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Adsorption of oil products using modified woodworking waste

Damir Afgatovich Kharlyamov* |**Gennady Vitalevich Mavrin** |**Ilnar Fargatovich Suleimanov**

Candidate of Technical Sciences, Docent, Department of Chemistry and Ecology, Naberezhnye Chelny Institute, Kazan Federal University, Russia

We obtained magnetic sorption material based on wood processing wastes by chemical modification. The elemental composition of the initial and modified samples was determined. It was revealed that magnetic sorption material had sorption properties regarding to oil products dissolved in an aqueous medium. Sorption properties at pH=4 and pH=7 on model solutions containing petroleum products under static conditions were studied. To establish the effect of temperature, the experiments were carried out in a thermostatic medium at temperatures of 15, 25 and 35 °C. It was established that in an acidic medium and with increasing temperature, the cleaning efficiency of model solutions decreased, which indicated the probablity of the physical adsorption. At pH=7 in an aqueous medium using the method of variable weights and constant concentrations, isotherms of oil products adsorption were constructed. According to the classification of Giles, received isotherms relate to L class (Langmuir class). The maximum adsorption capacity-0.0323 mmol/g was observed at a temperature of 15 °C and an increase in temperature to 35 °C adsorption capacity decreased to 0.0309 mmol/g. The calculations of thermodynamic parameters showed that the process of adsorption of oil products on the considered sorption material could be described by the Dubin-Radushkevich model, which was due to physical interaction. The Boyd's model was used to obtain insight into the mechanism of the physical adsorption kinetics. It was found that the kinetics of the processes of oil product adsorption on magnetic sorption material was limited by external diffusion.

KEYWORDS

Chemical modification; magnetic sorption material; waste wood fiber.

***Corresponding Author:**
Damir Afgatovich Kharlyamov
Email: kharlyamov@gmail.com
Tel.: +7-917-399-14-20

Introduction

Annually in the world more than 600 thousand tons of oil and oil products (OP) are discharged into water bodies. Sources of oil pollution of water are oil producing companies, oil pipelines, transportation of OP on tankers, as well as storage, processing and use of oil and OP. Individual water bodies contain more than a hundred cubic meters of oil pollution, although they are not only the main source of fresh water for humans, but also the habitat of many living organisms. The appearance of oil stains complicates the processes of photosynthesis in water due to the cessation of access of the sunlight, and also causes the death of plants and animals [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 its 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 possessing specific surface area, porosity and ion exchange properties [8–10]. Also it is worth mentioning that amongst offered SM there are those possessing specific properties [11–15], for example magnetic properties or ability to biodegrage. Promising way nowadays is using wood waste as SM for removal of different pollutants from water mediums. Many studies have offered investgation of kinetic and thermodynamic of adsorption, and written calculations about adsorption isotherms of pollutants according to different models. SM woodworking and logging wastes are used, as in their original state, so are they in state after modifications with various methods [16]. In terms of thermodynamic and kinetic properties of OP adsorption on magnetic composite sorption material (CSM) in the current study, chemical modification of wood fiber waste (WF) was obtained gathered after manufacture of MDF boards were determined. During the research, adsorption capacity was determined in relation to dissolved OP, formulated adsorption isotherms, determined thermodynamic and kinetic parameters of adsorption processes of OP on CSM. It was meant to discuss the efficiency of proposed method.

Material and methods

CSM were obtained from FW out of MDF boards manufactured by treating last with water solutions of ferrum chloride and ammonia [16,17], also with ultrasound at frequency of 35 kHz and 0.15 kW/cm2 in water medium. To research elemental composition of SM samples, energy-dispersive X-ray analyzer «JEOL» was used. Studying the sorption properties of SM in relation to OP was conducted in static conditions in neutral and acidic mediums. Model solutions of OP was received by intense mixing of diesel fuel and distillated water using high speed mechanical mixer. Next, mixing solution was left for upholding and splitting of water and organic phases was conducted. To formulate adsorption isotherms of OP, method of variable suspensions and constant concentrations was applied [18]. With the aim of determining possible mechanisms of sorption process passing experiments were conducted at different temperatures (15,25 and 35 °C). The received values of sorption capacity adsorption isotherms were formulated. To rate sorption properties of CSM depending on the time of contact in conical flask with volume of 100 mL 50 mL 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, after which SM was removed from the solution with magnet. Value of sorption capacity was calculated using next formula (1):

$$A = \frac{(C_0 - C) \cdot V}{m} \quad (1)$$

where C_0 is the initial concentration of OP, mmol/L; C denotes final concentration of OP, mmol/L; m signifies mass of suspension SM, g; V stands for volume of model solution, l.

To study the absorption mechanism, the experiments were conducted at different temperatures, and the graphs of adsorption capacity in relation to time of contact were sketeched.

Results and discussion

The process of obtaining CSM was based on sedimentation of magnetite (Fe3O4) on the surface of FW with help of ammonia water from solution, containing mix of chlorides of tri- and divalent ferrum under ultrasonic effect. According to the elemental analysis (Table 1), base components as for original sample (FW) and so for modified one (CSM)-were oxygen, carbon and nitrogen. The presence of small amount of calcium, silicon and ferrum in original fibers was explained by usage of binding components in its

manufactory, also sticking of mechanical particulates on its surface. After modification, noticeable rise of ferrum compounds mass fraction ocurred, which was connected to sedimentation of Fe3O4 [19]

TABLE 1 Elemental composition of materials

Sample	Mass fraction, %						
	O	C	N	Fe	Ca	Mg	Si
FW	39.0	35.2	24.3	0.15	0.28	0.25	0.08
CSM	38.2	33.1	22.4	5.28	0.22	0.14	0.03

Research on OP adsorption was conducted in static regime. Firstly, the equilibrium concentration of dissolved components DF after 2 h of contacting of CSM mass equal 1g with 50 mL of model solution with 14,2 mg/l concentration in neutral medium and 14,8 mg/l in acidic medium at temperatures of 15, 25 and 35 °C was determined. Measuring mass concentration of OP was conducted by OP analyzer. Calculated values of adsorption capacity SM CSM in relation to OP are presented in Table 2.

TABLE 2 Adsorption capacity of CSM in relation to oil products at static conditions

T, °C	Adsorption capacity, mmol/g	
	pH=4	pH=7
15	0.0314	0.0323
25	0.0308	0.0316
35	0.0291	0.0309

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

Using the method of variable suspensions and constant concentrations, adsorption isotherms of OP on SM CSM in neutral medium at temperatures 15, 25 and 35 °C (Figure 1) were formulated.

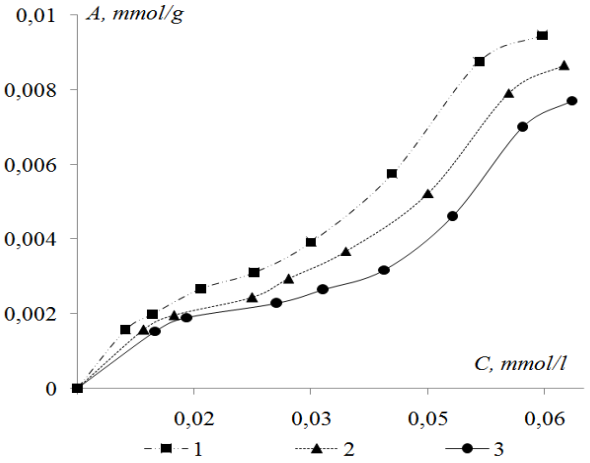

FIGURE 1 Adsorption isotherms of oil products on CSM at different temperatures: 1-15 °C; 2-25 °C; 3-35 °C

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. Giles isotherms relate to L class (Langmuir class). On the beginning stage, isotherms are characterized 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 [20].

TABLE 3 Results of processing adsorption isotherms of oil products on CSM at different temperatures (according to Dubin-Radushkevich, Freundlich and Langmuire models)

T, °C	Dubin-Radushkevich model	Freundlich model	Langmuire model
15	y=-0,2808x - 5,0589 (R^2=0,9935)	y=0,7945x + 1,1114 (R^2=0,9465)	y=3,5809x + 101,27 (R^2=0,9810)
25	y=-0,3351x - 5,1778 (R^2 = 0,9961)	y=0,8558x + 1,1096 (R^2=0,9509)	y=4,9782x + 98,608 (R^2=0,9812)
35	y=-0,3552x - 5,3346 (R^2=0,9950)	y=0,8372x + 1,2133 (R^2=0,9684)	y=5,8053x + 117,86 (R^2=0,9783)

Adsorption isotherms were 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 CSM 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 (2):

$$\Delta G^o = -R \cdot T \cdot \ln K_L \quad (2)$$

where R denotes universal gas constant J/(mol·K); T is 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} and K_{L2}), accordingly, by equation (3):

$$\Delta H^o = R \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \ln \frac{K_{L2}}{K_{L1}} \quad (3)$$

Entropy (ΔS^o, J/(mol·K)) was determined by formula (4):

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \quad (4)$$

Values of thermodynamic quantities for the studied processes are presented in Table 4. From the received data comes that adsorption processes of OP on SM CSM relate to process of physical adsorption.

Kinetic dependence of adsorption processes of OP on SM CSM, obtained in static conditions on model systems, is presented on a Figure 2 (initial concentration of OP in solution-1,40 mg/l, dosage of SM-1 g/L, time of contact-2 hours, temperature-25 °C).

TABLE 4 Values of thermodynamic quantities of the adsorption processes of oil products on CSM

T, °C	ΔS^o (J/(mol·K))	E	ΔG^o (kJ/mol)	ΔH^o
15	109,9	4,691	-8,015	
25	104,1	4,279	-7,211	23,72
35	101,0	4,186	-7,408	

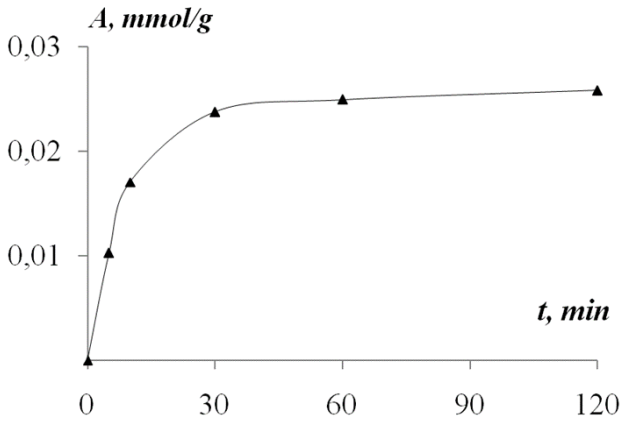

FIGURE 2 Kinetic dependence of adsorption processes of oil products on CSM

To determine the limiting stage of kinetic processes of physical adsorption, Boyd diffusion model was used. According to the given model, adsorption processes consist from two stages [aca]:

1) diffusion of sorbate on the surface of SM in solution (external diffusion);

-diffusion of sorbate in SM pores (internal diffusion).

To identify the limiting stage, the following dependencies were formulated (5):

$$-\lg(1-F) = f(t),\ A = f(t^{1/2})\ \&\ B_t = f(t) \qquad (5)$$

where F is degree of equilibrium in the system, defined as $F=A/A_\infty$, B_t denotes non-dimensional Boyd's parameter, was determined by table data (as a function from F) [19,22,23].

To describe contribution of external diffusion in the adsorption process, the following equation was used (6):

$$\gamma = \frac{3 \cdot D_e}{r_0 \cdot \delta \cdot K_p} \qquad (6)$$

where De is external diffusion coefficient; r0 denotes SM particulate radius, cm; δ signifies thickness of solution film around the SM granules (value of δ usually taken equal to 5·10-3 cm, determined by expression: δ = 1/u, where u is volumetric speed of the flow); K_p is coefficient of distribution ($K_p=A/C_e$); C_e is equilibrium concentration.

External diffusion coefficient (D_e) was calculated from tangent of straight line with a slope of -ln(1-F) - t by formula (7):

$$D_e = \frac{r_0 \cdot \delta \cdot \gamma \cdot A}{3 \cdot C_e} \qquad (7)$$

To rate contribution of internal diffusion, equation (8) was used:

$$A = k_d \cdot t^{\frac{1}{2}} + L \qquad (8)$$

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

For calculating non-dimensional Boyd's parameter (B_t), classic equation of internal diffusion (9) was used:

$$F = 1 - \frac{6}{\pi^2}\exp\left(-\frac{D_i \cdot \pi^2 \cdot t}{r^2}\right) \qquad (9)$$

where D_i is internal diffusion coefficient, cm^2/s; r - radius of SM seed, cm; t is time, min [24].

Internal diffusion coefficient (D_i) was determined by tangent of straight line with a slope of Bt - t (10):

$$B_t = \frac{D_i \cdot \pi^2 \cdot t}{r^2} \qquad (10)$$

Determining of external and internal diffusion constants was 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 Bi, equation (11) was used:

$$B_i = \frac{r \cdot D_e}{\delta \cdot K_p \cdot D_i} \quad (11)$$

If B_i<1 adsorption process is limited by external diffusion, if Bi>20 - internal diffusion, if 1<B_i<20 adsorption process passes in mixdiffusional regime.

Received adsorption isotherms of OP on SM CSM were processed within the framework of diffusion kinetic adsorption model. Coefficient Bi was determined by linearization of kinetic curves in coordinates -lg(l-F)=f(t), F=f($t^{1/2}$) and B_t=f(t). Results of this processing are presented in the Table 5.

TABLE 5 Values of coefficients Bi of oil products adsorption on sorption material CSM

Adsorption time, t (min)				
5	10	30	60	120
0.872	0.729	0.746	0.797	0.848

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

Conclusion

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

According to BDDT classification, received isotherms relate to 4th type of adsorption isotherms and describing polymolecular adsorption, which is characteristic for porous SM. Using Giles classification, isotherms relate to L class (Langmuir class). Received adsorption isotherms were 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 appeared to be due to physical interaction.

Kinetic dependence of adsorption processes of OP on SM MCSM was formulated. The optimal time of contact between sorption material and model solution was determined, amounted to 30 minutes.

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

Therefore, the results of study of the adsorption properties of magnetic composite sorption material presented in this work show that the researched material, obtained as a result of modification of woodworking waste, has a sufficiently high adsorption capacity (0.032 mmol/g), which in turn makes it possible to use the proposed sorption material for cleaning water objects from oil products. By processing the obtained adsorption isotherms, it was determined that the process of adsorption of petroleum products is best described by the Dubinin–Radushkevich equation. It was established that the processes of adsorption of oil products on the magnetic composite sorption material relate to the processes of physical adsorption, and the kinetics of the processes of adsorption of oil products is due to external diffusion.

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Orcid:

Damir Afgatovich Kharlyamov: https://orcid.org/0000-0002-7728-4502

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