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KINETIC, EQUILIBRIUM AND STATISTICAL ANALYSIS OF DIESEL FUEL ADSORPTIVE DESULFURIZATION

Abstract

Desulfurization of hydrocarbon fuels has lately become one of the most important processes in petroleum refining. Increasingly stringent environmental protection regulations mean that motor fuel producers must improve their existing technology and to start considering alternative ways of removing sulfur from fuels. It is very difficult for currently available technology to treat diesel fuel and achieve sulfur content of less than 10 mg kg^{-1}. The compounds that remain in fractions with 500 mg kg^{-1} sulfur, depending on the origin of the feed, are usually in the form of refractory compounds which are mainly alkyl-dibenzotiophenes with one or two alkyl groups on 4- and/or 6-positions. These compounds severely inhibit conventional hydrodesulfurization processes. Adsorption is a process that can be applied for diesel fuel desulfurization. The idea is to selectively separate less than 1 wt.% of fuel mass by selective adsorption for removing sulfur, and leave the 99 wt.% of non-sulfur-containing fuel mass untouched. Adsorptive desulfurization was carried out in laboratory apparatus designed for batch adsorption applying activated carbon and aluminium oxide. Kinetic and equilibrium analysis of the adsorption process was done. The results of these experiments showed that activated carbon had significantly better performance regarding the lowering of sulfur content and adsorption capacity. Statistical analysis of the data obtained from the experiments, carried out according to 2^3 factorial design, was used to determine the influence of time, initial sulfur concentration, activated carbon mass and their interactional effects on sulfur content and adsorption capacity.

1. Introduction

Sulfur, as well as sulfur compounds, from crude oil and oil fractions represent a problem within the petroleum refining and related industries ever since the very beginning of crude oil refining, and with sulfur being removed the quality of a product is improved which notably attributes to the economy of oil refining. In 2005 in the European Union the sulfur content in both fuels was limited to 50 mg kg^{-1}, and for

the year 2009 the reduction to 10 mg kg^{-1} of sulfur was prescribed. Alternative processes of desulfurization of motor fuels are becoming more and more important since many countries are introducing increasingly stringent environmental protection regulations. One of these promising new processes, which has been intensively studied, is adsorptive desulfurization. Adsorption has been described as a process of selective collecting and concentrating of certain molecules from gas or fluid on a solid surface of a substance which possesses adsorption properties. The principle of a new access to the process of removing sulfur is selective separation of less than 1% m/m of inlet quantity of fuel by selective absorption, and then the rest, which is 99% m/m of non-sulfur-containing fuel, is to be enabled to easily pass the system. Here we face a great challenge of finding the right adsorbent which will selectively adsorb sulfur compounds. [1,2]

Design of experiments (DOE) is a statistical method used to explain a particular process in a better way, to model the process, to improve the efficiency of the process and the quality of a product. DOE provides getting the data on the interaction among the factors and the way the whole system works, and these data could not be gained with experimenting by value varying of only one factor while the other factors are kept on constant values.[3-5]

This paper describes a method of adsorptive desulfurization of diesel fuel by using activated carbon and activated aluminium oxide as the adsorbent. The testing of the effects of adsorption process parameters on the efficiency of reducing sulfur content in diesel fuel and adsorption capacity has been carried out. The experiments were conducted based on 2^3 factorial design with 5 central points.

2. Experimental part

2.1 Process

Adsorption desulfurization of diesel fuel has been conducted by LAM A1 batch adsorption apparatus, as it is shown in the Figure 1.

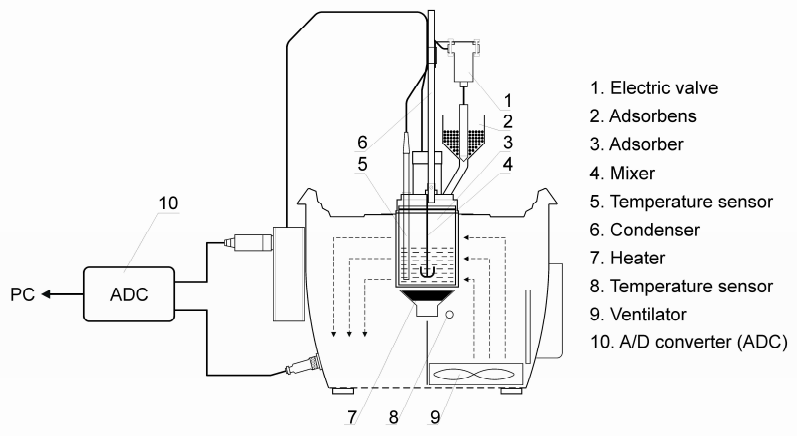

Figure 1: Adsorption apparatus LAM A1

The process has been carried out at 50 ℃ and atmosp heric pressure in the so called adsorbers. They are stainless steel tanks with volume of 250 ml.

The apparatus was controlled via computer (PC). The total amount of adsorbents needed for the experiments was being dried at 110 °C for 4 hours after which it was stored in a desiccator. The adsorbent particles were separated from the treated diesel fuel by filtrating in the filter paper Filtrak no. 391 via a Büchner funnel and a vacuum pump. The total sulfur content in the samples of diesel fuel is determined by wave dispersive x-ray fluorescence spectrometer (HRN EN ISO 20884).

2.2. Materials

The paper has tested two adsorbents: activated carbon (AC) and activated aluminium oxide (AO). Activated carbon showed the following properties: particle size 0.4-0.8 mm, bulk density 0.48 g cm^{-3}, specific surface 936 m^2 g^{-1} and pore volume 0.53 cm^3 g^{-1}. Activated aluminum oxide showed these properties: particle size 2,7 mm, bulk density 0,041 g cm^{-3} and specific surface 475 m^2 g^{-1}. The used raw material was diesel fuel taken after the hydrosulfurization and produced by INA-Oil Industry.

2.3 Kinetic analysis

In order to get better understanding of kinetics of adsorptive desulfurization, experimentally gained results were compared to the data gained from the regression analysis via empiric kinetic models. In the paper the kinetic modeling of the process of batch adsorption organic sulfur compounds from diesel fuel via Lagergren and Ho models was conducted. The following expressions show these models in integrated forms[6]:

$$\ln(q_e - q) = \ln(q_e) - k_1 t \quad (1)$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

The models are used with the premise that the adsorption of organic sulfur compounds from diesel fuel due to its low concentration can be observed as the adsorption of one component represented by sulfur content in fuel. The fact that also attributes to this is that these adsorbents are highly selective towards sulfur. A certain number of authors have successfully used this premise in similar studies.[7,8]

2.4 Balance analysis

Balance analysis of adsorptive desulfurization of diesel fuel is carried out by using Langmuir and Freundlich model. The following expression shows the linear form of Langmuir balance model:

$$\frac{C_e}{q} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)$$

Freundlich model which supposes the heterogeneous adsorption within differences of activated places has a linear form as follows[9,10]:

$$\ln q = \ln k_F + \frac{1}{n} \ln C_e \quad (4)$$

2.5. Statistical analysis

The modeling of adsorptive desulfurization was carried out by using 2^3 factorial design. Three process factors were simultaneously varied in the experiment: time (t, min), initial sulfur concentration (C_0, mg kg^{-1}) and mass of activated carbon (m_{AC}, g); the values are shown in the Table 1. Based on 2^3 factorial design during which the process factors are varied on the two levels (+1 i –1) 5 central points were added (0), which means that the experiments were conducted with the process factors whose values were arithmetic mean of upper and lower level (Table 2). In this way the influence of each factor was tested and their interaction within the process. The experiment design and statistic analysis were carried out via programme package Design-Expert© produced by Stat-Ease company.

Table 1: Levels of the factor values in the process

Inlet value	Level		
	–1	**0**	**+1**
x_1: t, min	20	60	100
x_2: C_0, mg kg-1	16,0	27,2	38,4
x_3: m_{C3}, g	2	3	4

Table 2: 2^3 factorial design of the experiment with 5 central points and the results

Std. No.	Ordinal number	x_1	x_2	x_3	C_p, mg kg^{-1}	q_p, mg g^{-1}
3	1	–1	+1	–1	27.7	0,2194
10	2	0	0	0	14.8	0,1695
12	3	0	0	0	15.2	0,1640
6	4	+1	–1	+1	7.6	0,0861
9	5	0	0	0	15.2	0,1640
7	6	–1	+1	+1	20.1	0,1876
11	7	0	0	0	15.4	0,1613
4	8	+1	+1	–1	25	0,2747
13	9	0	0	0	15.2	0,1640
8	10	+1	+1	+1	18.3	0,2060
2	11	+1	–1	–1	10.5	0,1128
1	12	–1	–1	–1	12.3	0,0759

5	13	–1	–1	+1	9.7	0,0646

3. Results and discussion

3.1 Kinetic analysis

The aim of the experiment was to compare the efficiency of removing sulfur from diesel fuel in the adsorption process with adsorbents: activated carbon and activated aluminum oxide.

The results show that adsorption efficiency of activated carbon is greater than that with activated aluminium oxide, as shown on Figure 2.

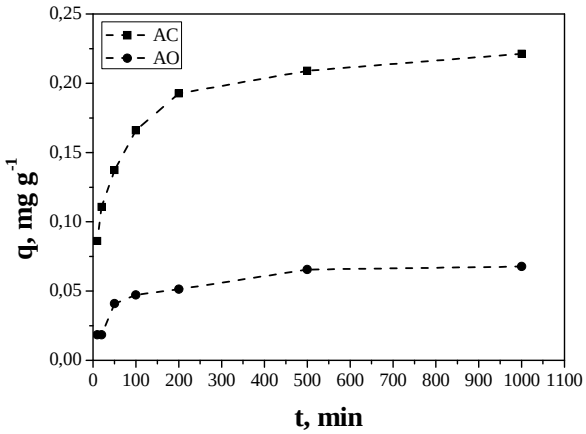

Figure 2: Dependence of adsorption capacity on time for tested adsorbents (T = 50 ℃, n_m = 300 min^{-1}, m = 2,00 g)

The data on dependence of adsorption capacity with time have been used for the kinetic analysis. The Figures 3 and 4 show the results of the analysis according to the empiric kinetic Lagergren and Ho model.

It is evident that the experimental data coincide better with the data gained via Ho model as opposed to the values gained via Lagergren model. The estimation via Lagergren model was conducted in a way that the left side of the expression (1) as balance adsorption capacity, q_e, of the used adsorbents included the values measured after 1000 min (AC: 0.2214 mg g^{-1}, AO: 0.0677 mg g^{-1}), when it was assumed that the balance of the system was reached. The values of the balance adsorption capacity calculated via Lagergren model (AC: 0.1074 mg g^{-1}, AO: 0.0469

mg g^{-1}) significantly differ from the adsorption values measured after 1000 min which confirms the inadequacy of that model.

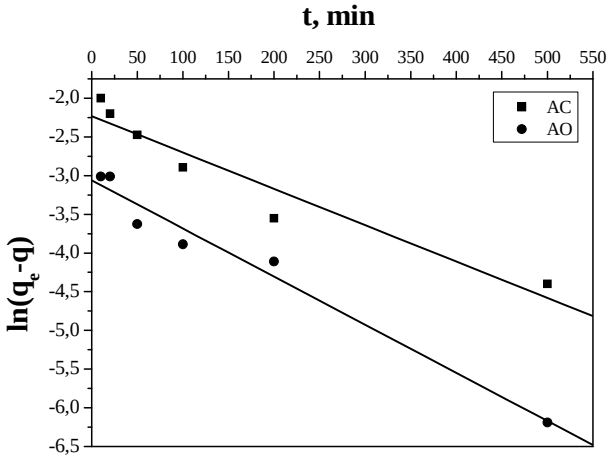

Figure 3: Lagergren model

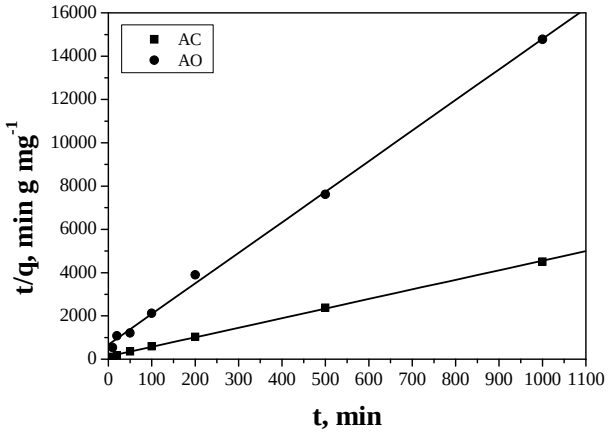

Figure 4: Ho model

Table 3. Coefficient of empirical kinetic models

Lagergren model			
Adsorbent	**k_1, min^{-1}**	**q_e, mg g^{-1}**	**R^2**
AC	0,00470	0,1074	0,9258
AO	0,00622	0,0469	0,9730
Ho model			
Adsorbent	**k_2, g mg^{-1} min^{-1}**	**q_e, mg g^{-1}**	**R^2**

AC	0,1532	0,2261	0,9994
AO	0,2964	0,0708	0,9981

The excellence of Ho model for describing the kinetics of adsorptive desulfurization of diesel fuel was confirmed by closeness of the estimated values of balance adsorption capacity (AC: 0.2261 mg g^{-1}, AO: 0.0708 mg g^{-1}) to the estimated capacity values after 1000 min where the values of correlation coefficients reach values almost equal to 1, (AC: 0.9994, AO: 0.9981), while the corresponding R^2 values of Lagergren model are smaller (AC: 0.9258, AO: 0.9730) which, once again, proves that this model is not adequate for describing this process.

3.2 Balance analysis

Balance analysis has been carried out based on the data of the dependence of adsorption capacity to initial sulfur concentration which is shown in the graph by using the adsorption isotherms for tested adsorbents (Figure 5). These isotherms show that the research of balance characterization gave the best results when activated carbon was used as the adsorbent.

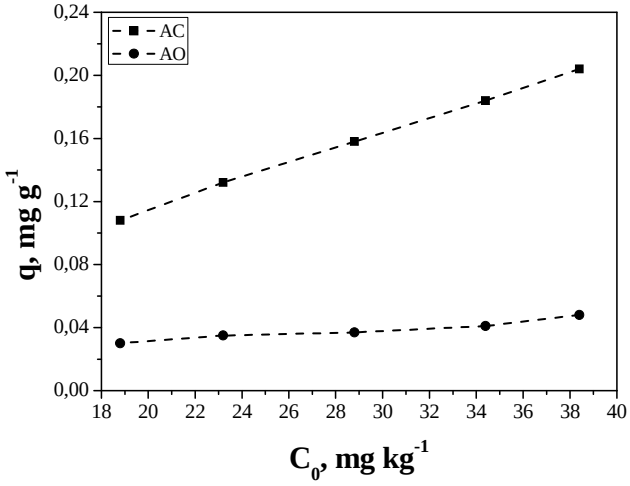

Figure 5: Adsorption isotherms for tested adsorbents

Figures 6 and 7 show the comparison of the data based on Langmuir and Freundlich models and the experimental values. It is evident that the experimental points are closer to the line or they are lying on it. The line represents Freundlich model which shows that this model is more suitable for describing the process of adsorption desulfurization and that here we deal with physical adsorption. The Table 4 show the constants of Langmuir and Freundlich models and the correlation coefficients, in fact R^2 values, which are larger with Freundlich model than with Langmuir model which confirms the fact that Freundlich model is more adequate. The values of the Freundlich constant *n* which is larger than 1 also confirms adequacy of this model

for describing the process of adsorptive desulfurization of diesel fuel and that the adsorption is of the physical nature.

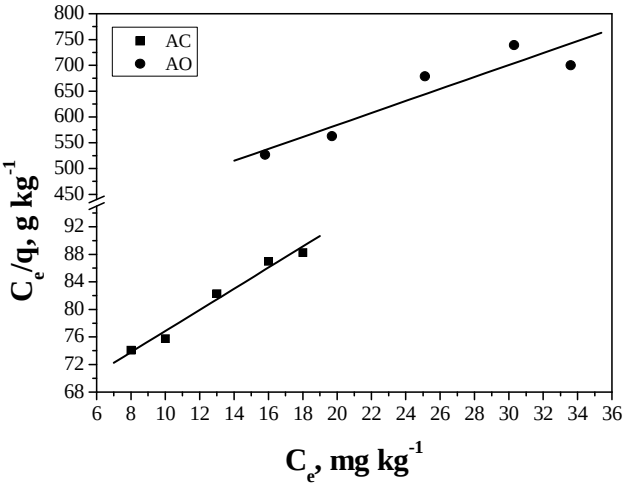

Figure 6: Langmuir model

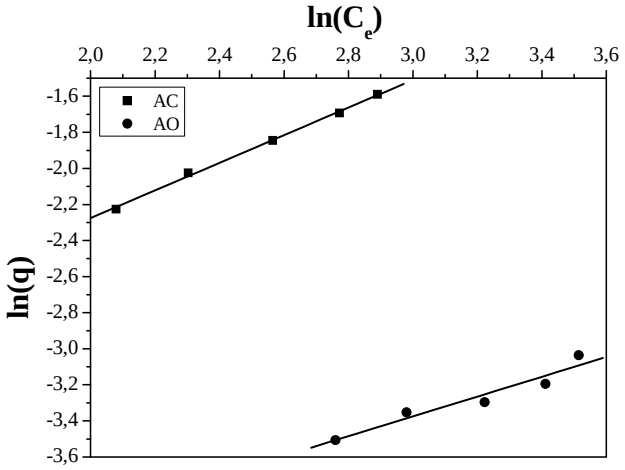

Figure 7: Freundlich model

Table 4: Constants of Langmuir and Freundlich models and correlation coefficients

Adsorbent	**Langmuir model**		
	k_L, kg mg^{-1}	**Q_m, mg g^{-1}**	**R^2**
AC	0,0250	0,6513	0,9783
AO	0,0330	0,0860	0,8624
	Freundlich model		
	k_F	**n**	**R^2**
AC	0,0222	1,3064	0,9978
AO	0,0066	1,8237	0,9336

3.3 Statistical analysis

The aim of the statistical analysis was to define the effect of the observed parameters and their interactions on the efficiency of removing sulfur from diesel fuel by using the process of adsorption. Since the previously mentioned balance and kinetic analysis proved that activated carbon is more efficient adsorption agent, the design of experiments with activated carbon was conducted. Design of experiments and the gained results are shown in the Table 2. The minimum value of residual sulfur in diesel fuel after the process of adsorption was 7.6 mg kg^{-1}, along with the value of the adsorption capacity of 0.0861 mg g^{-1}. The statistical analysis estimated the effects of certain parameters on the observed responses, which is shown in the Table 5.

Table 5: The estimated effects of factors and their interactions on measured value

Factor / interaction	**Total sulfur content**		**Adsorption capacity**	
	Effect, -	**Contribution to total effect, %**	**Effect, -**	**Contribution to total effect, %**
x_1	-2.10	2.22	0,0331	5,02
x_2	12.75	81.73	0,1371	86,40
x_3	-4.95	12.32	-0,0346	5,50
x_1x_2	-0.15	0.01	0,0038	0,07
x_1x_3	0.15	0.01	-0,0131	0,79
x_2x_3	-2.20	2.43	-0,0156	1,12
$x_1x_2x_3$	0.30	0.05	-0,0054	0,13

Based on these results (Table 5) we can determine the basic influences on sulfur content: time, x_1, initial sulfur concentration, x_2, mass of activated carbon, x_3 and the interactional effects of initial sulfur concentration and mass of activated carbon, x_2x_3.

Also, the basic influences of the factors on the adsorption capacity are: time, x_1, initial sulfur concentration, x_2, mass of activated carbon, x_3 and interaction between initial sulfur concentration and mass of activated carbon, x_2x_3 and interaction between time and mass of activated carbon, x_1x_3. Initial sulfur concentration showed

the greatest effect with the contribution of 81,73 % on sulfur content after the process of adsorption and with the contribution of 86,40 % on adsorption capacity.

4. Conclusion

The efficiency of removing sulfur from diesel fuel was tested using the process of adsorption. The adsorption was conducted on activated carbon and activated aluminium oxide. Activated carbon proved to be more efficient during the adsorption of sulfur compounds from diesel fuel when compared to aluminum oxide. The kinetic research, in the cases of both used adsorbents, established that experimental and calculated data coincide better when Ho model is being used. The balance characterization for both used adsorbents showed that the process of adsorption desulfurization is better described by Freundlich model and that here we have a case of physical adsorption. During kinetic and balance research better results are gained for the use of activated carbon. The test results on the efficiency of adsorptive desulfurization with activated carbon, conducted via factorial design with three factors on two levels and 5 central points, were statistically analyzed and therefore a significant influence of particular factors was determined within the process: time, mass of activated carbon and initial sulfur concentration as well as the interaction between initial sulfur concentration and mass of activated carbon and the interaction between the time and mass of activated carbon considering the sulfur content in diesel fuel and adsorption capacity.

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Nomenclature

C_e – balance sulfur content in diesel fuel, mg kg^{-1}
C_0 – initial sulfur concentration, mg kg^{-1}
k_F – Freundlich constant related to adsorption capacity,
k_L – Langmuir constant, g mg^{-1}
k_1 – adsorption rate constant of Lagergren model, min^{-1}
k_2 – adsorption rate constant of Ho model mg^{-1} min^{-1}
m – mass of adsorbent, g
m_{AC} – mass of activated carbon, g
n – Freundlich constant related to adsorption intensity
n_m – rpm of mixer, min^{-1}
Q_e – theoretical capacity of monomolecular layer, mg g^{-1}
q – quantity of adsorbed sulfur on adsorbent surface, mg g^{-1}
q_e – balance adsorption capacity, mg g^{-1}
T – temperature, K
t – time, min
x_1 – code expression for process duration time, -
x_2 – code expression for initial sulfur concentration, -
x_3 – code expression for mass of activated carbon, -

UDK	ključne riječi	key words
665.753.4	dizelsko gorivo	diesel fuel
665.662.2	rafinacija adsorpcijom	rafination by adsorbtion
665.666.4	uklanjanje sumpornih tvari, desulfurizacija	removal of sulfur containing substances
661.183.2	aktivni ugljen	activated carbon
661.183.8	aktivni aluminij oksid	activated alumina
541.123	kemijska ravnoteža u heterogenom sustavu	chemical equilibrium of heterogenous system
519.2	matematički statistički model procesa	process mathematical statistic model

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