A Design of Experiments Investigation of Adsorptive Desulfurization of Diesel Fuel

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Adsorptive desulfurization of diesel fuel was investigated applying two Design of Experiments (DOE) methods. The experiments were carried out in a batch adsorption system using Chemviron Carbon SOLCARB^{TM} C3 activated carbon as adsorbent. The first DOE method employed was a full factorial with three factors on two levels and five center points, and the second was Box-Behneken design with the same three factors but on three levels. The effects of individual factors and their interactions on sulfur concentration and sorption capacity were determined, and statistical models of the process developed. The first-order models predict the behavior of the system rather well but significant curvature was detected. Subsequently developed second-order models were able to give reasonably well descriptions of the system. The lowest achieved output sulfur concentration was 7.6 mg kg^{-1} with relatively low sorption capacity of 0.0861 mg g^{-1}.

Key words:
Design of Experiments, desulfurization, adsorption, diesel fuel, activated carbon

Introduction

Transport is an essential human activity and it has played an important role in the development of many societies. However, the environmental costs of this energy-intensive sector are also critical: e.g., it produces 20 % of all anthropogenic greenhouse gas emissions. While all modes of transport have an environmental impact, the major impact is from road transport.[1] That is why governments all over the world are implementing emission regulations limiting the production of carbon monoxide, hydrocarbons, NO_x, SO_x, and particulates from motor vehicles. In order to reduce the SO_x emissions as well as the whole spectrum of negative effects that sulfuric compounds have, legislation is being enforced limiting the concentration of sulfur in motor fuels. According to European Directive 2003/17/EC, the maximum allowed sulfur concentration in diesel and petrol fuels since January 2009 is 10 mg kg^{-1}, respectively. The introduction of fuels with a maximum sulfur concentration of 10 mg kg^{-1} will improve the fuel efficiency attainable with new, emerging vehicle technologies, and should be examined in the case of non-road mobile machinery and should lead to significant reductions in emissions of conventional air pollutants when used in existing vehicles.[2]

In our previous work,[3] the benefits of adsorptive desulfurization and the problems of conventional hydrodesulfurization processes it solves were described. This paper represents the continuation of the research into the removal of sulfur from diesel fuel by adsorbing organic sulfuric compounds on Chemviron Carbon SOLCARB^{TM} C3 activated carbon, which has been proven as an excellent adsorbent for such a task. The emphasis this time is on statistical analysis of data attained from carefully designed and executed experiments.

Design of Experiments (DOE) refers to the process of planning, designing and analyzing the experiment so that valid and objective conclusions can be drawn effectively and efficiently.

DOE can be described as a series of tests, in which purposeful changes are made to input factors, so that causes of significant changes in the output responses could be identified. It includes procedures of planning, designing and analyzing the experiment.[4] DOE is a powerful statistical tool for exploring new processes or gaining detailed understanding of existing ones, and then optimizing those processes. Basically, DOE is the use of particular patterns of experiments to generate a lot of information about a process while still using an absolute minimum of actual experiments to obtain the information. It has been widely accepted in the manufacturing industry for improving product performance and reliability, process capability and yield. Application of DOE for science is based on the fact that scientific research is mainly empirical and makes extensive use of experimentation.[5–7]

DOE eliminates the 'confounding of effects' whereby the effects of design variables are mixed up. Confounding of effects means we cannot correlate product changes with product characteristics.

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DOE helps us handle experimental error. Any data point may contain bad data, i.e. it is accurate within a certain range, it includes experimental error and is susceptible to the effects of variation in raw materials, test instruments, machine operators etc. DOE enables determination of the important variables that need to be controlled as well as the unimportant ones that may not need to be controlled. Also, it enables the measurement and quantification of interactions, which is very important, because this is not achievable by the one-factor-at-a-time (OFAT) experimentation methodology.[8]

Depending on the point of view, model equations describing chemical or physical processes, such as the adsorption process, attained by statistical analysis of experimental data applying DOE methodology, in relation to classical adsorption models, such as Langmuir or Freundlich models, have the advantage of not being burdened by the actual nature of the process and all the mechanisms involved. The statistical models are concerned only with the direct relations between the response variable(s), and the input factors and their interactions, and no theoretical assumptions are needed.

For example, the Langmuir model assumes that the surface of the adsorbent is homogeneous, the adsorption energy is constant over all sites, and the adsorption on the surface is localized, as well as that each site can accommodate only one molecule or atom.[9]

Of course, the fact that statistical models do not take into account the process itself, and mainly account for the consequences, can be interpreted as a flaw, along with the fact that they can only be used for predicting the behavior of the investigated system. However, statistical DOE methods can largely increase the efficiency of the experimental work and often strengthen previously obtained conclusions, as well as lead to new discoveries.

Numerous DOE designs and methods exist and are used for scientific research, of which we applied a factorial design and response surface methodology (RSM). There are many published reports describing the use of these DOE methods for investigating various adsorption processes and our previous work is part of that group as well.[3,10–13]

Materials and methods

Adsorbent and diesel fuel

The adsorbent used was Chemviron Carbon SOLCARB™ C3 activated carbon whose initial characteristics were: particle diameter, d_p, 1.0–2.0 mm, bulk density, ρ, 0.48 g cm^{-3}, specific surface area, a, 936 m^2 g^{-1}, pore volume, 0.53 cm^3 g^{-1}. Activated carbon was ground and sieved to the particle diameter between 0.40–0.80 mm. This particle diameter was chosen because of the problems in handling smaller particles although, reportedly,[3] better results were achieved with particle dimeters of less than 0.20 mm, and because the influence of particle diameter in this range is relatively small and satisfactory effectiveness can be achieved with average particle diameters of around 0.60 mm. One more reason for this choice was the possible future use of the obtained experimental data in column experiments for which particle diameter between 0.40–0.80 mm are ideally suited for use in available column design. The diesel fuel used in this work was blended from several hydrodesulfurized gas oils, collected at different times from the Rijeka Refinery, INA-Industrija nafte d.d., Croatia, with the aim to achieve the same basic physical and chemical properties (Table 1) including initial total sulfur concentration, as the diesel fuel used in our previous work.[3]

Table 1 – *Physical and chemical properties of diesel fuel*

Property		Value
cetane number		51.0
cetane index		46.0
density at 15 °C/kg m^{-3}		820.0
polycyclic aromatic hydrocarbons, w/%		2.1
total sulfur concentration/mg kg^{-1}		27.0
ignition point/°C		> 55
kinematic viscosity at 40 °C/mm^2 s^{-1}		3.98
distillation:	distilled until 250 °C, φ/%	< 40
	distilled until 300 °C, φ/%	75
	end of distillation/°C	342

Adsorption experiments

Adsorptive desulfurization experiments were carried out using semiautomatic laboratory apparatus LAM A1 (Fig. 1) developed for batch adsorption. The process was conducted at 50 °C under ambient pressure in stainless steel adsorbers. Total capacity of adsorbers was 250 cm^3 and volume of diesel fuel, V_D, was 50 cm^3. The LAM A1 apparatus was controlled via personal computer (PC).

Activated carbon samples were dried for 4 h at 110 °C, after which they were transferred to the desiccator for storage. Removal of activated carbon particles from the treated diesel fuel was carried out by filtration through Filtrak filter paper no. 391 using Buchner funnel and vacuum pump. Total sulfur concentration was measured using wave dispersive

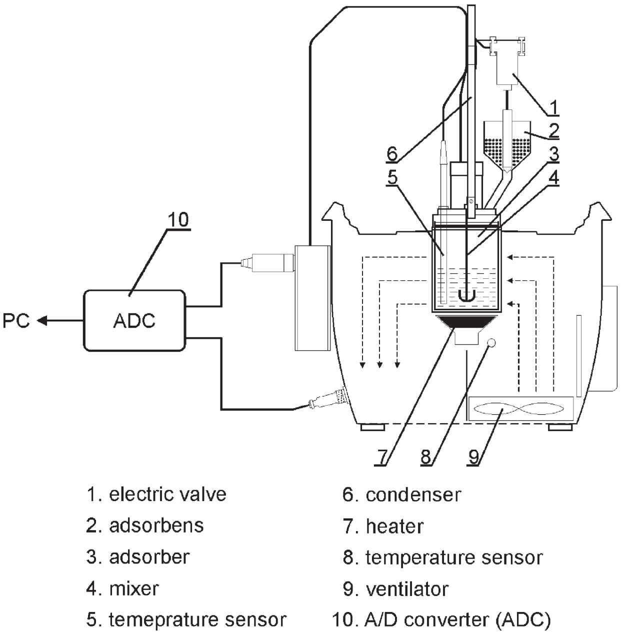

Fig. 1 – *LAM A1 batch adsorption apparatus*

X-ray fluorescent spectrometer according to the ISO 20884 standard method.

The value of adsorption capacity, q, was calculated using the following equation:

$$q = \frac{\rho_D V_D (C_0 - C_{i,exp})}{m_{C3}} \tag{1}$$

where ρ_D is diesel fuel density, and V_D is the diesel fuel sample volume.

Factorial experimental design

Many experiments involve the study of the effects of two or more factors. In general, factorial designs are most efficient for this type of experiment. Factorial experimental design can be described as a sequence of trials or runs where in each experiment all the possible factor level combinations are investigated.[7] In this part of the study we employed a 2^3 full factorial experimental design with 5 replicates at the center point. The experimental design was comprised of 13 experiments in total. Time, initial sulfur concentration and adsorbent mass were chosen as independent variables, so-called factors, and the output sulfur concentration and sorption capacity were dependent response variables. The dependence of the output sulfur concentration and sorption capacity on time was tested in order to clarify previously acquired data[3] where the one-factor-at-a-time experiments showed moderate effect and the results of statistical analysis indicated rather small effect.

The initial sulfur concentration and adsorbent mass were set as factors in order to further investigate and verify their seemingly largest effects on the said responses. The center point replicates were chosen to verify any change in the estimation procedure, as a measure of precision property and to see whether any significant curvature in the design space exists. The levels of the parameters with their actual and coded values are presented in Table 2.

Table 2 – *Actual and coded values of factors*

Factor	Value	Level		
		lower	center	higher
time/min	actual(t)	20	60	100
	coded(X_1)	–1	0	+1
initial sulfur concentration/mg kg^{-1}	actual(C_0)	16.0	27.2	38.4
	coded(X_2)	–1	0	+1
adsorbent mass/g	actual(m_{C3})	2.00	3.00	4.00
	coded(X_3)	–1	0	+1

Development of the 2^3 full factorial experimental design with 5 replicates at the center point was carried out using Design-Expert©, a DOE software from Stat-Ease, Inc., and is presented in Table 3.

Table 3 – *2^3 full factorial experimental design with 5 replicates at the center point*

Std. No.	Run No.	X_1: t/min	X_2: C_0/mg kg^{-1}	X_3: m_{C3}/g	$C_{i,exp}$/mg kg^{-1}	$q_{i,exp}$/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	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

Response surface methodology

Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes.

Most applications of RSM are sequential in nature. That is, at first some ideas are generated concerning which factors or variables are likely to be important in the response surface study.[14] For this purpose, we used the results of our previous study[3] and the results of the first part of this work. There are many reasons for using RSM for research and the most important is the need to conduct experiments efficiently by a proper choice of design, in order to determine operating conditions according to the optimal response based on a set of controllable variables.[15]

Box-Behnken designs (BBD) are a family of efficient three-level designs for fitting second-order response surfaces. This class of design is based on the construction of balanced incomplete block designs. An example of a balanced incomplete block design with three treatments and three blocks is given in Table 4.

Table 4 – *Balanced incomplete block design with three treatments and three blocks*

Block	Treatment		
	1	2	3
1	X	X	
2	X		X
3		X	X

The pairing together of treatments 1 and 2 symbolically implies, in the response surface setting, that variables X_1 and X_2 are paired together in a 2^2 factorial (scaling ± 1) while X_3 remains fixed at the center ($X_3 = 0$). The same applies for blocks 2 and 3, with a 2^2 factorial being represented by each pair of treatments, while the third factor remains fixed at 0.[14]

The developed $k = 3$ Box-Behnken design with 5 center points, that we applied, consists of 17 runs as presented in Table 5. As in factorial experiments, time, initial sulfur concentration and adsorbent mass were chosen as independent variables, while output sulfur concentration and sorption capacity were chosen as dependent response variables.

The BBD is ideally suited for scientific studies that require RSM and three evenly spaced levels. Thus, the BBD is an efficient option and indeed an important alternative to the central composite design (CCD). Another important characteristic of the BBD is that it is a spherical design.

Table 5 – *Three-factor BBD with 5 center points*

Std. No.	Run No.	X_1: t/min	X_2: C_0/mg kg^{-1}	X_3: m_{C3}/g	$C_{i,exp}$/mg kg^{-1}	$q_{i,exp}$/mg g^{-1}
11	1	0	–1	1	8.4	0.0779
12	2	0	1	1	21.8	0.1702
5	3	–1	0	–1	19.6	0.1558
4	4	1	1	0	24.1	0.1954
14	5	0	0	0	14.8	0.1695
1	6	–1	–1	0	10.9	0.0697
10	7	0	1	–1	29.3	0.1866
6	8	1	0	–1	18.0	0.1886
15	9	0	0	0	15.2	0.1640
3	10	–1	1	0	27.1	0.1544
8	11	1	0	1	13.0	0.1456
9	12	0	–1	–1	9.4	0.1353
16	13	0	0	0	15.2	0.1640
13	14	0	0	0	15.4	0.1613
17	15	0	0	0	15.2	0.1640
2	16	1	–1	0	9.0	0.0957
7	17	–1	0	1	15.8	0.1169

In our example for the $k = 3$ case, all of the points are so-called "edge points" (i.e. points that are on the edges of the cube) and are at a distance $\sqrt{2}$ from the design center. There are no factorial points or face points. Fig. 2 displays the BBD for $k = 3$. The BBD involves all edge points but the entire cube is not covered. In fact, there are no points on the corner of the cube or even a distance $\sqrt{3}$ from the design center. This is because the BBD was not meant to be a cuboidal and its use is best suited for situations in which the aim is not to predict the responses at the extremes or at the corners of the cube, as was the case with this work.[14]

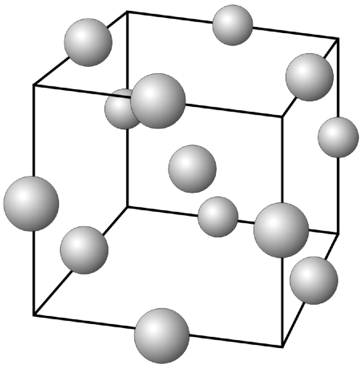

Fig. 2 – *Three factor BBD with a center point*

Results and discussion

Factorial design analysis

The first step in a factorial design analysis is the calculation of the average effects of process factors and their interactions on the response variables (Table 6). In a two-level factorial design, the average effect of a factor can be defined as the change in response produced by a change in the level of that factor averaged over the levels of other factors.

Table 6 – *List of effects*

Factor/ Interaction	Output sulfur concentration		Sorption capacity	
	effect/–	contribution/%	effect/–	contribution/%
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

For example, the average effect of time on output sulfur concentration was calculated using the following equation:

$$\text{Effect }(X_1) = \frac{2}{n2^k}(C(1,-1,-1) + C(1,1,-1) + C(1,-1,1) + C(1,1,1) - C(-1,-1,-1) - C(-1,1,-1) - C(-1,-1,1) - C(-1,1,-1)) \tag{2}$$

$$\text{Effect }(X_1) = \frac{2}{1\times 2^3}(10.5 + 25.0 + 7.6 + 18.3 - 12.3 - 27.7 - 9.7 - 20.1) = -2.10$$

where n is the number of runs for each experiment, i.e. for each combination of factor levels, and k is the number of factors.

The interaction effect of two factors, for example X_1 and X_2, can be defined as the average difference between the effect of factor X_1 at the high level of factor X_2 and the effect of X_1 at the low level of X_2.[7]

The values of the effects in Table 6 suggest that all the individual factors and interaction between initial sulfur concentration and adsorbent mass have a substantial influence on the output sulfur concentration. In the case of sorption capacity, the largest contribution to the overall effect have again individual factors, and the interaction between initial sulfur concentration and adsorbent mass with the addition of the interaction effect between time and initial sulfur concentration.

These effects were isolated as main effects and used as variables for multiple regression analysis of experimental data from Table 3.

Design-Expert© software was used to develop model eqs. (3a) and (3b), and eqs. (4a) and (4b) which describe the dependence of output sulfur concentration in treated diesel fuel (coded: Y_C, actual: $C_{i,cal}$ (mg kg^{-1})) and sorption capacity (coded: Y_q, actual: $q_{i,cal}$ (mg kg^{-1})) on the main effects.

$$Y_C = 16.40 - 1.05X_1 + 6.37X_2 - 2.48X_3 - 1.10X_2X_3 \tag{3a}$$

$$C_{i.cal} = 1.9036 - 0.0263t + 0.8638C_0 + 0.1964m_{C3} - 0.0982C_0m_{C3} \tag{3b}$$

$$Y_q = 0.15 + 0.017X_1 + 0.069X_2 - 0.017X_3 - 0.0065X_1X_3 - 0.0078X_2X_3 \tag{4a}$$

$$q_{i.cal} = -0.0723 + 0.0009t + 0.0082C_0 + 0.0115m_{C3} - 0.0002t\,m_{C3} - 0.0007C_0m_{C3} \tag{4b}$$

The validation of model eqs. (3a) and (3b), and eqs. (4a) and (4b) was performed by analysis of variance (ANOVA) and the results are presented in Table 7, where F-value is used for comparing model variance with residual (error) variance. If the variances are close to being equal, the ratio will be close to one and it is less likely that any of the factors will have a significant effect on the response. The F-value is calculated by model mean square divided by residual mean square.

P-value is defined as probability of seeing the observed F-value if the null hypothesis is true (there is no factor effect). Small probability values call for rejection of the null hypothesis. The probability equals the proportion of the area under the curve of the F-distribution that lies beyond the observed F-value. The F distribution itself is determined by the degrees of freedom associated with the variances being compared.[16] For both model equations, the F-values of 1487.23 and 418.39 imply the models are significant. P-values of less than 0.0500 indicate that coefficients of both model equations are significant.

The R^2 values for total sulfur concentration and sorption capacity model equations are 0.9988 and 0.9971, respectively.

This means that both model equations can account for more than 99 % of the variability. Moreover, the ability of the model equations to describe the real behavior of total sulfur concentration in diesel fuel and sorption capacity during adsorption

Table 7 – *ANOVA results for eqs. (3a) and (3b), and eqs. (4a) and (4b)*

Source	Sum of squares, –	Degrees of freedom, –	Mean square, –	F-value, –	P-value, –
Total sulfur concentration					
X_1	8.82	1	8.82	133.64	< 0.0001
X_2	325.12	1	325.12	4926.14	< 0.0001
X_3	49.01	1	49.01	742.50	< 0.0001
X_2X_3	9.68	1	9.68	146.67	< 0.0001
model	392.63	4	98.16	1487.23	< 0.0001
curvature	4.73	1	4.73	71.68	< 0.0001
total	397.82	12	—	–	–
residual	0.46	7	0.066	–	–
Sorption capacity					
X_1	$2.185 \cdot 10^{-3}$	1	$2.185 \cdot 10^{-3}$	106.32	< 0.0001
X_2	0.038	1	0.038	1828.78	< 0.0001
X_3	$2.393 \cdot 10^{-3}$	1	$2.393 \cdot 10^{-3}$	116.45	< 0.0001
X_1X_3	$3.416 \cdot 10^{-4}$	1	$3.416 \cdot 10^{-4}$	16.62	0.0065
X_2X_3	$4.887 \cdot 10^{-4}$	1	$4.887 \cdot 10^{-4}$	23.77	0.0028
model	0.043	5	$8.600 \cdot 10^{-3}$	418.39	< 0.0001
curvature	$3.847 \cdot 10^{-4}$	1	$3.847 \cdot 10^{-4}$	18.71	0.0050
total	0.044	12	–	–	–
residual	$1.233 \cdot 10^{-4}$	6	$2.055 \cdot 10^{-5}$	–	–

is tested by fitting the calculated against measured values (Figs. 3a and 3b). The straight line represents the ideal case when the calculated total sulfur concentration and sorption capacity are equal for the same values of 3 varied parameters. The points diverge very slightly from the line, which means that the calculated data fits very well with the experimental results. When testing for possible curvature in the system, the F-values of 71.68 and 18.71 were obtained. These F-values indicate the nonlinearity and the existance of significant curvature in the relationships between responses and process factors. Such results were the main indicators of the need to further study this system and to apply another method capable of uncovering the nature of this curvature. The three individual factors that were found to have the main effect on both responses were further investigated in the second part of this work by the response surface methodology.

BBD analysis

The statistical analysis of experimental data from Table 5 was performed by Design-Expert© software to determine the factor levels, while the second order polynomial model eqs. (5a) and (5b), and eqs. (6a) and (6b) were developed to describe the relations between the output sulfur concentration and sorption capacity and the three process parameters: time, initial sulfur concentration and adsorbent mass.

$$\begin{aligned} Y_C = 15.16 - 1.16X_1 + 8.08X_2 - \\ - 2.16X_3 + 1.00X_1^2 + 1.62X_2^2 + \\ + 0.44X_3^2 - 0.28X_1X_2 - 0.30X_1X_3 - 1.63X_2X_3 \end{aligned} \tag{5a}$$

$$\begin{aligned} C_{i.cal} = 5.38 - 0.06t + 0.49C_0 - 0.44m_{C3} + \\ + 6.22 \cdot 10^{-4}t^2 + 0.01C_0^2 + 0.45m_{C3}^2 - \\ - 6.14 \cdot 10^{-4}t\, C_0 - 7.50 \cdot 10^{-3}t\, m_{C3} - 0.15C_0m_{C3} \end{aligned} \tag{5b}$$

$$\begin{aligned} Y_q = 0.16 + 0.01X_1 + 0.041X_2 - 0.019X_3 - \\ - 0.013X_1^2 - 0.022X_2^2 + 4.142 \cdot 10^{-4}X_3^2 + \\ + 3.750 \cdot 10^{-3}X_1X_2 - 1.025 \cdot 10^{-3}X_1X_3 + 0.010X_2X_3 \end{aligned} \tag{6a}$$

$$\begin{aligned} q_{i.cal} = 0.0243 + 1.2451 \cdot 10^{-3}t + 0.0102C_0 - \\ - 0.0453m_{C3} - 8.2880 \cdot 10^{-6}t^2 - \\ - 1.7926 \cdot 10^{-4}C_0^2 + 4.1417 \cdot 10^{-4}m_{C3}^2 + \\ + 8.3705 \cdot 10^{-6}t\, C_0 - 2.5625 \cdot 10^{-5}t\, m_{C3} + \\ + 9.1518 \cdot 10^{-4}C_0m_{C3} \end{aligned} \tag{6b}$$

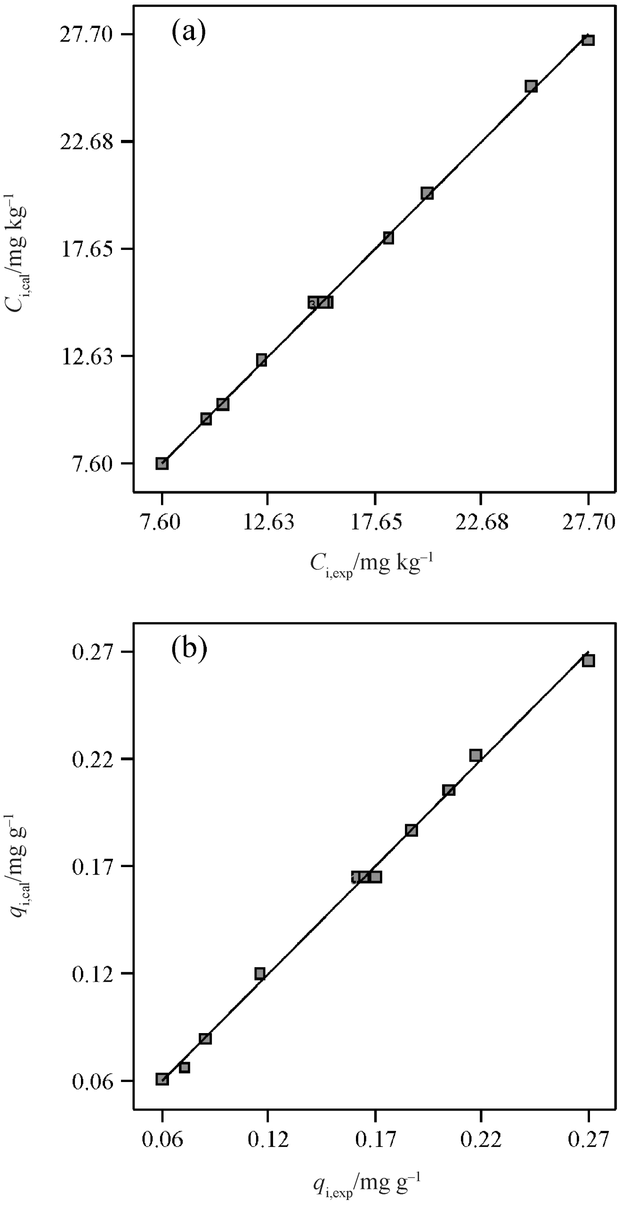

Fig. 3 – *Factorial design – calculated vs. measured values of (a) output sulfur concentration and (b) sorption capacity*

Table 8 – *ANOVA results for eqs. (5a) and (5b)*

Source	Sum of squares, –	Degree of freedom, –	Mean square, –	F-value, –	P-value, –
Total sulfur concentration					
X_1	10.81	1	10.81	103.03	< 0.0001
X_2	521.65	1	521.65	4971.43	< 0.0001
X_3	37.41	1	37.41	356.54	< 0.0001
X_1^2	4.17	1	4.17	39.73	0.0004
X_2^2	11.05	1	11.05	105.31	< 0.0001
X_3^2	0.83	1	0.83	7.95	0.0258
X_1X_2	0.30	1	0.30	2.88	0.1333
X_1X_3	0.36	1	0.36	3.43	0.1064
X_2X_3	10.56	1	10.56	100.66	< 0.0001
model	598.55	9	66.51	633.81	< 0.0001
total	599.28	16	–	–	–
residual	0.73	7	0.10	–	–

Table 9 – *ANOVA results for eqs. (6a) and (6b)*

Source	Sum of squares, –	Degree of freedom, –	Mean square, –	F-value, –	P-value, –
Sorption capacity					
X_1	$2.062 \cdot 10^{-3}$	1	$2.062 \cdot 10^{-3}$	56.00	0.0001
X_2	$1.300 \cdot 10^{-2}$	1	$1.300 \cdot 10^{-2}$	365.16	< 0.0001
X_3	$3.034 \cdot 10^{-3}$	1	$3.034 \cdot 10^{-3}$	82.41	< 0.0001
X_1^2	$7.404 \cdot 10^{-4}$	1	$7.404 \cdot 10^{-4}$	20.11	0.029
X_2^2	$2.129 \cdot 10^{-3}$	1	$2.129 \cdot 10^{-3}$	57.82	0.0001
X_3^2	$7.222 \cdot 10^{-7}$	1	$7.222 \cdot 10^{-7}$	0.02	0.8926
X_1X_2	$5.625 \cdot 10^{-5}$	1	$5.625 \cdot 10^{-5}$	1.53	0.2563
X_1X_3	$4.203 \cdot 10^{-6}$	1	$4.203 \cdot 10^{-6}$	0.11	0.7454
X_2X_3	$4.203 \cdot 10^{-4}$	1	$4.203 \cdot 10^{-4}$	11.41	0.0118
model	$2.200 \cdot 10^{-2}$	9	$2.449 \cdot 10^{-3}$	66.52	< 0.0001
total	$2.200 \cdot 10^{-2}$	16	–	–	–
residual	$2.577 \cdot 10^{-4}$	7	$3.682 \cdot 10^{-5}$	–	–

The validation of eqs. (5a) and (5b), and eqs. (6a) and (6b) was performed by ANOVA and the results are presented in Tables 8 and 9. The P-values of coefficients indicate that terms X_1X_2 and X_1X_3 for both responses are insignificant; for sorption capacity, the term X_3^2 is insignificant as well. The comparison of factorial design and BBD models reveals very good analogy regarding the significance of individual factors and their interactional effects. The only descrepancy that occurred for sorption capacity regarding the interactional effect between time and adsorbent mass, was when in the case of factorial design model it was determined to have a significant effect, while in the case of BBD model the term X_1X_3 was deemed insignificant. The reason why this term and others with less significance were included in the BBD equation was in order to satisfy the model hierarchy. Generally, it is hard to expect that the interaction between time and mass will have an effect on either sulfur concentration or sorption capacity; therefore, it is safe to say that a smaller value of this effect determined during the BBD analysis is closer to its actual significance.

The significance of both BBD model equations is confirmed by F-values of 633.81 and 66.52, respectively. The R^2 value of eqs. (5a) and (5b) is 0.9988 which is equal to the R^2 value of eqs. (3a) and (3b), while the R^2 value of eqs. (6a) and (6b) is 0.9884 which is only slightly less than the R^2 value of equations eqs. (4a) and (4b). All these R^2 values are very close to unity and it can be said that the developed empirical models can adequately account for almost all the variability in the system.

The validity of eqs. (5a) and (5b), and eqs. (6a) and (6b) can be further tested, as in the previous analysis, by fitting calculated against measured values of output sulfur concentration and sorption capacity (Figs. 4a and 4b). The points on Figs. 4a) and 4b) diverge very slightly from the straight line, which means that the calculated data fits very well with the experimental results.

These results confirm the validity of eqs. (5a) and (5b), and eqs. (6a) and (6b) and their adequacy for describing the behavior of the investigated system, i.e. the adsorptive desulfurization of diesel fuel.

The best way to visualize this is by graphical presentation of response surfaces and contour plots (Figs. 5a and 5b, Figs. 6a and 6b, Figs. 7a and 7b).

The graphs in Figs. 5a, 6a and 7a indicate that the magnitude of influence on output sulfur concentration is as follows $C_0 > m_{C3} > t$. The same cannot entirely be said for sorption capacity for which the order of influence is $C_0 > t > m_{C3}$. Also, it can be seen on Figs. 5a, 6a and 7a that output sulfur concentration dependence on t and m_{C3} is adversely

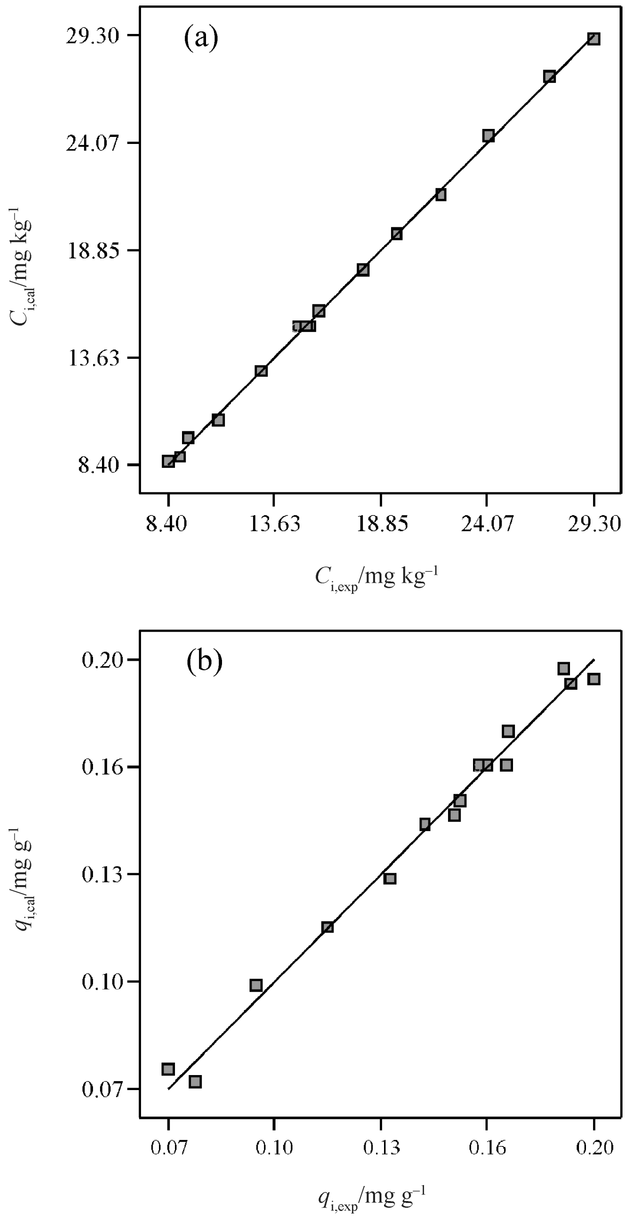

Fig. 4 – *BBD – calculated vs. measured values of (a) output sulfur concentration and (b) sorption capacity*

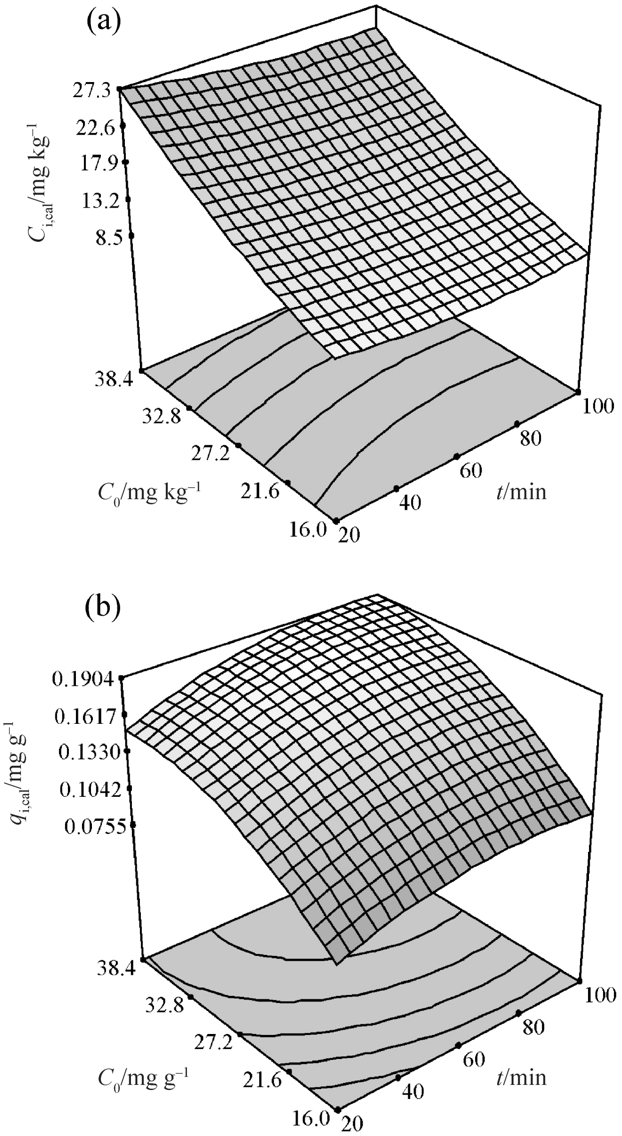

Fig. 5 – *Response surface and contour plots of (a) output sulfur concentration and (b) sorption capacity vs. time and initial sulfur concentration (m_{C3} = 3.00 g)*

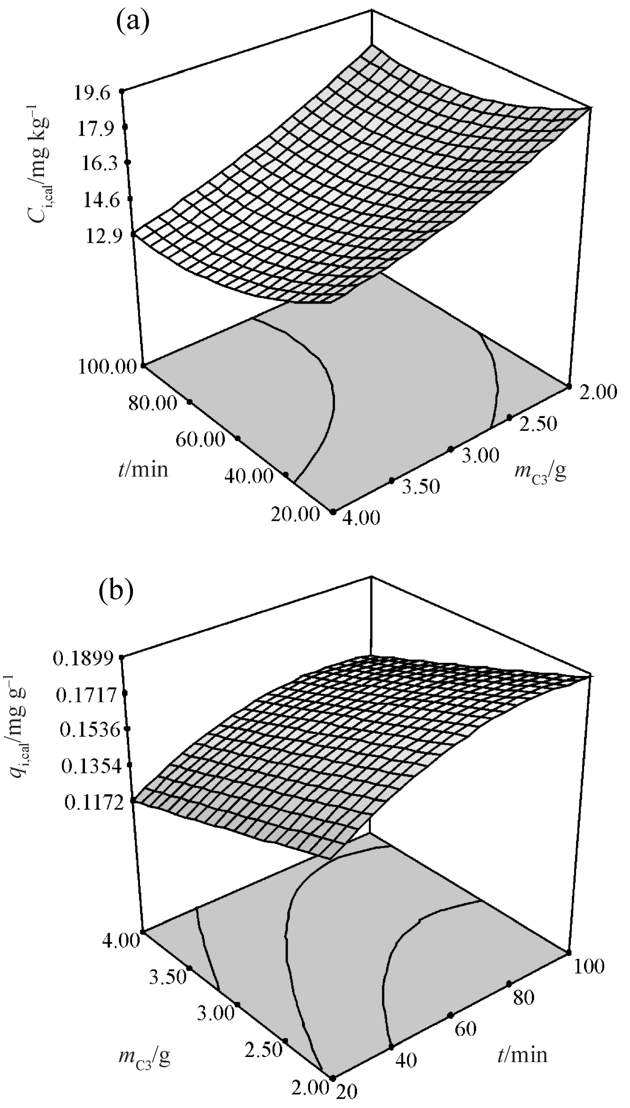

Fig. 6 – *Response surface and contour plots of (a) output sulfur concentration and (b) sorption capacity vs. time and adsorbent mass (C_0 = 27.2 mg kg^{-1})*

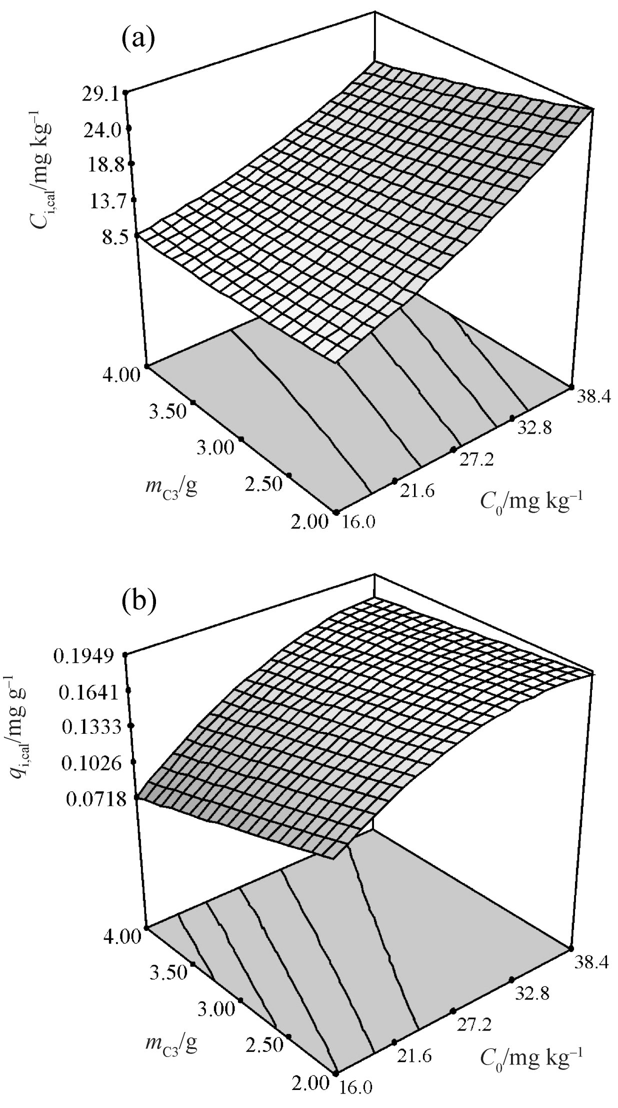

Fig. 7 – *Response surface and contour plots of (a) output sulfur concentration and (b) sorption capacity vs. initial sulfur concentration and adsorbent mass (t = 60 min)*

proportional, i.e. with the increase in time and adsorbent mass, the concentration decreases while it is proportional with regard to C_0 when the increase of initial sulfur concentration is causing the increase in output concentration. At the same time, sorption capacity's dependence on t and C_0 is proportional, i.e. increase in t and C_0 causes an increase in capacity, while it is adversely proportional with regard to m_{C3} when the increase of adsorbent mass is causing the decrease in sorption capacity. These results are in compliance with previously published data and conclusions, viz. in our previous work,[3] and the work of Bakr *et al.*[17] Additionally, when comparing the extent of effects at particular factor levels, almost all of them follow the same pattern, i.e. the extent of the factors' effect on responses is the same at the lower and higher level. The only ones that stand out are the effects of time and adsorbent mass on output sulfur concentration (Figs. 5a and 7a), where time and adsorbent mass have very little effect at a lower level of C_0, while at higher level of C_0 their effects are greater.

These observations mean that the higher sulfur concentration diesel fuel, targeted for adsorptive desulfurization, could be successfully treated by making relatively small adjustments to other process parameters which would then cause larger positive effects, i.e. larger decrease in output sulfur concentration.

Adding to that is the fact that, in many cases of different feedstock, conventional hydrodesulfurization processes encounter difficulties in trying to lower the sulfur concentration to below certain levels, especially to below 10 mg kg^{-1}, risking damage to the physical and chemical properties of diesel fuel. Hua *et al.*[18] determined that the proportion of dibenzothiophene to total sulfur in hydrofined diesel oil reaches as high as 84.2 %, which indicates that dibenzothiophenes are the sulfur compounds most difficult to remove during the hydrofining process. Also, Wang and Prins[19] discuss many aspects of the problems associated with hydrodesulfurization of dibenzothiophene, 4,6-dimethyldibenzothiophene, and their hydrogenated intermediates. In addition, it was reported that upgrading the HDS unit itself in order to achieve the desired ultra-low sulfur levels in fuels would require more than a three-fold increase in the HDS catalyst volume/reactor size, resulting in enormously high operating costs.[20,21]

The economic and technical viability of the adsorptive desulfurization of diesel fuel as a downstream upgrade to the conventional HDS at this stage of research and development is rather unclear, although positive signs are visible. The only large-scale commercial desulfurization process in operation involving adsorption is the S Zorb process. The S Zorb process is a reactive adsorption process where the sulfur atom is removed from the molecule and is bound by the adsorbent, while the hydrocarbon part is returned to the final product with no structural changes.[22] A 6 000 BPSD (Barrels Per Stream Day) gasoline unit is in operation at the ConocoPhillips Borger refinery since April 2001, while overall the S Zorb technology is licensed to 42 sites.[23] Hagiwara and Echizen[24] in their survey evaluated several FCC gasoline desulfurization processes including hydrodesulfurization processes Octgain 125, Octgain 220, and Scanfining from Exxon-Mobil; Prime G from IFP; CDHydro and CD-HDS from CDTech; and S Zorb from ConocoPhillips, and these results are shown in Table 10.

The analysis of data in Table 10 indicates that, out of the evaluated desulfurization processes in terms of economic viability, the S Zorb adsorptive desulfurization process from ConocoPhillips and the CDTech HDS process, are better than other candidates for commercial implementation.[24]

The potential of commercial application of diesel fuel desulfurization on SOLCARB C3 activated carbon was explored in our work[25] with a fixed bed adsorpiton column. We determined that for an 11.8-hour long treatment of around 10^4 kg h^{-1} of hydrodesulfurized gas oil with sulfur concentration, C_0, of 27.0 mg kg^{-1} and average output total sulfur concentration, C, of 4.2 mg kg^{-1}, the adsorption column of 17.32 m in height with one 93.5 t load of activated carbon SOLCARB C3, would be needed. In addition, it was suggested that in order to enable continuous 24-hour processing, an extra column of the same dimensions and adsorbent load would have to be used, and that during down time the saturated adsorbent would be regenerated by thermal treatment at high temperatures in the presence of

Table 10 – *List of FCC gasoline desulfurization processes*[24]

Parameters	Octgain 125	Octgain 220	Exxon Scanfining	Prime G	CDTech	S Zorb
processing capacity/bbl day^{-1}	15 000	31 000	25 000	24 000	30 000	25 000
investment/million $US	14.9	23.8	16.8	21.7	18.5	13.8
hydrogen consumption/m^3 m^{-3}	66	23	14	22	18	12
power consumption/kWh m^{-3}	12.6	9.4	3.8	8.2	2.8	4.4
steam use/kg m^{-3}	–	214	128	180	70	13
home-use fuel/dm^3 m^{-3}	13.6	5.8	2.4	1.5	5.3	6.3
catalyst cost/$US bbl^{-1}	0.43	0.22	0.22	0.01	0.25	0.27
cooling water/t m^{-3}	6.0	5.4	3.2	3.1	1.3	3.1
yield loss/%	5	0.7	0	0.8	0	0
octane loss/–	0	0.1	1.0	1.3	1.0	0.75
required capacity/10^3 m^3 year^{-1}	22 558	23 175	23 093	23 049	23 093	23 148
construction index	877	696	607	815	557	500
depreciation index	175	139	121	163	111	100
variable index	207	119	134	119	102	100
evaluation index	382	259	256	282	214	200

steam and/or carbon dioxide. These values were determined to be supported by literature[26–28] indicating that there is a real possibility for this process finding actual application in the refining industry. However, further research is needed, particularly towards increasing adsorbent effectiveness, selectivity and applicability, as well as additional work on modeling, optimization and scale-up of the fixed bed adsorption system.

As an example of the potential of the adsorption technology applied as an upgrade to the existing HDS process as well as its implementation and integration possibilities and economic viability, presented will be the SK Corporation of Korea HDS pretreatment technology for the production of ultralow sulfur diesel (ULSD) with adsorptive pretreatment to remove the nitrogen compounds from the middle-distillate-range petroleum fractions.

Lee *et al.*[29] showed that the total ISBL (In Side Battery Limits) investment cost for a stand-alone grass roots SK process is estimated to be US$400/bpsd (barrels per stream day) for the first quarter of year 2003, for plant capacities in the range of 25 000 to 30 000 bpsd at a US Gulf Coast location. Only minor modifications are required for the existing HDS unit to couple SK pretreatment process upstream of the HDS unit. The investment cost is approximately US$300/bpsd for a 60 000-bpsd capacity unit. The total utility consumption of the process with fired heater design is as follows:

– fuel: 0.01 FOEB (Fuel Oil Equivalent Barrel);
– cooling water: 1.0 t;
– electricity: 0.4 kW (per barrel of feed).

An alternative stream stripping design is also available. The adsorbent is expected to last over two years with little or no losses. The predicted adsorbent cost is $0.10 per barrel of charge regardless of unit capacity. Solvent losses are in the range of about $0.02 per barrel of feed. Pretreated feed consumes approximately 10 to 20 % less hydrogen in the HDS unit at the same product outlet sulfur level. These savings result primarily from the less severe operating conditions required and the significant reduction in denitrification requirements. The less severe operating conditions are also expected to result in a longer HDS catalyst life and a higher HDS product yield. The investment and operating cost can be lowered substantially if the pretreatment unit is heat-integrated directly with the downstream HDS unit. A pretreatment unit was integrated with an HDS unit in a recent case study. It was estimated that the investment cost would be lowered by approximately 25 % with significant operating cost savings.

The total utility consumption of the integrated steam stripping case is as follows:

– steam: 0.01 t;
– cooling water: 0.6 t;
– electricity: 0.33 kW (per barrel of feed).

To determine the cost-effectiveness of the SK pretreatment process, a number of case studies were made comparing pretreatment with a conventional HDS unit revamp. In general, the additional operating costs for pretreatment translate into a slightly higher breakeven capital cost for a revamp. How much higher is very site specific and is influenced by a number of factors, of which the most critical appears to be HDS hydrogen consumption costs.

The SK process, therefore, becomes most attractive for older, lower pressure units that require extensive revamping costs, which are obviously very site specific and therefore must be developed on a case-by-case basis together with site-specific operating costs. The SK process would also appear to be attractive for a new grass root unit due to the increased capital cost for a high-pressure unit vs. a low-pressure HDS unit.[29]

Conclusions

Adsorptive desulfurization of diesel fuel was investigated by applying two DOE methods, three factor two-level factorial design and $k = 3$ Box-Behneken design. The factorial design analysis confirmed the relevance of the investigated process parameters: time, initial sulfur concentration and adsorbent mass, and yielded first-order model equations that were statistically and graphically tested and proved capable of predicting the behavior of the system rather well.

The analysis included testing for curvature in the system, which was determined to be significant. This result established the need for further testing to uncover the nature of this curvature and describe the system more accurately.

The experiments conducted according to BBD and subsequent multiple regression analysis, resulted with the development of second-order model equations for predicting output sulfur concentration and sorption capacity. ANOVA was carried out and the models' significance was determined to be reasonable. The analysis of these three-dimensional graphical interpretations of the models as well as model coefficients, showed that, within the experimental test range, the input sulfur concentration had the greatest effect on output sulfur concentration and sorption capacity, while comparatively smaller gains in positive direction, i.e. towards the lowering of output sulfur concentration, could be achieved by increasing process time and adsorbent mass. At the same time, the increase of adsorbent mass caused the decrease in sorption capacity but this negative trend was overshadowed by the fact that the main goal of a 10 mg kg^{-1} or less sulfur concentration was achieved and more sulfur was actually being removed.

The lowest achieved output sulfur concentration was 7.6 mg kg^{-1} with relatively low sorption capacity of 0.0861 mg g^{-1} at lower level of input sulfur concentration and higher levels of time and adsorbent mass.

List of symbols

a – specific surface area, m^2 g^{-1}
$C_{i,\,cal}$ – calculated total sulfur concentration in treated diesel fuel, mg kg^{-1}
$C_{i,\,exp}$ – experimental total sulfur concentration in treated diesel fuel, mg kg^{-1}
C_0 – initial sulfur concentration, mg kg^{-1}
d_p – particle diameter, mm
k – number of factors, –
m_{C3} – adsorbent mass, g
n – number of runs for each experiment, –
q – sorption capacity; amount of adsorbed sulfur on the adsorbent, mg g^{-1}
$q_{i,\,cal}$ – calculated sorption capacity, mg g^{-1}
$q_{i,\,exp}$ – experimental sorption capacity, mg g^{-1}
R^2 – correlation coefficient, –
t – time, min
V_D – volume of diesel fuel sample, cm^3
X_1 – coded time, –
X_2 – coded input concentration, –
X_3 – coded adsorbent mass, –
Y_c – coded total sulfur concentration in treated diesel fuel, –
Y_q – coded sorption capacity, –

Greek letters

ρ – bulk density, g cm^{-3}
ρ_D – diesel fuel density, g cm^{-3}

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