs with coordinates - lg (l - F) = f (t), F = f ($t^{1/2}$) and B_t = f (t). To calculate coefficient B_i was used equation:

$$B_i = \frac{r \cdot D_e}{\delta \cdot K_p \cdot D_i}$$

If $B_i<1$ adsorption process is limited by external diffusion, if $B_i>20$ - internal diffusion, if $1<B_i<20$ adsorption process passes in mix diffusional regime [25].

Received adsorption isotherms of OP on SM MCSM were processed within the framework of diffusion kinetic adsorption model. Coefficient B_i was determined by linearization of kinetic curves in coordinates -lg(l-F)=f(t), F=f(t1/2) and B_t=f(t). Results of this processing are presented in the Table-5.

Table-5. Values of coefficients B_i of oil products adsorption on sorption material MCSM.

Adsorption time, t (min)				
5	**10**	**30**	**60**	**120**
0,8719	0,7312	0,7453	0,7958	0,8473

As it is seen from data, presented in the Table-5, kinetic of adsorption processes of OP on SM MCSM is limited by external diffusion, because of values of coefficients B_i in researched amounts of tine are < 1.

4. CONCLUSIONS

During experiments adsorption capacity of MCSM was determined in relation to dissolved OP at different temperatures and pH of the medium. It was determined that the rise of temperature leads to lowering of adsorption capacity, what tells about possible physical forces holding oil products on the surface of sorption material. In acidic medium occurs lowering of sorption capacity.

According to BDDT classification, received isotherms relate to 4th type of adsorption isotherms and describing polymolecular adsorption, which is characteristic for porous SM. By Giles classification isotherms relate to L class (Langmuir class). Received adsorption isotherms worked out within Langmuire, Dubin-Radushkevich and Freundlich models. By presented calculations it was determined what Dubin-

Radushkevich model describes adsorption process better than any other.

Calculated thermodynamic constants confirmed that adsorption process of OP on SM MCSM appear due to physical interaction.

Formulated kinetic dependence of adsorption processes of OP on SM MCSM. Determined optimal time of contact between sorption material and model solution, which amounted to 30 minutes.

Received adsorption isotherms of OP on SM MCSM were processed within the framework of diffusion kinetic adsorption model, it is also revealed what kinetic of adsorption processes of OP on SM MCSM is limited by external diffusion.

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