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LIQUID-PHASE SORPTION OF OIL BY CARBONIZED RICE HUSKS: IMPACT OF GRAIN SIZE DISTRIBUTION ON THE SORPTION KINETICS

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ABSTRACT

The use of sorbents, obtained from renewable wastes to purify the hydrosphere from various hazardous pollutants is an innovative approach with multiplied environmental effect. In this regard, there is interest in the processing of rice husks and converting them into an effective biosorbent for purification of water from oil pollution.

By slow pyrolysis of rice husk at 480°C pyrolysis charcoal was obtained. The product was divided into fractions with sizes in the range from 0,4 to 2,0 mm. Each fraction was tested with respect to adsorption of crude oil from water surface gravimetrically and as emulsified in aqueous media by a batch-method.

The aim of this study was to determine the influence of the factor "granulometry of the adsorbent" on the sorption kinetics and efficiency of the material for both cases of contamination. An attempt had been made the kinetics of the process to be described by kinetic models, most often used for adsorption from aqueous media: Lagergren's equation; second order kinetics equation; Weber-Morris's diffusion equation and Elovich equation.

Keywords: rice husks, pyrolysis, oil contamination, adsorption, kinetic.

INTRODUCTION

As one of the main energy sources of the modern economy, crude oil has a noticeable negative impact on the ecosystems of the geosphere and the hydrosphere. The effect is mainly related to the extraction, transporting and processing of oil. Regardless of the development and employment of low-waste technologies in oil refineries; upgrading of petroleum production technology; improvement of the processes for storage and transportation of oil and petroleum products; advanced activities for localization and elimination of accidental spills, as a whole pollution of water reservoirs with crude oil remains dangerously high [1]. Recognizing the high degree of risk, EU adopted a number of directives and decisions for the prevention and control of pollution [2, 3]. Implementation of these directives is a serious challenge and requires improving the existing technology.

Adsorption has been proven as an effective method for removal of oil and oil products from water medium. The high cost of commercial synthetic sorbents stimulates the interest for finding inexpensive and available raw materials for their production. Such huge amounts materials are some of the renewable bio-wastes.

Among the promising by-products for the synthesis of biosorbents are the rice husks, the annual accumulation of which creates serious environmental problems.

The naturally created in the rice husks lignin cellulose matrix with dispersed therein amorphous SiO_2 in pyrolysis changes their own phase, structural, textural and surface-chemical characteristics. As a result, the solid pyrolysis residue acquires properties which make it a potential adsorbent [4-9]. The transformation of rice husks into an effective adsorbent for the purification of water from oil and oil products multiplies the environmental effect of their processing.

Oil in aqueous media forms films, aggregates and emulsions. The cleaning of oil films and aggregates by a combination of mechanical and adsorption methods is an efficient and good practice. Whereas purification of crude oil emulsions in water is a difficult process due to the stability of the system oil-water [10].

In our previous work the sorption kinetics of oil and oil products from water surface by pyrolyzed rice husks was determined [11]. The influence of granulometry; bulk density of the pollutant and the presence of oleophilic surface functionalities on the process rate was estimated. As an extension of these studies it is interesting to study the adsorption kinetics of small amounts of oil in the emulsion state from aqueous medium with the same adsorbent used in the previous investigation [11].

Purpose of the present study was to determine the influence of the bulk density on the sorption kinetics and efficiency of the sorbent for surface and emulsion contaminations. An attempt had been made to describe the kinetic region of operation of the process, for both cases of sorption by different kinetic models, such as: Lagergren's equation (pseudo-first order kinetic); second order kinetics equation; Weber-Morris's diffusion equation and Elovich equation.

EXPERIMENTAL

Preparation of the sorbent, sample characterizations and adsorption studies

The adsorbent has been prepared by a slow pyrolysis of rice husks, from Pazardjik region in Bulgaria (harvested in 2008) at 480 °C. The conditions of the process; the methods for characterization; the structural and phase characteristics including the type and the quantity of the finely dispersed fluids were described in details in our previous works [5, 11]. The relationship between the amount of sorbed oil from water surface and the time, for sorbents with different granulometric composition was determined by the methodology, described in details in [11].

Experiments for adsorption of oil from aqueous medium were carried out by adsorbent with sieve fractions of dimensions ranging between 0,40 and 2,0 mm. The sorption capacity of the adsorbents for crude oil was investigated with aqueous emulsions of the pollutant. Crude oil was obtained from the field Dolni Dabnik (Bulgaria). It has bulk density 0,833 g cm^{-3} at 20 °C. The principle of the experiments was as follows: 1,000 g of pyrolyzed rice husk were mixed with 400 ml water with concentration of oil 400 mg ml^{-1} in a 500 ml capacity flask The flasks, contain the suspension were agitated for a predetermined time interval - from 5 to 40 minute, to reach a stable equilibrium, in normal conditions with a laboratory stirrer at 100 rpm. At the end of agitation the suspension was filtered and the crude oil concentration into the solution was determined spectrophotometrically at maximum absorbance wave length $\lambda = 262$ nm using a Cary 100 Scan UV-Visible Spectrophotometer.

Kinetics studies

The sorption of oil, spilled on the water surface or emulsified in aqueous medium using a solid-state adsorbent is as a heterogeneous process, occurring in the system sorbent/oil/water. This means that its rate will depend not only on the interaction between the sorbent and the sorbate, but also on the rate of diffusion to and into the volume of the sorbent; on the phenomena on the inter-phase boundary; on the interaction of the water with the sorbate, etc. The realization of the actual act of adsorption, either physical or chemical, forms the kinetic step of the process. While the external (bulk phase) and/or the internal (pore) mass transfer, determine the so called "diffusion step" of the process. Hereby, the overall rate of the process will depend on the speed of the slowest stage. Upon reaching steady state, the rate constants of the two processes remain different and their ratio determines whether the process is occurring in the kinetic, diffusion or in the transition region.

The phenomenological mechanism of sorption from solutions is described on the basis of the concepts, previously introduced for the sorption from gas phase and these are amended in view of the specific conditions in the case of liquid phase. The linear least squares method is the one used most often in order to select a suitable kinetic equation, giving good correlation between experimentally determined data and the theoretically estimated values. The mathematical principle of the method is not too complicated and it can be applied even in the cases when the relation between the practically evaluated quantity and its calculated value is not really linear, but it can be approximated to such dependence.

The sorption, as any real equilibrium process, is a function of the time. Therefore, the main evidence about the adsorption properties of the material can be derived from the dependence between the amount of adsorbed substance and the time interval at constant temperature, $q_t = f(t)_T$.

The quantity of oil adsorbed from water surface per unit mass of adsorbent, according to the method described in [14] was determined by the dependencies:

$$V_{t,ads} = \pi R^2 \cdot h_t \,, \qquad (1)$$

where: $V_{t,ads}$ is the volume of the material which has adsorbed oil for the time t, cm^3; h_t – depth of penetration of crude oil/oil product inside the layer of the adsorbent for the time t, cm; R - radius of the layer, cm.

The mass of the sorbent G_t, in grams, soaked with sorbate for time interval t is:

$$G_{t,ads} = V_{t,ads} \cdot \rho_{ads} \,, \qquad (2)$$

and

$$q_t = G_{t,ads.} \cdot C_{ads} \,, \qquad (3)$$

where: q_t is the quantity of oil, adsorbed for time t, g; ρ_{ads} – bulk density of the sorbent, g cm^3; C_{ads} – adsorption capacity of the material, g g^{-1}.

The adsorption of contaminants of various properties from an aqueous medium can be described by different kinds of kinetic models [12,13]. For the purposes of our investigation we applied several of the most often used equations, describing the occurrence of the process in the kinetic or in the diffusion region:

Pseudo-first order kinetics

Processes, occurring in the kinetic region, which can be described by kinetic equations of a pseudo-first order, usually the model of Lagergren is used [14]:

$$\frac{dq_t}{dt} = k_L \left(q_e - q_t\right) \qquad (4)$$

where: q_e is the sorbate amount, adsorbed on the material after reaching equilibrium for time interval t_e, g; k_L – Lagergren's rate constant, min^{-1}.

The equation (4) is integrated within the boundaries $q_t = 0$ at $t = 0$ and $q_t = q_e$ for $t = t_e$:

$$\lg\left(q_e - q_t\right) = \lg q_e - \left(\frac{k_L}{2{,}303}\right) \cdot t \qquad (5)$$

The rate constant, k_L is determined by the slope of the linear dependence $\lg\left(q_e - q_t\right) vs. (t)$.

Second order kinetics

A second order equation is also applicable to the kinetic region [14]:

$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t\right)^2 \qquad (6)$$

where: k_2 is the second order rate constant of adsorption, mg g^{-1} min^{-1}.

After integrating equation (6) one obtains:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 \cdot q_e^{\,2}}\right) + \left(\frac{t}{q_e}\right), \qquad (7)$$

The initial rate of sorption, $\left(k_2 \cdot q_e^{\,2}\right)$, together with the second order rate constant, $\left(k_2\right)$ are determined through linear regression of the dependence $t/q = f(t)$, at constant temperature.

Intraparticle diffusion model

The possibility that the diffusion might be the only rate-determining step of the adsorption is judged by the linear dependence of Weber-Morris [15]:

$$q_t = k_i \cdot \sqrt{t} + C \qquad (8)$$

where:

C is a coefficient, accounting the bonding effect between the layers;

k_i – the rate constant of the process, mg g^{-1} $min^{-1/2}$.

If the experimental data are describing not , but in fact - a multilinear dependence, this means that the sorption is influenced by two or more rate-determining steps, i.e. the process is occurring in the transition region.

Elovich equation

This is one of the most often used models to describe the kinetics of sorption when there are valence interactions between the adsorbent and the sorbate, i.e. chemisorption [16]:

$$\frac{dq_t}{dt} = a \cdot \exp\left(-bq_t\right) \qquad (9)$$

where: a is the initial rate of sorption, mg g^{-1} min^{-1}; b – a desorption constant, g mg^{-1}.

Chen и Cayton developed further the equation of Elovich by assuming that $a \cdot b \cdot t >>> t$ [17]. Applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t_e$ they obtained the equation:

$$q_t = \left(\frac{1}{b}\right) \cdot \ln\left(ab\right) + \left(\frac{1}{b}\right) \cdot \ln t \qquad (10)$$

The constants a and b in the exponential dependence of Elovich are determined from the intersection and the slope of the plotted dependence - $q_t vs. \ln t$. When the correlation between the sorption capacity and the constant b is negative, it is accepted that the adsorbent does not retain the sorbate. The positive value of the constant gives evidence for occurring of sorption [18].

RESULTS AND DISCUSSION

In order to determine the influence of the granulometry upon the sorption kinetics of crude oil from an aqueous medium and a water surface at a constant temperature the adsorption curves were obtained for each fraction, Fig.1a and Fig.1 b:

The shape of the kinetic curves exhibits that in the case of oil sorption from water surface for the various fractions of the adsorbent the process is accomplished in two-steps. The rate of the first step depends on the ratio of the gravitational and capillary forces, while that of the second step – on the structural characteristics and the oleophilicity of the adsorbent.

During adsorption from an aqueous medium the equilibrium for each fraction is achieved gradually over time, as the kinetic curves for all fractions of the adsorbent are identical in form. The influence of particle size distribution on the adsorption kinetics is expressed very clearly. In this case, the adsorption will depends only on the structure and surface characteristics of the sorbent. Moreover, applying intensive stirring favors the contact between the sorbent and the pollutant.

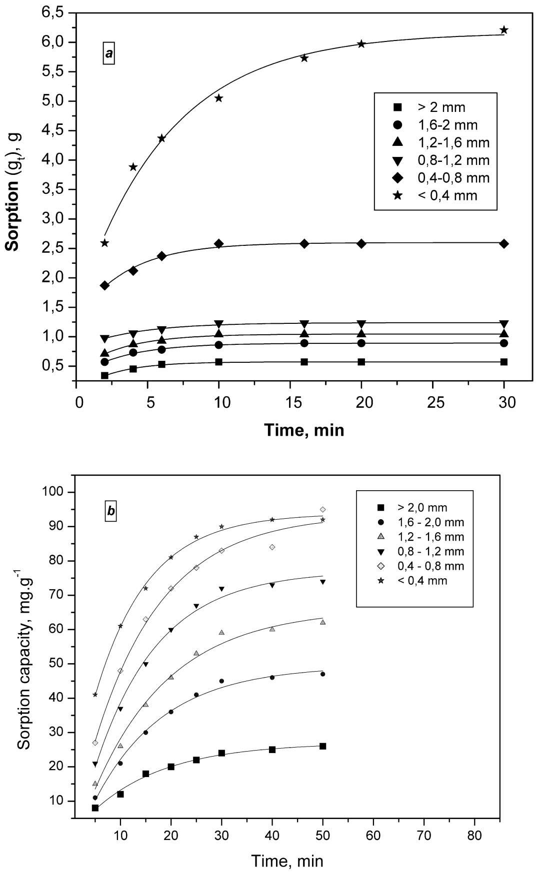

Fig. 1. Dependence of the adsorbed amount on the contact time using different granulometric fractions of pyrolyzed rice husks: (*a*) for adsorption of oil from water surface and (*b*) from an aqueous medium.

The adsorption equilibrium when cleaning crude oil from water surface is reached almost three times faster than when the sorption occurs into the aqueous medium. The time interval for reaching the adsorption-desorption equilibrium determines the efficiency of the adsorbent.

In the case of adsorption of oil from water surface, the particle size of the pyrolyzed rice hulls affects the adsorption of the oil layer mainly for fractions with dimensions less than 0.8 mm.

The applicability of the used kinetic equations with respect to the adsorption characteristics presented in Figures 1a and 1b was verified by plotting the following dependencies: pseudo-first order $lg\ (q_e\text{-}q_t) = f(t)$ and second order $t/q_e = f(t)$ kinetics; intra-particle diffusion $q_t = f(\sqrt{t})$ and valence interactions within the system q_t vs $ln\ t$, Figs. 2-5. The statistical data for the linear regression at each ratio are listed in Tables 1- 4.

The low values of the standard deviation and the high correlation coefficients (above 0,99), respective for fractions with dimensions in the range of 1.6 to 0,4 mm, indicate that the sorption kinetics of oil from the water surface with this granulometric brand of pyrolyzed rice husk satisfies the Lagergern equation.

The same is valid for the adsorption of oil from aqueous media with grain size fractions of the solid pyrolysis residue from 1.6 to 0.8 mm.

According to the obtained statistical data for linear regression it is more adequate to apply a second order kinetic equation for both instances of the sorption. The model describes satisfactorily the process occurring in the kinetic region for each one of the fractions of the pyrolyzed rice husks.

The possibility that the diffusion might be the rate limiting stage in regard to the entire process was evaluated by the equation of Weber-Morris, Fig. 4.

As can be seen from the values of the correlation coefficients for each fraction, the diffusion in both cases of adsorption of oil cannot be assumed as a rate limiting step.

The obtained data relating to the application of various mathematical models showed that whatever the fractional composition of the pyrolyzed rice husks was, the adsorption of crude oil from the water surface or aqueous medium occurred mainly in the kinetic region.

According to some authors, the applicability of the second order kinetic model is an indication of sorption occurring through interactions between valence forces

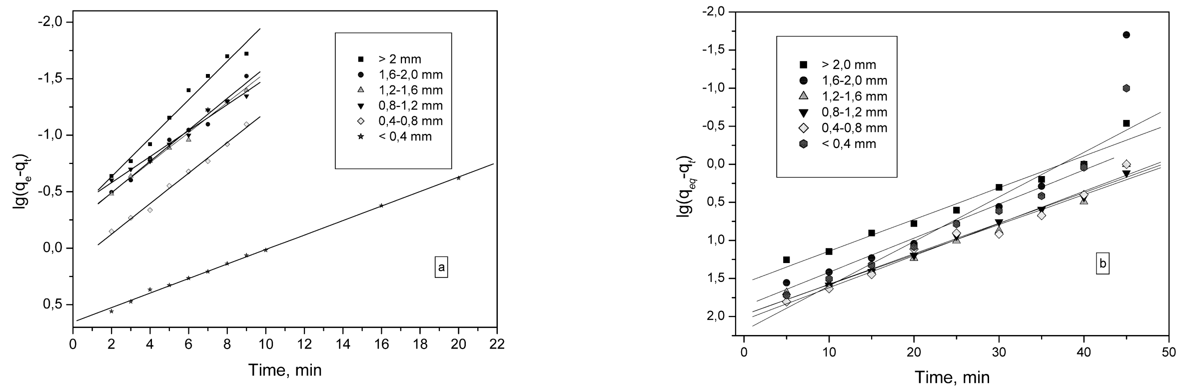

Fig. 2. Lagergren plots for adsorption of oil by the various fractions of pyrolyzed rise husks: (*a*) from water surface and (*b*) from an aqueous medium.

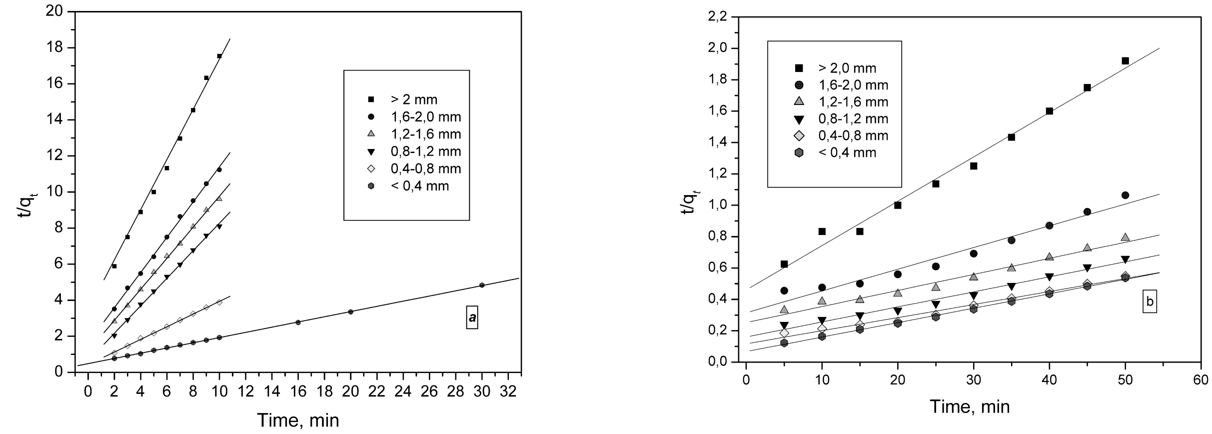

Fig. 3. Test of second order kinetic equation for the sorption of oil by different fractions of pyrolyzed rise husks: (*a*) from water surface and (*b*) from an aqueous medium.

of the surface functionalities of the adsorbent and of the sorbate [19 - 23]. The possibility that the adsorption was occurring in the system water/oil/pyrolyzed rice husks, also involving the participation of some other forces, beside the Van deer Wail's, was estimated by applying the Elovich equation. The reason for this are given by the facts that: 1) the thermal destruction of rice husks is associated with deposition of compounds on the surface of the solid pyrolysis residue, possessing functional groups of different reactivity: carbonyl; carboxylic; hydroxyl, etc. and 2) the solid pyrolysis residue by its nature is a natural hybrid material C/SiO_2. The carbon atoms in it are in the sp^2-hybridization state, while the amorphous silica is characterized by the presence of reactive siloxane and silanol groups [5, 24].

The results from applying the Elovich's model to describe the kinetics of light oil sorption by the fraction of 1.6-2.0 mm pyrolyzed rice husks from water surface, as well as from aqueous media are presented on Fig. 5a and 5b. The parameters of the linear regression are listed in

The data obtained do not confirm the assumption that in the oil sorption by pyrolyzed rice husks act forces other than Van der Waals adsorption interaction ones.

CONCLUSIONS

The kinetics of sorption of oil from water surface using fractionated pyrolyzed rice husks has been investigated by the method of sorbate penetration inside the layer of the sorbent and from an aqueous medium - by a batch-method.

The adsorption depends on the grain size distribution of the pyrolyzed rice husks and this effect is more pronounced for oil sorption from an aqueous medium.

Some of the most often applied models have been used to describe the kinetics and the mechanism of the process. It has been found out that the oil sorption kinetics is most adequately described by a second order kinetic equation, irrespective of the grain size of the pyrolyzed rice husks. It follows that the process of oil

Table 1. Parameters of the linear regression, values of the rate constants and theoretical values of the adsorbed amount of oil at equilibrium is reached, for pseudo-first order kinetics in both cases of sorption.

Granulometric composition, *mm*	Equilibrium quantities of sorbed oil,*g* (from the water surface)		*SD	**R^2	***k_1
	$q_e^{exp.}$	$q_e^{theor.}$			
> 2,0	0,57	0,51	0,0649	0,9795	0,3919
1,6-2,0	0,89	0,61	0,0518	0,9806	0,3203
1,2-1,6	1,04	0,59	0,0401	0,9872	0,3061
0,8-1,2	1,23	0,45	0,0420	0,9813	0,2648
0,4-0,8	2,58	1,39	0,0330	0,9916	0,3104
< 0,40	6,21	4,52	0,0167	0,9980	0,1480

*SD-standard deviation; **R^2-correlation coefficient; ***k_1-Lagergren rate constant.

Granulometric composition, *mm*	Equilibrium quantities of sorbed oil , *mg* (from an aqueous medium)		*SD*	R^2	k_1
	$q_e^{exp.}$	$q_e^{theor.}$			
> 2,0	26,0	36,1	0,1134	0,9667	0,0960
1,6-2,0	47,0	162,6	0,4652	0,8091	0,1506
1,2-1,6	63,1	94,2	0,1003	0,9706	0,0907
0,8-1,2	75,7	110,7	0,0412	0,9952	0,0926
0,4-0,8	91,0	120,5	0,0998	0,9745	0,0974
< 0,40	93,1	108,7	0,268	0,9109	0,1374

Table 2. Parameters of the linear regression, values of the rate constants and theoretical values of the adsorbed amount of oil at equilibrium for second order kinetics equation for oil removal from aqueous state by different fractions of pyrolyzed rice husks

Granulometric composition, *mm*	Equilibrium quantities of sorbed oil,*g* (from water surface)		*SD*	R^2	k_2
	$q_e^{exp.}$	$q_e^{theor.}$			
> 2,0	0,57	0,68	0,2211	0,9973	0,7257
1,6-2,0	0,89	1,02	0,1176	0,9982	0,5765
1,2-1,6	1,04	1,16	0,0979	0,9984	0,6358
0,8-1,2	1,23	1,31	0,0999	0,9980	0,9077
0,4-0,8	2,58	2,85	0,0396	0,9985	0,2925
< 0,40	6,21	6,94	0,0204	0,9998	0,0427

Granulometric composition, *mm*	Equilibrium quantities of sorbed oil, *mg* (from aqueous medium)		*SD*	R^2	k_2
	$q_e^{exp.}$	$q_e^{theor.}$			
> 2,0	26,0	35,3	0,0489	0,9884	17.10^{-4}
1,6-2,0	47,0	71,9	0,0438	0,9628	$6,13.10^{-4}$
1,2-1,6	63,1	98,0	0,0252	0,9769	$4,13.10^{-4}$
0,8-1,2	75,7	104,2	0,0205	0,9827	$5,75.10^{-4}$
0,4-0,8	91,0	120,5	0,0179	0,9825	$6,06.10^{-4}$
< 0,40	93,1	108,7	0,0068	0,9979	12.10^{-4}

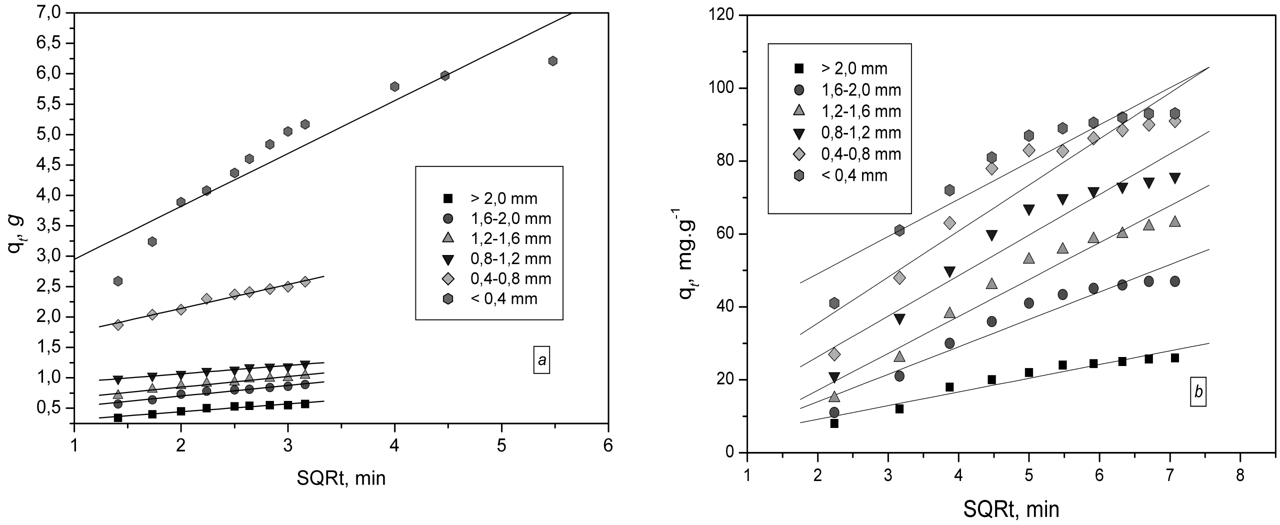

Fig. 4. Test of Weber-Morris model for sorption of oil by different fractions of pyrolyzed rice husks: (*a*) from water surface and (*b*) from an aqueous medium.

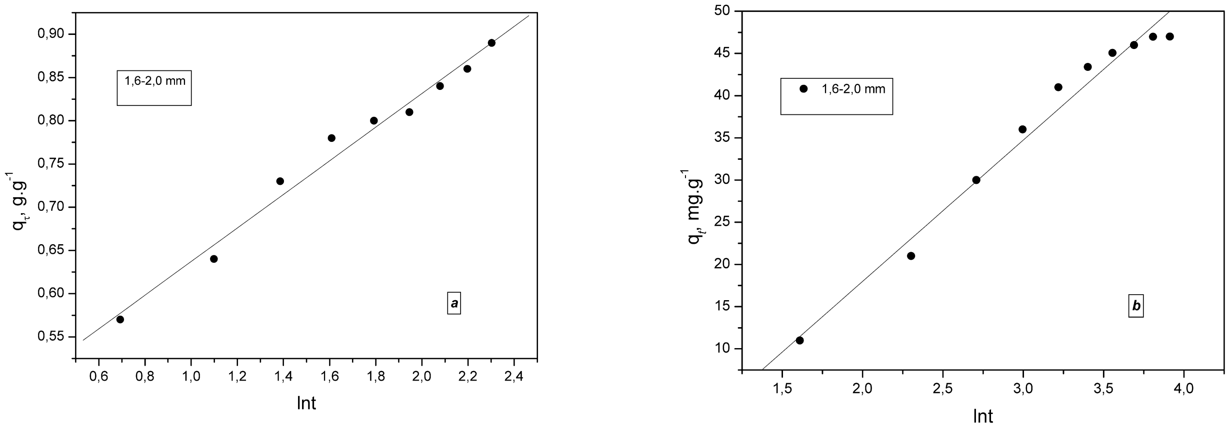

Fig. 5. Elovich equation plots for adsorption of oil by different fractions of pyrolyzed rice husks: (*a*) from water surface and (*b*) from an aqueous medium.

Table 3. Parameters of the linear regression for the diffusion model in both cases of sorption.

Granulometric composition, *mm*	Parameters of the linear regression *(water surface)*					
	Coefficients		Average square error		*SD*	*R*^{2}
	$a\left(k_i\right)$	b	σ_a	σ_b		
> 2,0	0,1832	0,1293	0,0312	0,0127	0,0213	0,9366
1,6-2,0	0,3535	0,1738	0,0341	0,0139	0,0233	0,9571
1,2-1,6	0,5000	0,1739	0,0316	0,0130	0,0216	0,9630
0,8-1,2	0,7905	0,1376	0,0159	0,0065	0,0108	0,9846
0,4-0,8	1,3513	0,3946	0,0526	0,0214	0,0359	0,9797
< 0,40	2,0820	0,8690	0,3117	0,0985	0,3869	0,8862

Granulometric composition, *mm*	Parameters of the linear regression *(aqueous medium)*					
	Coefficients		Average square error		*SD*	*R*^{2}
	$a\left(k_i\right)$	b	σ_a	σ_b		
> 2,0	1,6506	3,7552	1,9276	0,3677	1,7464	0,9287
1,6-2,0	-1,0547	7,5248	4,0226	0,7672	3,6445	0,9232
1,2-1,6	-3,1320	10,1290	4,4243	0,8438	4,0084	0,9474
0,8-1,2	4,0795	11,1281	6,3476	1,2107	5,7509	0,9135
0,4-0,8	10,2846	12,6356	8,5783	1,6361	7,7718	0,8817
< 0,40	28,6986	10,2043	7,0036	1,3358	6,3452	0,8794

Table 4. Linear regression parameters for sorption of oil in an aqueous state obtained by application of the model of Elovich.

Sorption	**Parameters of the linear regression**					
	Coefficients		Average square error		*SD*	*R*^{2}
	a	**b**	$\boldsymbol{\sigma_a}$	$\boldsymbol{\sigma_b}$		
Water surface	1,8570	0,2465	0,0375	0,0201	0,0545	0,9624
Aqueous medium	-15,472	16,737	2,7438	0,8584	1,8882	0,9794

sorption from an aqueous medium takes place predominantly in the kinetic region.

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