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Kinetics and mechanism of oil and oil products sorption from water surface onto pyrolyzed waste biomass

S. A. Uzunova[1], I. M. Uzunov[2*], D. R. Mehandjiev[2], V. B. Toteva[1]

[1] *University of Chemical Technology and Metallurgy - Sofia, 8 St.Kl.Ohridski Blvd., 1756 Sofia, Bulgaria*
[2] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G.Bonchev Str., bl.11, 1113 Sofia, Bulgaria*

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In the present study an attempt was made to describe the kinetics and mechanism of oil and oil products sorption from aqueous surface on pyrolyzed rice husks. The pseudo-first order and second order kinetic models, Elovich equation and intraparticle diffusion model were applied to describe the kinetics and estimate the rate-limiting stage of the process. The best-fit model was selected based on the linear regression method. The effect of the sorbent granulometry, the density of oil pollutants and the presence of surface functionalities on sorption kinetics was investigated.

Keywords: Rice husks; Pyrolysis; Oil spills; Sorption; Kinetics

INTRODUCTION

The industrial activity, being an integral part of the development of contemporary society, is associated with significant and most often uncontrolled environmental pollution with all the ensuing consequences. The persistent hydrocarbons are some of the dangerous contaminants. They are transferred into the hydrosphere by oil or oil products. Oil mining and processing, as well as transportation and storage of oil products are very often accompanied by oil spillage, due to various reasons. It has been established that large amounts of aromatic, aliphatic and naphthenic acids, alcohols, phenols and aliphatic ketenes are formed as a result of photolytic oxidation of oil in aqueous medium [1,2]. The high toxicity of oil spills is mainly due to the water-soluble compounds of this group. In spite of all the measures taken to reduce pollution, the extent of contamination of water basins with oil products still remains dangerously high. The quantity of oil and oil products spilled in the World Ocean amounts to about 6 millions of tons annually [3].

During the recent years different mechanical, photochemical and physicochemical processes are being applied to solve the problems arising from oil spillages. Among the physicochemical processes the adsorption turns out to be the most effective technology with proven wide-scope potential for the treatment of polluted waters [4-9].

Recently, the application of adsorption methods combines well with the problem to utilize various waste biomasses from the agriculture and foodstuff production industry through converting the by-products into efficient biosorbents – an alternative to the commercial sorbents [8, 10-14]. The advantage is their availability and preparation with relatively low production expenses. An example in this respect is the processing of rice husks waste into efficient adsorbents for purification of water from various contaminants [15-19].

The studies on the options to apply biosorption as an alternative method for the purification of water are focused in three main directions: screening of efficient biosorbents; optimization of the process parameters and elucidation of the kinetics and mechanism of sorption [11, 14, 20-23].

The effectiveness of a specific sorbent in regard to the removal of various oil products from water depends on its structural and surface properties [8, 24]. A real challenge in the field of adsorption would be to study and determine the kinetics of the process. The latter is related to the adsorption capacity of the material and the adsorption mechanism. The knowledge of the kinetics of sorption could permit to evaluate the minimal time interval for complete saturation of the adsorbent; the required height of the sorbent layer, sufficient to eliminate an oil spill with a certain thickness, as well as the theoretical maximum adsorption capacity of the layer.

The influence of the chemical composition, the residual fluid components and the porosity on the adsorption capacity of carbonized rice husks towards heavy oils was examined by Kumagai et al. They also discussed the predominant mechanism of oil

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* To whom all correspondence should be sent:
E-mail: uzunov_iv@svr.igic.bas.bg

adsorption by the husks and described a procedure to enhance the sorption capacity [24].

The sorption of accidental spillage of oil products using a sorbent on the basis of waste wood fibers and the corresponding exponential kinetic model were studied by Konseisayo et al. [25].

The kinetic dependences recently published by Kamenshchikov et al. [26] and Dedov [27] for different types of sorbents revealed that the sorption of oil products from water surface follows a two-step mechanism.

Although there are some available publications describing the adsorption of oil and oil products from the water surface, the kinetics of the process, based on utilization of pyrolyzed rice husks has not been studied yet.

The aim of the present investigation was to determine the effect of the granulometry of adsorbent prepared by pyrolysis of rice husks; the density of the oil products and the content of surface functionalities on the kinetics and mechanism of sorption. The present work represents an attempt to apply some known kinetic equations to the sorption of oil and oil products from water surface. The adsorption study was carried out using a method different from the most often applied batch-methods.

MATERIALS AND METHODS

Preparation of the sorbents

The adsorbent was prepared by slow pyrolysis of rice husks at 480°C, under stationary conditions. The experiments were performed in a tubular stainless steel electrically heated reactor, positioned vertically, equipped with temperature controllers, under a residual pressure of 1.33 Pa. The reactor had a heated zone of dimensions 240 mm (L) × 40 mm (ID) × 170 mm. The liquid products were collected in a trap between the reactor and a vacuum pump, maintaining a temperature of 2-3°C. Then the temperature in the reactor was increased linearly from room temperature up to 480° C at a heating rate of 4° min^{-1} and retention time 4 hours. The so obtained solid pyrolysis residue is characterized by 253 $m^2.g^{-1}$ B.E.T. specific surface area, assessed by N_2 adsorption; porosity 56.8 % and average pore diameter of 0.781 μm, determined by Hg-porosimetry [28]. The amount of the fluids, which were extracted with acetone was estimated at 4.2 % w/w, as the oleophilic compounds predominated in the eluent [28].

Six samples with a different fractional composition were obtained from the starting material, as follows: below 0.4; 0.4÷0.8; 0.8÷0.12; 1.2÷1.6; 1.6÷2.0 and greater than 2.0 mm, designated as: PRH-1; PRH-2; PRH-3; PRH-4; PRH-5; PRH-6, respectively. These samples were used to determine the influence of the bulk density of the composite material on the kinetics of sorption of the oil or oil products.

Methodology for determining the kinetics of sorption

Pre-weighed adsorbent is filled into a glass tube of height 10.0 cm and diameter 1.0 cm, on the bottom of which is mounted a grid with aperture size smaller than the smallest particle size. The glass tube is immersed in a beaker, filled **only** with oil or oil product forming a layer with a depth of 5 mm. The rate of sorption was determined from the data giving the relationship between the time and the height of oil product penetration into the adsorbent layer.

Methodology for determining the sorption capacity with respect to oil or oil products

Blank test: Stainless steel grid, which has about 100–150 apertures per square centimeter and mass M_1 is immersed into crude oil or oil product for 10 min. The grid is drained from excess of the liquid for 10 min and then weighed (M_2). The difference between (M_2 - M_1) is the mass of oil (oil product) retained by the empty grid.

Pre-weighed 1.00 g sorbent is placed on the clean grid. The grid with sorbent (M_3) was: (i) immersed into the oil product for 10 min; (ii) allowed to drain the excess liquid for 10 min; (iii) weighed (M_4). The difference between (M_4 - M_3) gives the mass of oil/oil product which was retained by the grid and the sorbent. The difference (M_4 - M_3) - (M_2 - M_1) is the mass of oil absorbed by the sorbent. The sorption capacity (C_{ads}) of the material was calculated in g g^{-1} (grams of sorbed oil per gram of sorbent) or in percentage by the equation:

$$C_{ads} = \frac{(M_4 - M_3) - (M_2 - M_1)}{M_3 - M_1}, \qquad (1)$$

The method is described in details by Angelova et al. [29].

The bulk density of the investigated samples was determined in accordance with BDS EN 13041:2011.

As test-pollutants in the kinetic study were used oil products with different densities, namely: gasoline (BDS 17374-95); diesel (BDS 8884-89); motor oil (BDS 9785-89); light crude oil (Georgia) and heavy crude oil (Bulgaria).

Kinetic studies

The sorption is a real equilibrium process and appears to be a function of the time. This means that the main evidence about the adsorption properties of the material could be derived from the dependence between the amount of adsorbed substance and the time at constant temperature, $q_t = f(t)_T$ where: q_t is the quantity of oil/oil product adsorbed for time *t*, g;

The amount of the adsorbed oil, corresponding to the level of its penetration into the sorbent layer, using the data for the bulk density of the sorbent and its adsorption capacity was calculated by the equations**:**

$$V_{t,ads} = \pi R^2 \cdot h_t \, , \tag{2}$$

where: $V_{t,ads}$ is the volume of the material which adsorbs oil/oil product for time *t*, cm^3;

h_t – height of penetration of oil/oil product inside the layer of adsorbent for time *t*, cm;

R - radius of the layer, cm.

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

$$G_{t,ads} = V_{t,ads} \cdot \rho_{ads} \, , \tag{3}$$

and

$$q_t = G_{t,ads.} \cdot C_{ads} \, , \tag{4}$$

where: q_t is the mass of adsorbed oil/oil product 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 sorption of oil or oil products from the water surface using a solid-state adsorbent is a heterogeneous process which occurs in the system sorbent/oil/water. This means that its rate will depend on: (i) the interaction between sorbent and sorbate; (ii) the rate of diffusion toward and inside the sorbent; (iii) the phenomena on the interphase boundary; (iv) the interaction of water with the sorbate, etc. The realization of the actual act of adsorption, either physical or chemical, forms the kinetic step of the process. The diffusion step of the process is determined by the external and/or the internal mass transfer. Hereby, the overall process velocity 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 determined the region in which the process took place - kinetic, diffusion or transition.

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 were amended in view of the specific conditions in the case of liquid phase. The method of linear regression is the one used most often in order to select a suitable kinetic equation, which gives good correlation between experimental data and the theoretically estimated values. The mathematical principles of the method are not too complicated and it can be applied even in cases when the relation between the practically evaluated parameter and its calculated value is not really linear, but it can be approximated to such dependence.

The adsorption of various contaminants from water can be described by different kinetic models [30,31]. In our investigation several of the most often used equations were applied. They describe the occurrence of the process in the kinetic or in the diffusion region, namely:

Pseudo-first order kinetics

Usually the model of Lagergren [32] is used for processes which could be described by kinetic equations of pseudo-first order and occurring in the kinetic region. After integration within limits $q_t = 0$ at $t = 0$ and $q_t = q_e$ for $t = t_e$ the equation can be presented as follows**:**

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

where:

q_e is the sorbate amount retained by the material after reaching the equilibrium for time interval t_e, g;

k_L – Lagergren rate constant, min^{-1}.

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

Second order kinetics

The second order equation is also applicable to the kinetic region [32]. An integrated form of the equation was used**:**

$$\frac{t}{q_t} = \left(\frac{1}{k_2 \cdot {q_e}^2}\right) + \left(\frac{t}{q_e}\right), \tag{6}$$

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

Both, the initial rate of sorption, $(k_2 \cdot {q_e}^2)$ and the second order rate constant, (k_2) are determined by linear regression of the dependence $t/q = f(t)$, at constant temperature.

Intra-particle diffusion model

The possibility of diffusion to be the only rate-determining step of the adsorption can be verified via the linear equation of Weber-Morris [33]:

$$q_t = k_i \cdot \sqrt{t} + C \, , \tag{7}$$

where: C is a coefficient which accounts for the bonding effect between layers; k_i – rate constant of the process, mg.g^{-1}.min$^{-1/2}$.

If the experimental data do not describe a straight but a multi-linear dependence, this means that the sorption is influenced by two or more rate-determining steps, i.e. the process occurs in the transition region.

The diffusion coefficient of the sorbate inside the pores of the adsorbent is calculated (assuming spherical form of the adsorbent particles) by the equation:

$$t_{1/2} = 0{,}03 \cdot \frac{r_0^2}{D} \quad , \qquad (8)$$

or

$$D = 0{,}038 \cdot \frac{r_0^2}{t_{1/2}} \quad , \qquad (9)$$

where: D is a diffusion constant which depends on the porous structure of the sorbent, cm^2.s^{-1};

r_0 - particle radius, cm;

$t_{1/2}$ – time interval in which half of the sorption process proceeds before reaching equilibrium, s.

Elovich equation

This equation is the most often used model to describe the kinetics of sorption in case when there are valence interactions between the adsorbent and the sorbate, i.e. chemisorption [34]:

$$\frac{dq_t}{dt} = a \cdot \exp(-bq_t), \qquad (10)$$

where: a is initial rate of sorption, mg.g^{-1}.min^{-1};

b – desorption constant, g.mg^{-1}.

Chen et al. (1980) accepted $a \cdot b \cdot t >>> t$ and further developed the equation of Elovich [35]. Applying the limits $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t_e$ they obtained the equation:

$$q_t = \left(\frac{1}{b}\right) \cdot \ln(ab) + \left(\frac{1}{b}\right) \cdot \ln t\,, \qquad (11)$$

The constants a and b in the exponential equation of Elovich are determined on the basis of 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 that sorption occurs [36].

RESULTS AND DISCUSSION

Sorption of crude oil

Light crude oil of density 0.833 g.cm^{-3} at 20° C, was used as a sorbate to determine the influence of sorbent granulometry upon the sorption kinetics. The data for the bulk density of each fraction of the pyrolyzed rice husks, the percentage distribution of the fractions, as well as their sorption capacity, are presented in Table1.

Table 1. Particle size distribution and oil sorption capacity of the fractions of rice husks pyrolyzed at 480°C

Granulometry, mm	Distribution, %	Sample	Bulk density, g.cm^{-3}	Oil sorption capacity, g.g^{-1}
> 2,0	15	PRH-6	0.072	6.667
2.0-1.6	21	PRH-5	0.076	8 .771
1.6-1.2	19	PRH-4	0.084	8.247
1.2-0.8	25	PRH-3	0.106	5.909
0.8-0.4	20.8	PRH-2	0.182	4.363
< 0.4	8.1	PRH-1	0.293	4.215

The adsorption kinetic curves obtained at constant temperature depending on the adsorbent granulometry are presented in Fig.1.

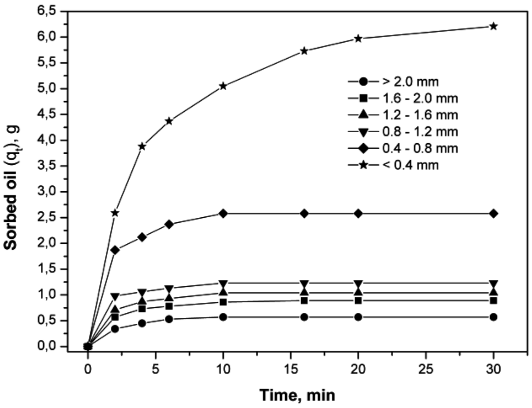

Fig. 1. Dependence between the adsorption and the contact time for pyrolyzed rice husks with different particles size

The shape of the kinetic curves exhibits that the sorption of crude oil by various fractions of the adsorbent is accomplished in two steps. The rate of the first step depends on the ratio between the gravitational and capillary forces, while that of the second step – on the structural characteristics and the oleophilicity of the adsorbent. The time interval for reaching the adsorption-desorption equilibrium is a very important characteristic because it determines the efficiency of the adsorbent [25,27, 37].

The structure of the adsorbent layer can be regarded as a system consisting of capillaries, inside which the process of sorption occurs in two orthogonal directions. In the case of small size fractions, the formed transportation channels possess dimensions, comparable to the pore size of the adsorbent. The impedance, related to the transport of the sorbate inside the layer of the adsorbent is increasing. Thereupon in capillaries having hydrophobic surface, the capillary effect is in action. As a result, the sorbate rises up to a level higher than the initial one [28]. The horizontal capillary translocation of the oil/oil product also depends on the atmospheric pressure. The condition is: the thickness of the oil layer should exceed that of a monomolecular layer. Hereby, the atmospheric pressure and the pressure of the oil layer are summed up within and beyond the area of the adsorbent. The resultant pressure causes coercive external diffusion, which leads to initial filling of the structural cavities within the adsorbent. The opposite – in case of a fraction with large size, wide transportation channels are formed through which the oil product quickly penetrates inside the sorbent layer and reaches the active surface of the material.

The applicability of the used kinetic equations with respect to the adsorption characteristics, presented in Table 1 and the experimental results was verified by plotting the following functions: $\lg(q_e - q_t) = f(t)$; $t/q_e = f(t)$; $q_t = f(\sqrt{t})$, Figures 2(a); 2(b) and 2(c).

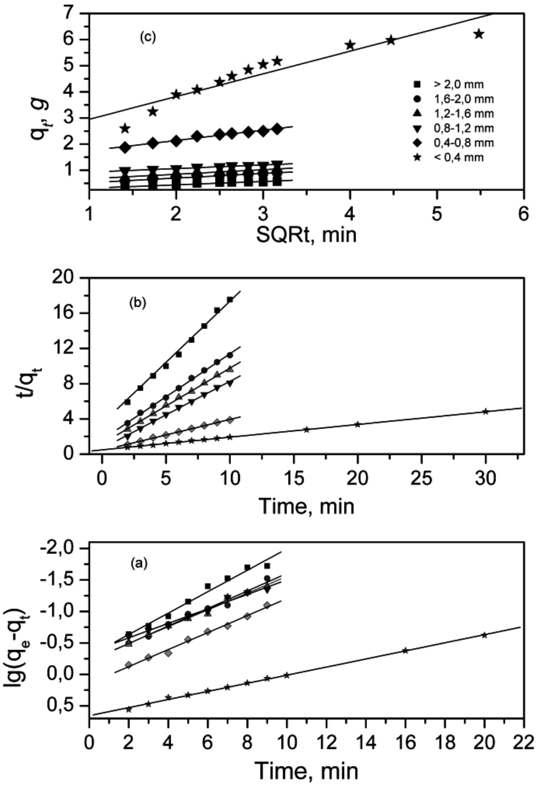

Fig. 2. Test of kinetic equations for the sorption of oil by pyrolyzed rise husks with different granulometry: (a) Lagergren plots; (b) second order kinetics equation; (c) Weber-Morris equation

The statistical data for the linear regression corresponding to the equations are listed in Tables 2, 3 and 4.

Table 2. Parameters of the linear regression for pseudo-first order kinetics, rate constants and theoretical values of the adsorbed amount of oil in equilibrium

Samples	Equilibrium quantities of sorbed oil,g		$^{*}SD$	$^{**}R^2$	$^{***}k_1$
	$q_e^{exp.}$	q_e^{theor}			
PRH-6	0.57	0.51	0.0649	0.9795	0.3919
PRH-5	0.89	0.61	0.0518	0.9806	0.3203
PRH-4	1.04	0.59	0.0401	0.9872	0.3061
PRH-3	1.23	0.45	0.0420	0.9813	0.2648
PRH-2	2.59	1.39	0.0330	0.9916	0.3104
PRH-1	6.12	4.52	0.0167	0.9980	0.1480

*SD-standard deviation; $^{**}R^2$-correlation coefficient; $^{***}k_1$-rate constant

Table 3. Parameters of the linear regression for second order kinetics equation, rate constants and theoretical values of the adsorbed amount of oil in equilibrium state

Samples	Equilibrium quantities of sorbed oil,g		SD	R^2	k_2
	q_e^{exp}	q_e^{theo}			
PRH-6	0.57	0.68	0.2211	0.9973	0.7257
PRH-5	0.89	1.02	0.1176	0.9982	0.5765
PRH-4	1.04	1.16	0.0979	0.9984	0.6358
PRH-3	1.23	1.31	0.0999	0.9980	0.9077
PRH-2	2.58	2.85	0.0396	0.9985	0.2925
PRH-1	6.21	6.94	0.0204	0.9998	0.0427

Table 4. Parameters of the linear regression for the diffusion model

Sample	Parameters					
	coefficients		average square error		SD	R^2
	$a(k_i)$	b	σ_a	σ_b		
PRH-6	0.57	0.51	0.1832	0.1293	0.0213	0.9366
PRH-5	0.89	0.61	0.3535	0.1738	0.0233	0.9571
PRH-4	1.04	0.59	0.5000	0.1739	0.0216	0.9630
PRH-3	1.23	0.45	0.7905	0.1376	0.0108	0.9846
PRH-2	2.59	1.39	1.3513	0.3946	0.0359	0.9797
PRH-1	6.12	4.52	2.0820	0.8690	0.3869	0.8862

As can be seen, the obtained statistical results from the linear regression and the theoretical values of adsorbed amount of oil in the equilibrium state, revealed that the process is most adequately described by a second order kinetic equation. This means that the sorption of oil by pyrolyzed rice husks occurs in the kinetic region, regardless of the bulk density of the sorbent (R^2>0, 99).

As it was already pointed above, the adsorption is also influenced by some other processes, whereupon the rate-determining step could be single or more than one. The probability the diffusion to be the rate limiting stage of the process could be evaluated with the equation of Weber-Morris. The obtained data of the correlation coefficients for each fraction reveal that in this case the diffusion cannot be assumed as a rate limiting step. In order to evaluate the role of diffusion within the total rate of the process, the coefficient of diffusion *D* was determined by applying equations (9) and (10) for the fraction of size 0.40 mm. The shape of the granules of the fraction can be approximated to spheres. The calculated diffusion coefficient amounts to 5.3×10^{-5} cm^2.s^{-1}. The value is by two orders of magnitude smaller than the rate of penetration of the oil inside the adsorbent (6.5×10^{-3} cm.s^{-1}, at $t_{1/2}$ and at constant cross section of the layer). This fact confirms the substantial effect of the internal (pore) diffusion on the total rate of the process of sorption [29].

The obtained parameters of linear regression for the applied models, as well as the values of the rate constants showed that whatever be the fractional composition of the pyrolyzed rice husks, the adsorption of crude oil occurs mainly in the kinetic region.

The complex mechanism of oil sorption from the water surface was also confirmed by some authors. They have shown that the applicability of the second order kinetic model is an indication of sorption which proceeds through interaction between the valence forces of the surface functionalities of the adsorbent and those of the sorbate [38-42].

Influence of the dispersed fluids on the kinetics of sorption

The experiment was carried out with the fraction PRH-5 of solid pyrolysis residue and light crude oil ($\rho^{20°} = 0.833$ g.cm^{-3}). It was established that after the quantitative extraction of the finely dispersed fluids by the solid pyrolysis residue, the quantity of oil adsorbed for time interval t decreased considerably, Fig. 3.

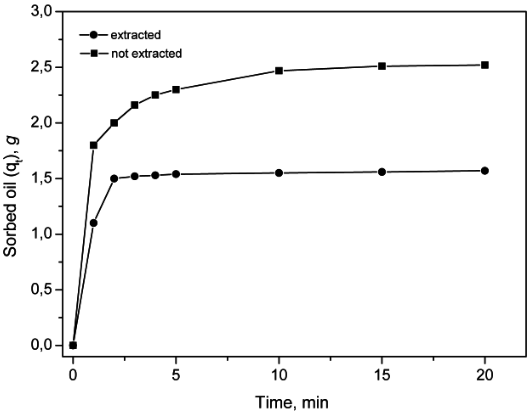

Fig. 3. Effect of the fluids dispersed on the solid pyrolysis residue upon the amount of adsorbed oil depending on the contact time.

The obtained result shows that the kinetics and mechanism of oil sorption are substantially influenced by the chemistry of the sorbent surface.

The possibility the adsorption in the system water/oil/pyrolyzed rice husks to occur with participation of other forces, beside those of Van der Waals was estimated by applying the Elovich equation. The equation was applied to describe the sorption of oil with extracted and with unextracted pyrolyzed rice husks. The results are presented in Fig. 4.

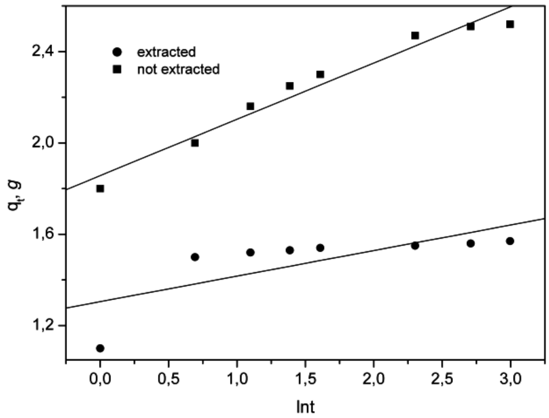

Fig. 4. Plots of the Elovich equation for adsorption of oil with extracted and not extracted pyrolyzed rice husks.

The relevant parameters of the linear regression are listed in Table 5.

The obtained comparative data unambiguously prove the influence of surface functionalities on the oil sorption process. The solid pyrolysis residue by its nature is a natural C/SiO$_2$ hybrid material. It contains carbon atoms in the sp^2-hybridization state and reactive siloxane groups belonging to amorphous silica. Furthermore, the thermal destruction of rice husks is associated with deposition upon the surface of the solid pyrolysis residue of alkanes, cycloalkanes and arenes, as well as compounds possessing functional groups with different reactivity. This promotes the interaction of petroleum hydrocarbons with the sorbent [28,43].

It was established that the extraction of the fluids, deposited on the solid pyrolysis residue, leads to a change in the porosity of the material [29].

Table 5. Parameters of linear regression for the Elovich model, concerning extracted and unextracted rice husks

Sorbent (PRH)	Parameters					
	coefficients		average squared error		*SD*	R^2
	a	*b*	σ_a	σ_b		
Unextracted	1.8570	0.2465	0.0375	0.0201	0.0545	0.9624
Extracted	1.3046	0.1120	0.0792	0.0425	0.1152	0.5411

The adsorbent used in the present investigation possesses a high percentage of pores with sizes of 1-50 µm, as well as above 50 µm. After extraction with acetone, the quantity of the pores of dimensions 1-50 µm is increased with 9% at the expense of the pores with size > 50 µm. The effect is due to the fact that a part of the volatile pyrolysis products completely fills up the pores with smaller size. The likelihood for changing the region of occurrence of the adsorption, associated with this fact was checked by using the second order equation.

The obtained results demonstrated a good correlation between the model and the experimental data for both samples, Fig. 5 and Table 6.

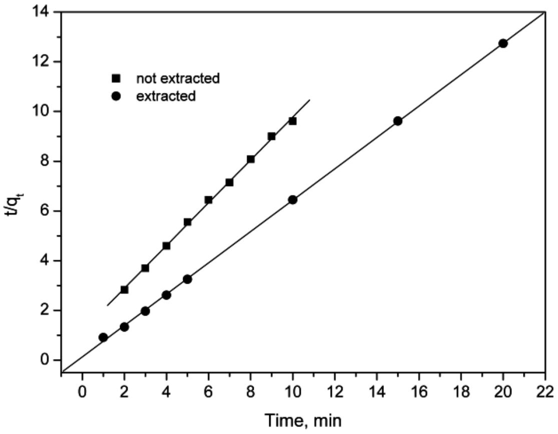

Fig. 5. Test of second order kinetic equation for the sorption of oil on extracted and not extracted pyrolyzed rice husks

Table 6. Parameters of the linear regression for second order kinetic equation, rate constants and theoretical values of the adsorbed amount of oil in equilibrium state for adsorption with extracted and not extracted PRH

Sorbent (pyrolyzed rice husks)	Equilibrium quantities of sorbed oil,g		*SD*	R^2	k_2
	$q_e^{exp.}$	$q_e^{theor.}$			
Extracted	2.52	1.58	0.0979	0.9984	0.3427
Not extracted	1.57	1.16	0.0736	0.9998	3.1547

The change in the porosity of the material does not lead to any drastic change in the rate of diffusion. In sum, the increase in the quantity of small pores does not hinder the diffusion of the oil into the sorbent structure and the process actually occurs in the kinetic region.

Influence of the density of the oil product on the kinetics of sorption

The investigation was carried out using oil products possessing low (ρ^{20° = 0.768); medium (ρ^{20° = 0.886) and high density (ρ^{20° = 0.973). Data about the characteristics of the used oil products, including the adsorption capacities of pyrolyzed rice husks were reported by Angelova et al. [44]. Unfractionated pyrolyzed rice husks were used as the adsorbent under investigation. The percentage distribution of the granulometric fractions in the solid pyrolysis residue is presented in Table 1.

The dependences between the adsorbed amount of oil or oil product, q_t and the time are presented in Fig.6.

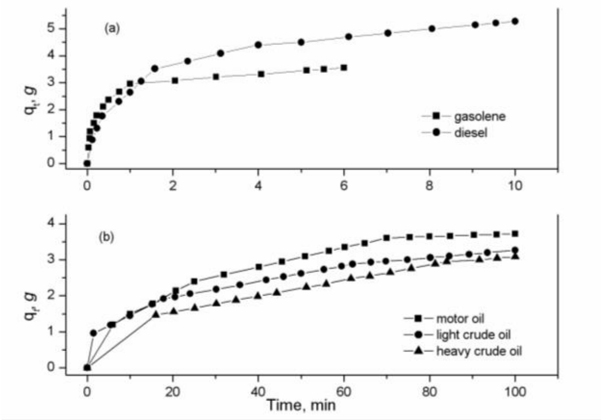

Fig. 6. The effect of oil products density upon the adsorption kinetics

The obtained results prove that the rate of reaching adsorption-desorption equilibrium depends on the density of the hydrocarbon pollutant and the relation is hyperbolical.

Upon increasing the density of the oil product, which is a gravitational characteristic, a partial compensation from the oppositely directed capillary forces appears. As a result, the adsorbed amount of heavy distillate oil products is smaller. In the case of products with low bulk density a high rate of sorption is observed during the first 10 – 15 min after the initial contact between sorbent and sorbate. After this period, the rate decreases until adsorption-desorption equilibrium is reached.

In order to determine the region in which the adsorption process is occurring depending on the density of the oil products, the same equations, already mentioned above were used:

Kinetic equation of pseudo-first order

The plotted dependences $\lg(q_e - q_t) = f(t)$ for the sorption of oil products of different density are illustrated in Figure 7.

In Table 7 are listed the relevant parameters of the linear regression and the theoretical values of the adsorbed amount in the equilibrium state.

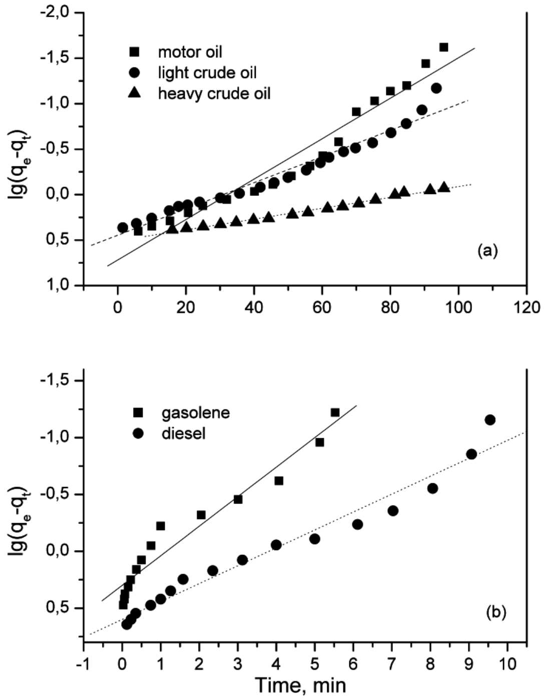

Fig. 7. Lagergren equation for adsorption of oil and oil products by pyrolyzed rice husks

Table 7 Parameters of the linear regression for pseudo-first order kinetics, rate constants and theoretical values of the adsorbed amount when equilibrium is reached, concerning oil products of different density

Petrochemicals	Equilibrium quantities of sorbed pollutant, g		*SD*	*R*^{2}	*k*$_1$
	q$_e^{exp.}$	q$_e^{theor.}$			
Gasoline	3.56	1.99	0.1309	0.9438	0.5985
Diesel	5.28	3.97	0.1025	0.9654	0.3627
Motor oil	3.72	5.22	0.1493	0.9505	0.0511
Light crude oil	3.27	2.79	0.0835	0.9626	0.0332
Heavy crude oil	3.09	3.21	0.0164	0.9892	0.0138

Second order kinetic equation

The plotted dependences $t/q_t = f(t)$ for the various oil products are presented in Fig. 8. The parameters of the linear regression are listed in Table 8.

Table 8. Parameters of the linear regression for second order kinetics, rate constants and theoretical values of the adsorbed amount in equilibrium state

Petrochemicals	Equilibrium quantities of sorbed pollutant, g		*SD*	*R*^{2}	*k*$_2$
	q$_e^{exp.}$	q$_e^{theor.}$			
Gasoline	3.56	3.60	0.0271	0.9982	1.2365
Diesel	5.28	5.65	0.0365	0.9968	0.1758
Motor oil	3.72	4.60	0.5044	0.9943	0.0096
Light crude oil	3.27	3.64	1.0479	0.9850	0.0172
Heavy crude oil	3.09	4.23	1.0668	0.9740	0.0058

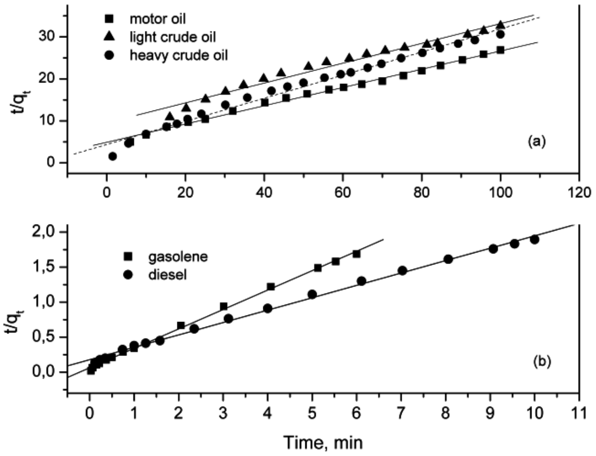

Fig. 8. Test of second order kinetic equation for the adsorption of oil products possessing different densities.

Intra-particle diffusion model

An attempt to apply the model based on diffusion as the only adsorption rate limiting step, in regard to oil products of different densities, has led to the results, presented in Fig.9 (a,b) and Table 9.

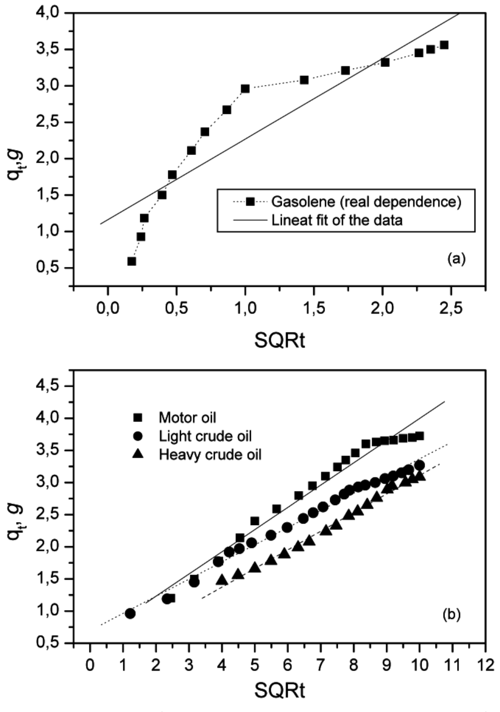

Fig. 9. Test of the Weber-Morris model for the adsorption of: (a) gasoline and (b) motor oil; light and heavy oil with pyrolyzed rice husks.

The results obtained relating to the adsorption of various oil products from water surface by pyrolyzed rice husks, indicated the following:

(i) In spite of the different densities of the oil products the sorption from water surface is occurring in the kinetic region and is described adequately by a second order equation;

(ii) The values of the correlation coefficients for light and heavy crude oils, obtained for the diffusion equation, converge to unity but the rate constants of diffusion are by one order of magnitude higher than those for physical adsorption. This means that the process actually occurs in the kinetic region.

Table 9. Statistical data originating from the Weber-Morris equation for adsorption of oil products of different densities

Petro-chemicals	Parameters					
	coefficients		average squared error		*SD*	R^2
	a	*b*	σ_a	σ_b		
Motor oil	0.5403	0.3557	0.1062	0.0145	0.1416	0.9710
Light crude oil	0.6962	0.2672	0.0398	0.0057	0.0661	0.9906
Heavy crude oil	0.2131	0.2899	0.0475	0.0062	0.0482	0.9926

CONCLUSIONS

The kinetics of sorption of oil and oil products from water surface using fractionated and unfractionated pyrolyzed rice husks was investigated by the method of penetration of the sorbate in the layer sorbent.

The obtained results demonstrated that the fractions of pyrolyzed rice husks can be successfully used for purification of marine oil spills. It was found that the finest fraction has the best adsorption ability.

Some equations which are often applied were used to describe the kinetics and mechanism of the process. Their use in the case of sorption of oil and oil products from water surface was shown. It was found out that the kinetics of sorption of the studied oil and oil products could be adequately described by a second order kinetic equation, irrespective of the grain size of the pyrolyzed rice husks or the bulk density of sorbate.

By applying the Elovich equation the role of the fluids finely dispersed on the solid pyrolysis residue during the sorption of oil and oil products from the water surface was confirmed.

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КИНЕТИКА И МЕХАНИЗЪМ НА СОРБЦИЯ НА НЕФТ И НЕФТОПРОДУКТИ ОТ ВОДНА ПОВЪРХНОСТ ВЪРХУ ПИРОЛИЗИРАНА ОТПАДНА БИОМАСА

С. А.Узунова[1], И. М.Узунов[2*], Д. Р. Механджиев, В. Б. Тотева[1]

[1] Химико-технологичен и металургичен университет-София, бул.”Св. Кл.Охридски” 8, 1756 София
[2] Институт по обща и неорганична химия-БАН, ул.”Акад. Г.Бончев”, бл.11, 1113 София

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(Резюме)

Настоящето изследване е опит да се изследват кинетиката и механизма на сорбция на нефт и нефтопродукти от водна повърхност с пиролизирани оризови люспи. За определяне на кинетиката и скоростоопределящия етап на процеса бяха използвани кинетични модели от псевдо-първи и втори порядък; уравнение на Елович, както и дифузионен модел. Приложимостта на уравненията бе оценена по статистическите данни на метода на линейна регресия. Бяха изследвани ефектите на: гранулометрията на сорбента, относителната плътност на нефтените замърсители и наличието на повърхностни функционални групи в сорбента върху кинетиката на адсорбция.