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# Adsorption of thiophene and its polyaromatic derivatives from model fuel on pyrolyzed rice husks: kinetics and equilibrium

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Kinetics of fuel adsorptive desulphurisation was studied using a model fuel containing thiophene, benzothiophene, and dibenzothiophene of initial total sulphur content ($S_{in}$) of 415, 218, and 111 wppm over pyrolyzed rice husks (PRH) under batch mode conditions. Total sulphur content was determined by X-ray fluorescence analysis. Second order kinetics, intraparticle diffusion model, and Elovich equation were used to analyse kinetic data. It was found that a second-order kinetics model adequately described adsorption of the three sulphur compounds on pyrolyzed rice husks. The equation provided the best fit between calculated and experimentally determined values of adsorption capacity. Value differences varied between 1.3% for $S_{in}$ 111 ppm and 5.9% for $S_{in}$ 415 ppm. Adsorption affinity of the three sulphur compounds as well as equilibrium adsorption capacity of pyrolyzed rice husks were investigated by determination of adsorption isotherm. Analysis of experimental data was conducted by using the isotherms of Langmuir, Temkin, and Freundlich. Data from multiple linear regression analysis pointed out that Freundlich isotherm described most adequately the adsorption equilibrium of polyaromatic sulphur heterocycles in the system fuel/PRH.

**Key words:** desulphurization, adsorption, aromatic sulphur heterocycles, pyrolyzed rice husks, kinetics, adsorption isotherm.

## INTRODUCTION

Depletion of the fossil fuel deposits, periodically emerging economic or political crises, and environmental pollution in recent decades imposed demand and development of alternative energy sources. However, the part of energy obtained from fossil feedstocks remains significant, more than 82% and half of them are produced from the crude oil [1]. Intense oil production worldwide leads to depletion of old and commissioning of new oil fields, containing increasingly high sulphur quantity. This in turn leads to new challenges related to technological and environmental problems in removal of the sulphur compounds in oil refinery streams. Conventional hydrodesulphurisation (HDS) of high sulphur feedstocks is unable to ensure sulphur levels, close to the limit ones whereas preserving other important quality indicators, such as content of polycyclic arenes, cetane number, density, etc. The process is not effective with respect to the deep removal of the polycyclic aromatic sulphur compounds such as thiophene (T) and its derivatives. Hereby, the sulphur compounds are passed into the industrial and automotive fuels. This leads to emissions of sulphur oxides, with all the resulting harmful effects on the environment and human health. The presence of organic sulphur compounds in the automotive fuels also reduces largely catalyst system efficiency in modern cars. In addition, the tendency in recent years aimed at developing the so-called ‘hydrogen economy’ is closely connected with the production of fuel cells but they require <1 ppm sulphur-hydrogen containing feeds [2]. Considering the importance of the problem concerning the emissions of sulphur oxides EU adopted a number of directives and decisions to control total sulphur in fuels [3,4]. Implementation of these directives is a major challenge and requires improving of the existing purification technologies to minimize sulphur content in petroleum derivatives. In addition to their effectiveness, the methods must ensure well-balanced prices of the final products. Research in the field over the last decade has been focused on the development of alternative methods for deep or ultra-deep fuel purification from sulphur. Most often these methods accompany conventional purification by HDS and provide fuels production with a total sulphur content of up to and below 10 ppm. The so-called non-HDS based desulphurisation processes refer to desulphurisation by extraction [5–8], olefinic alkylation of thiophenic sulphur (OATS process) [9], selective oxidative desulphurisation [10], and desulphurisation *via* precipitation [11].

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Among the alternative methods for the purification of fuels, particular attention is given to the method of adsorptive desulphurisation (ADS), which is based on selective adsorption of organic sulphur compounds from the fuel onto different by nature solid adsorbents [12–14]. The process is provided under soft conditions, such as moderate temperature and atmospheric pressure. Additional advantages of the process are high efficiency, molecular hydrogen free process, simple technology and equipment, complex, inexpensive capital and operating costs, and high level of labour safety. Extraction of the adsorbed organic sulphur compounds and their subsequent utilization provide a real ecological solution for regulation of a part of the refinery hazardous wastes. Recently published results concerning adsorptive desulphurisation confirm that heterogeneous adsorption is an attractive method for improving the quality of hydrocarbon fuels [15–22]. The method provides low content of sulphur and polyaromatic compounds content in the fuels in order to meet the requirements of modern quality standards. The ADS method is also attractive by the fact that various inexpensive and available raw materials are increasingly used for production of effective adsorbents [16–22]. From this point of view processing of rice husks waste to obtain proper materials for selective adsorption of aromatic sulphur compounds from fuels is of interest. Kumagai and co-workers have reported removal of dibenzothiophenes from kerosene on rice husk activated carbons in terms of their textural and chemical characteristics [23]. Uzunova *et al.* [24] have investigated some factors of influence upon selective adsorption of thiophene on pyrolyzed rice husks (PRH).

The purpose of the present study was to determine adsorption kinetics of a model fuel mixture of thiophene, benzothiophene (BT), and dibenzothiophene (DBT) of different initial sulphur concentration in solution onto pyrolyzed rice husks. Some kinetic models were used, such as second order kinetics; intraparticle diffusion model, and Elovich equation for data analysis to determine phenomenological adsorption mechanism of aromatic sulphur heterocycles (ASHs) onto pyrolyzed rice husks. The kinetics is directly related to achieving adsorption equilibrium in the system PRH/fuel. Adsorption affinity with respect to the mixture of the three sulphur compounds and equilibrium adsorption capacity of pyrolyzed rice husks were determined by use of adsorption isotherm.

Such an investigation deep inside the nature of the adsorptive desulphurisation by pyrolyzed rice husks offers a possibility to optimize the process from laboratory conditions to industrial scale-up.

## MATERIALS AND METHODS

### *Preparation and characterization of pyrolyzed rice husks*

The material used in the investigation was prepared by slow pyrolysis of rice husks provided from Pazardzhik region (Bulgaria). Rice husks prewashed several times with water and dried at 110 °C were pyrolyzed at 480 °C in a fixed bed stainless steel reactor under vacuum of 1.33 Pa. The heating rate was 4 $°C.min^{-1}$, the retention time being 3 h. Porous structure of the material was determined by mercury porosimetry. For the purpose, a Micromeritics AutoPore 9200 apparatus was used. The specific surface area was assessed by BET nitrogen adsorption measured by a Strohlein Area Meter static volumetric device. Ash content of the pyrolyzed rice husks was determined by thermogravimetric analysis on a SETARAM LABSYS Evo apparatus in a corundum crucible at a heating rate of 10 $°C.min^{-1}$ in air. Structural characteristics of the pyrolyzed rice husks are summarized in table 1.

**Table 1. C**haracteristics of the pyrolyzed rice husks

| Characteristics | Value |
|---|---|
| total pore volume, $cm^3.g^{-1}$ | 1.05 |
| porosity, % | 57.1 |
| total pore surface, $m^2g^{-1}$ | 5.9 |
| average pore diameter, µm | 0.72 |
| bulk density, $kg.m^{-3}$ | 102 |
| BET specific surface area, $m^2.g^{-1}$ | 253 |
| mass yield**,** wt % | 38 |
| carbonaceous material/ash wt. ratio | 0.96 |

As can be seen, the samples are characterized by high specific surface area, over 50% porosity, and total pore volume of 1.0 $cm^3.g^{-1}$. A differential pore size distribution shows that the porous structure of the pyrolyzed rice husks is formed predominantly by mesopores and macropores (Fig. 1) [25].

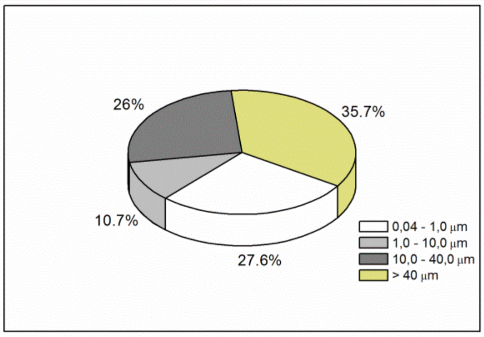

Fig. 1. Percentage of pore size distribution *vs.* total pore volume.

### *Adsorptive desulphurisation*

*Preparation of model fuel.* To determine the influence of initial sulphur content and contact time on adsorption kinetics, model fuel (MF) samples containing total sulphur of 415, 218, and 111 wppm were prepared by mixing thiophene, benzothiophene, and dibenzothiophene in octane at a 1:1:1 mass ratio. Fuel samples containing total sulphur of 415, 950, 1945, and 4600 wppm were prepared for determination of adsorption isotherm. The mixtures were percentage of pore size distribution having in mind that sulphur content in the thiophene, benzothiophene, and dibenzothiophene was 38.1, 23.9, and 17.4 mass%, respectively.

The three sulphur compounds and octane were Sigma Aldrich pure grade. Initial solutions were prepared by placing the required amount of thiophene, benzothiophene, or dibenzothiophene in a flask and octane was added up to a total weight of 100 g. Sulphur percentage in the solutions was determined by Sindie OTG Sulfur Analyzer using monochromatic wavelength dispersive X-ray fluorescence.

*Adsorption in batch mode.* Adsorption experiments were carried out at a constant temperature of 20 °C. Batch mode adsorption was provided by contacting 25.00 ml model fuel (specific gravity of 0.7 $g.cm^{-3}$) with 3.00 g of adsorbent placed in a stoppered Erlenmeyer flask. The suspensions were agitated on a rotary shaker for 120, 240, 360, 480, and 1440 min. An adsorption isotherm was obtained in order to investigate PRH adsorption capacity and affinity at equilibrium. The time required to reach adsorption equilibrium in the system fuel/PRH at 20 °C was determined by kinetic study.

The mixtures were agitated by shaking for 24 h to attain the equilibrium state. After that, the mixtures were filtered and the filtrates were analysed by XRF to determine adsorbed sulphur amount on the pyrolyzed rice husks. All measurements were performed in triplicate and the arithmetic average $\overline{S_{eq}}$ was calculated.

The adsorption capacity at equilibrium, $a_e$, was calculated according to the following equation:

$$a_e = \frac{(S_{in} - S_{eq})M}{m}, mg/g \qquad (1)$$

where $S_{in}$ and $S_{eq}$ are the initial and equilibrium sulphur concentration in the fuel (ppmw-S), respectively, $M$ is fuel mass (kg), and $m$ is adsorbent mass (g).

A quantitative measure of PRH efficiency and adsorption capacity is the degree of desulphurisation, φ, which was calculated by the formula:

$$\varphi = \frac{(S_{in} - S_{eq})}{S_{in}} \cdot 100, \% \qquad (2)$$

*Kinetic equations*. Phenomenological kinetic models are used to establish the rate-limiting step of the adsorption process. Rate-limiting processes for adsorption, occurring in the system liquid/solid usually are diffusion, mass transfer, or possibly chemical interaction between adsorbent and adsorbate. The accuracy of each kinetic model is a function of independent (input) parameters that affect output (measured) parameters. To select the most appropriate kinetic equation for which theoretically calculated and experimentally determined data have the best fit, the multiple linear regression (MLR) method is most commonly used. By establishing the adsorption kinetics, it is intended to optimize the process via regulating the conditions for its performance.

*Second order kinetics.* A second order equation is applicable to the kinetic region [26]. It usually describes bimolecular reactions with both reactants' concentrations decreasing with time. In this case, one can accept the second decreasing concentration is that of the surface active sites of the adsorbent. The mathematical expression is:

$$\frac{da_t}{dt} = k_2\left(a_e - a_t\right)^2, \qquad (3)$$

where $k_2$ is the second order rate constant of adsorp-tion, $mg.g^{-1}.min^{-1}$.

After integrating equation (3) one obtains:

$$\frac{t}{a_t} = \left(\frac{1}{k_2 \cdot a_e^{\,2}}\right) + \left(\frac{t}{a_e}\right), \qquad (4)$$

Initial rate of sorption ($k_2 \cdot a_e^2$) and second order rate constant ($k_{2)}$ were determined through linear regression method by the slope and interception of the dependence $t/a_t = f(t)$.

*Intraparticle diffusion model.* Adsorption velocity depends on the diffusion of the sulphur compounds toward and from the surface of the adsorbent. Mass transfer rate is a function of the concentration gradient in the liquid/solid system. In the case when diffusion is a rate-depending step, the process is described satisfactorily by the Weber-Morris equation [27]:

$$a_t = k_{id} \cdot \sqrt{t} + C, \qquad (5)$$

where $C$ is a coefficient accounting the bonding effect between layers and $k_{id}$ is a process rate constant, $mg.g^{-1}.min^{-1/2}$. The values of $C$ and $k_{id}$ are determined by the plot dependence $a_t = f(t^{1/2})$.

*Elovich equation*. This is one of the most often used models to describe chemisorption kinetics (Eq.

6) [28]. It is also successfully applied to describe the initial adsorption step and multilayer adsorption on a high heterogeneous surface area. The equation is empirical and does not refer to any particular mechanism:

$$\frac{da_t}{dt} = \alpha \cdot \exp\left(-ba_t\right), \tag{6}$$

where $\alpha$ is the initial rate of sorption, mg.g$^{-1}$.min$^{-1}$, and $b$ is desorption constant, g.mg$^{-1}$. Chen and Clayton [29] developed further the equation of Elovich, accepting the assumption ($\alpha.b.t$) >>> 1. For the boundary conditions $a_t = 0$ at $t = 0$ and $a_t = a_e$ at $t = t_e$, Eq. 7 was derived:

$$a_t = \left(\frac{1}{b}\right) \cdot \ln\left(\alpha b\right) + \left(\frac{1}{b}\right) \cdot \ln t, \tag{7}$$

where: $b$ is a constant referred to surface coverage and activation energy of chemisorption mg.g$^{-1}$, $\alpha$ is equilibrium rate constant, mg.g$^{-1}$.min$^{-1}$. The constants α and $b$ in the exponential equation (7) are determined from the intercept and the slope of the dependence $a_t$ *vs* ln*t*. In the case when the correlation between the adsorption capacity and the constant $b$ is negative it is assumed that the adsorbent does not retain the adsorbate.

## RESULTS AND DISCUSSION

### *Adsorption kinetics*

Adsorption ability of pyrolyzed rice husks from model solutions containing different initial amount of thiophene, benzothiophene, and dibenzothiophene is presented in figure 2.

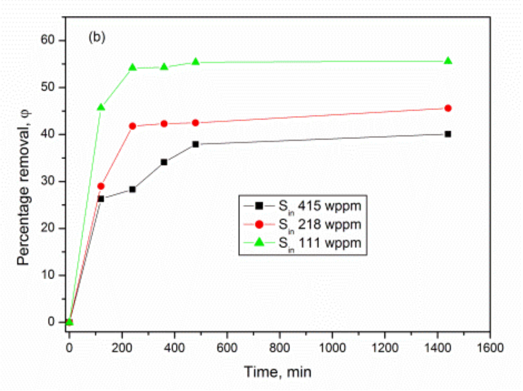

Fig. 2. Adsorption kinetics of aromatic sulphur heterocycles from model fuel on pyrolyzed rice husks.

The type of kinetic curves shows that the process of adsorption of a mixture of thiophene and its aromatic derivatives from fuel on pyrolyzed rice husks was carried out at two distinct stages. The first of them had duration of about 240 min. and is characterised by a sharp increase in the rate of adsorption. During this stage, a desulphurisation rate between 28 and 54 mass% was achieved depending on the initial content of total sulphur in the fuel. The second stage is related to saturation of the active adsorption sites giving rise to reduction in velocity of the process and establishment of adsorption-desorption equilibrium. The degree of desulphurisation varied between 1 and 12 mass%. The observed relationships are directly related to the structural characteristics of pyrolyzed rice husks. The rate to achieve adsorption-desorption equilibrium determines adsorbent effectiveness, i.e. duration of the first stage is of practical significance.

In order to investigate the dependence between input parameters (initial sulphur concentration in the fuel and contact time between adsorbent and adsorbate) and adsorption rate (output parameter) the above-mentioned four kinetic models were applied to analyse the experimental data. These phenomenological models describe the mechanism by which the adsorption of aromatic sulphur heterocycles from fuel on pyrolyzed rice husks occurred. Model parameters and multiple linear statistics are presented in table 2.

**Table 2.** Kinetic parameters for thiophene, benzothiophene, and dibenzothiophene adsorption from model fuel

| Kinetic constants | Initial sulphur content ,wppm | | |
|---|---|---|---|
| | 415 | 218 | 111 |
| Second order kinetics | | | |
| a$_{e,calc}$, mg.g$^{-1}$ | 1.033 | 0.602 | 0.366 |
| a$_{e,exp}$, mg.g$^{-1}$ | 0.971 | 0.581 | 0.361 |
| k$_2$, g.mg$^{-1}$.min$^{-1}$ | 0.0110 | 0.033 | 0.177 |
| R$^2$ | 0.998 | 0.999 | 1.000 |
| Elovich equation | | | |
| b, mg.g$^{-1}$ | 6.794 | 13.49 | 43.74 |
| 1/b | 0.1472 | 0.074 | 0.029 |
| α, mg.g$^{-1}$.min$^{-1}$ | 0.096 | 0.197 | 210.1 |
| R$^2$ | 0.876 | 0.692 | 0.601 |
| Intraparticle diffusion model | | | |
| C | 0.244 | 0.174 | 0.137 |
| K$_{id}$, mg.g$^{-1}$.min$^{-1/2}$ | 0.0245 | 0.014 | 0.005 |
| R$^2$ | 0.757 | 0.671 | 0.567 |

According to the linear regression statistics obtained, high values as 99% of the determination coefficient indicate that adsorption is best fitted to a second order kinetics equation for different initial sulphur concentrations in the fuel. For this kinetic model, a very good match was observed between calculated and experimentally determined values for adsorption capacity, $a_e$. Value deviation varied from 1 to 6%. On increasing the initial sulphur content in the model fuel the rate constant $k_2$ decreased by more than one order of magnitude. This is probably due to: (i) competitive adsorption of the three sulphur compounds and (ii) mutual hindrance (steric effects) in the occupation of the active sites on the surface.

Furthermore, with increasing the initial sulphur concentration in the fuel the electrostatic interaction between active adsorption centres decreased causing a decrease in adsorption affinity between adsorbent and adsorbate. As a result, the adsorbed amount decreased from 56% (111 wppm) to 40% (415 wppm). The second order kinetics model indicates that adsorption probably takes place also with the participation of valence forces, i.e. by specific interactions between adsorbent active sites and adsorbate.

Low values of the determination coefficient for the diffusion kinetic model indicate that diffusion cannot be considered a rate-limiting step. The general conditions, when the mass transfer of adsorbate to the adsorbent surface and into its porous structure is rate-determining, are the following: the correlation coefficient ($R^2$) values are close to 1, and the graphic dependence passes through the origin of the coordinate system, the constant *C* value being negative. If the experimental data describe not a straight-line dependence, but in fact, a multi-linear one as in the case, this means that sorption is influenced by two or more rate-determining steps, i.e. the process occurs in the kinetic or in the transition region.

Positive values of the constants calculated by Elovich equation give evidence that an active sorption process is really proceeding [29].

### *Adsorption isotherms*

A quantitative measure for maximum depth of fuel purification from sulphur compounds is the adsorption capacity value in equilibrium state. An experimental adsorption isotherm obtained in the concentration range from 415 to 4600 wppm of total sulphur is presented in figure 3. It is obvious that the amount of sulphur adsorbed on pyrolyzed rice husks increased as sulphur initial concentration was increased.

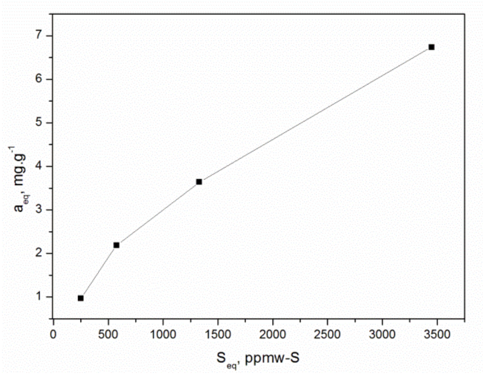

Fig. 3. Adsorption isotherm for simultaneous adsorption of thiophene, benzothiophene, and dibenzothiophene from model fuel.

Adsorption data were analysed using three models:

*Langmuir isotherm model.* The Langmuir model describes nonlinear adsorption and it is based on the assumption that the process is carried out on a homogeneous surface through the formation of a monolayer by the adsorbate without any interaction between the adsorbed molecules. Langmuir equation has the form:

$$\frac{S_{eq}}{a_e} = \frac{1}{K_L\,.a_\infty} + \frac{S_{eq}}{a_\infty} \qquad (8)$$

where $S_{eq}$, ppmw-S; $a_e$, mg.g$^{-1}$; $a_\infty$ is maximum adsorption capacity required to form a monolayer on the adsorbent surface, mg.g$^{-1}$; $K_L$- is Langmuir constant, kg.mg$^{-1}$, related to the energy of adsorption. The values of $K_L$ and $a_\infty$ are determined by the relationship:

$$S_{eq}/a_e = f\,(S_{eq}) \qquad (9)$$

*Freundlich isotherm model.* This empirical model is based on the assumption that the distribution of adsorption heat on the surface of the adsorbent is not homogeneous. Eq. 10 represents the linear form of the Freundlich isotherm:

$$\log a_e = \log K_F + (1/n).\log S_{eq}\,, \qquad (10)$$

where $K_F$, mg.g$^{-1}$, is the constant of Freundlich isotherm and it is an approximate indicator of adsorption capacity; *1/n* is a function of adsorption strength. The values of 1/*n* and $K_F$ are determined from the slope and intercept of the following relationship, Eq. 11:

$$\log a_e = f\,(\log S_{eq}) \qquad (11)$$

Values of adsorption intensity, *n*, between one and ten indicate favourable physical adsorption [31,32].

*Temkin isotherm model.*

The model of Temkin is based on the assumption that the energy of all molecules adsorbed in the monolayer decreases linearly in height. The linear dependence of the model is the following (Eq. 12):

$$a_e = B.\ln A + B.\ln S_{eq} \qquad (12)$$

The values of the isotherm constants *A* and *B* were determined from the slope and intercept of the graphical dependency (Eq. 13):

$$a_e = f\,(\ln S_{eq}), \qquad (13)$$

where *B* is coefficient related to the heat of adsorption (J/mol) and *A* is Temkin isotherm equilibrium binding factor (kg/g).

Values of the adsorption constants, coefficients for each adsorption isotherm as well as coefficients of determination, $R^2$, calculated by the multiple linear regression method and standard deviation, $S_{RE}$, are given in table 3.

**Table 3**. Isotherms constants and statistical criteria for the adsorption process

| Isotherm | Parameters |
|---|---|
| Langmuir | |
| $a_\infty$ | 8.33 |
| $K_L$ | $4.1\times10^{-4}$ |
| $R^2$ | 0.906 |
| $S_{RE}$ | 62.4 |
| Freundlich | |
| $K_F$ | 0.019 |
| n | 1.39 |
| 1/n | 0.72 |
| $R^2$ | 0.987 |
| $S_{RE}$ | 0.05 |
| Temkin | |
| B | 2.2 |
| A | $5.2\times10^{-3}$ |
| $R^2$ | 0.952 |
| $S_{RE}$ | 0.67 |

According to statistical data, the adsorption of thiophene and its derivatives from fuel is reasonably described by the Freundlich and Temkin isotherms. As can be seen both models provide good correlations for the adsorption, however, the Freundlich isotherm describes the process more adequately. The Freundlich model is valid for heterogeneous surfaces and predicts an increase in concentration of the species adsorbed on the solid surface if species concentration in the liquid phase is increased. Therefore, the adsorption of thiophene and its derivatives on pyrolyzed rice husks obviously takes place on a heterogeneous surface, which may expose various adsorption sites having different affinity to thiophene, benzothiophene, and dibenzothiophene. The equilibrium heat capacity, *B*, calculated from Temkin isotherm is low. The heterogeneity parameter, *1/n*, determined from the Freundlich isotherm is > 1, which indicates favourable adsorption of aromatic sulphur heterocycles onto pyrolyzed rice husks. The process is carried out with predominant participation of non-specific interactions between adsorbent and adsorbate.

## 4. CONCLUSIONS

The material obtained by slow pyrolysis of renewable agricultural waste as rice husks can successfully be used for additional purification of fuels by adsorptive desulphurisation as a concomitant method of conventional hydrodesulphurisation.

Adsorption of a mixture of thiophene and thiophene aromatic derivatives from model fuel in the studied concentration range predominantly occurred in the kinetic region and is adequately described by a second order kinetics equation. Calculated and experimentally obtained values for adsorption capacity of pyrolyzed rice husks varied from 1 to 6%.

An increase of the initial sulphur content in model fuel caused a decrease of the rate constant of the process by more than one order of magnitude. Probably, this is due to competitive adsorption of the three sulphur compounds and steric effects upon occupation of the active adsorption sites. As a result, adsorbate affinity to the adsorbent was decreased and the adsorbed amount was reduced from 55.6% to 40%.

The equilibrium adsorption of thiophene and its derivatives from fuel was reasonably described by Freundlich isotherm. According to the theory, the model is valid for heterogeneous surfaces and predicts an increase in adsorbate concentration on the solid surface when the concentration of adsorbing entities in the liquid phase is increased. Therefore, adsorption of thiophene and its derivatives on pyrolyzed rice husks takes place on a heterogeneous surface, which may expose various adsorption sites having different affinity to thiophene, benzothiophene, and dibenzothiophene.

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# АДСОРБЦИЯ НА ТИОФЕН И НЕГОВИ АРОМАТНИ ПРОИЗВОДНИ ОТ МОДЕЛНО ГОРИВО ВЪРХУ ПИРОЛИЗИРАНИ ОРИЗОВИ ЛЮСПИ: КИНЕТИКА И РАВНОВЕСИЕ

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(Резюме)

Изследвано е адсорбционното десулфуриране на горива чрез използване на моделно гориво, съдържащо смес от тиофен, бензотиофен и дибензотиофен при изходно общо съдържание на сяра ($\mathrm{S_{in}}$) 415, 218 и 111 wppm с пиролизирани оризови люспи (ПОЛ) в статични условия. Общото съдържание на сяра в разтвора беше определено чрез рентгенов-флуоресцентен анализ. Кинетиката на процеса бе определена чрез използване на уравнение от втори порядък, дифузионен модел и уравнението на Елович. Установено е, че кинетичният модел от втори порядък описва адекватно адсорбцията на трите серни съединения върху пиролизирани оризови люспи. Това уравнение осигурява и най-добро съвпадение между пресметнатите и експериментално определени стойности на адсорбционния капацитет. Разликата между тях варира от 1.3% при $S_{in}$ 111 ppm до 5.9% за $S_{in}$ 415 ppm. Адсорбционният афинитет на трите серни съединения, както и равновесният адсорбционен капацитет на пиролизирани оризови люспи, бяха определени чрез снемане на адсорбционна изотерма. Опитните данни бяха анализирани чрез използване на изотермите на Лангмюр, Фройндлих и Тьомкин. Данни от регресионния анализ показаха, че изотермата на Фройндлих най-адекватно описва адсорбционното равновесие на полиароматните серни хетеро-циклични съединения в системата гориво/ПОЛ.