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SCREENING AND RESPONSE SURFACE MODELING OF WATER VAPOR ADSORPTION FROM WET AIR IN PACKED BED OF SILICA GEL USING D-OPTIMAL DESIGN

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ABSTRACT. The experimental design methodology was applied for screening and response surface modeling of adsorption of water vapors from air on a fixed bed of silica gel grains. The variables considered were the air flow rate, temperature, air relative humidity and drying time. The D-optimal design allowed developing a quadratic model as a functional relationship between packed-bed adsorption efficiency and the independent variables. It was found that all factors considered have an important effect in the degradation efficiency of the organic matter**.**

Keywords: *D-optimal design, response surface modeling, air drying; adsorption; fixed bed.*

INTRODUCTION

Mathematical modeling of gas drying by adsorption in fixed bed was approached in a several papers reported in literature [1-9]. Theoretical studies suggested analytical mathematical models available when the process takes place in fixed bed of adsorbent under isotherm regime [1-4] and adiabatic or non-adiabatic regime respectively [5-9]. The suggested models are based on linear and non-linear equilibrium equations, considering the external and internal diffusion. However, due to the assumed hypothesis, the applicability of analytical models is limited, and their correlation rather weak.

The present work presents a preliminary study of applying experimental design screening and modeling at gas drying by adsorption in fixed bed of silica gel under non-isothermal and non-adiabatic conditions. It was decided to use D-optimal design, as this is an effective method for obtaining maximum information with a minimum of experiments, and to determine which factors significantly influence the measured variables. Air flow rate, temperature, air relative humidity and drying time were considered as independent variables,

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while packed-bed adsorption efficiency was selected as response. A quarter polynomial model was suggested, tested and validated using experimental data unemployed in the D-optimal design.

RESULTS AND DISCUSSION

Several results obtained at air drying by adsorption in fixed bed of ordered silica gel under various experimental conditions are shown in Figure 1. The normalized concentration of water vapors in air at the output of a packed bed column as determined from psychrometric measurements is plotted as a function of the adsorption time.

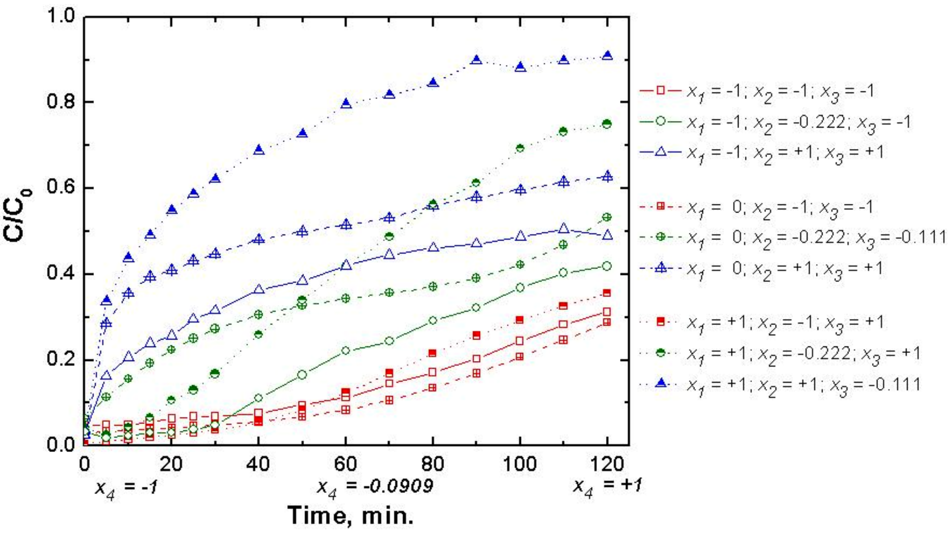

Figure 1. Several breakthrough curves achieved at air drying in fixed bed of silica gel at ranges of flow rate between 0.6 $m^3 \cdot h^{-1}$ and 1.2 $m^3 \cdot h^{-1}$, temperature from 20 to 38 °C and air relative humidity between 40 and 85 %.

The experimental data (Table 7) were analyzed by the Multi Linear Regression (MLR) method [10] to fit the second-order polynomial equation [11]:

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i \cdot x_i + \sum_{i=1}^{4} \beta_{ii} \cdot x_i^2 + \sum_{i=1}^{3} \sum_{j>i}^{4} \beta_{ij} \cdot x_i \cdot x_j + \varepsilon \qquad (1)$$

where β_0, β_i, β_{ii}, and β_{ij} are regression coefficients (β_0 is a constant term, β_i is a liner effect term, β_{ii} is a squared effect term, β_{ij} and is an interaction effect term) and Y is the predicted response value. MLR is based on finding the regression model that minimizes the residual sum of squares of the response.

A D-optimal experimental design generated by the MODDE software with 20 runs and 2 replicates considered (Table 1) was employed for screening and response surface modeling. The algorithm used by this software is the modified Federov algorithm [12] with the Bayesian modification [13]. D-optimal designs select points from the candidate set that maximize the determinant of the coded model matrix *X'X*, which is equivalent to maximizing the volume of *X'X*.

As response for modeling, the packed-bed adsorption efficiency, *Y,* was considered and calculated by the following expression:

$$Y = \frac{1}{\tau_{\exp}} \int_0^{\tau_{\exp}} \left(1 - \frac{C}{C_0}\right) d\tau \qquad (2)$$

where C_0 (kg m^{-3}) is the initial concentration of water vapors in air, C (kg m^{-3}) is the concentration of water vapors in air at the column output; and τ_{exp} – adsorption time (min.). The experimental results of the packed bed adsorption efficiency, *Y*, were determined according to planned initial conditions and reported in the last column of Table 1.

Table 1. Experimental design and results of the fractional design.

Run No.	Input variables								Response
	Flow rate, m^3/h	x_1	Temp., °C	x_2	Rel. humid., %	x_3	Time, min.	x_4	Y, non-dimens.
1	0.9	0	20	-1	40	-1	10	-1	0.96673
2	1.2	+1	27	-0.222	40	-1	10	-1	0.96625
3	0.6	-1	38	+1	40	-1	10	-1	0.92096
4	0.6	-1	20	-1	60	-0.111	10	-1	0.95083
5	1.2	+1	38	+1	60	-0.111	10	-1	0.71292
6	1.2	+1	20	-1	85	+1	10	-1	0.98991
7	0.6	-1	27	-0.222	85	+1	10	-1	0.94981
8	0.9	0	38	+1	85	+1	10	-1	0.76118
9	1.2	+1	20	-1	40	-1	60	-0.09	0.96354
10	0.6	-1	27	-0.222	40	-1	60	-0.09	0.91802
11	0.9	0	20	-1	85	+1	60	-0.09	0.95442
12	0.6	-1	20	-1	40	-1	120	+1	0.94049
13	0.6	-1	38	+1	40	-1	120	+1	0.70795
14	1.2	+1	38	+1	40	-1	120	+1	0.36872
15	1.2	+1	20	-1	60	-0.111	120	+1	0.66062
16	0.9	0	27	-0.222	60	-0.111	120	+1	0.67160
17	0.6	-1	20	-1	85	+1	120	+1	0.86288
18	1.2	+1	20	-1	85	+1	120	+1	0.85197
19	0.6	-1	38	+1	85	+1	120	+1	0.61635
20	1.2	+1	38	+1	85	+1	120	+1	0.35360
21	1.2	+1	38	+1	85	+1	120	+1	0.36195
22	1.2	+1	38	+1	85	+1	120	+1	0.34647

Screening is the first stage of an investigation where the goal is just to identify the important factors. The MODDE software allowed determining the coefficients of the second order fitting equation, which was analyzed based on the above-mentioned statistical criteria. In particular, the suitability of the screening model was tested by the ANOVA test. Table 2 summarizes the obtained results.

Table 2. Analysis of variance (ANOVA) for the screening modeling.*

Source of variation	Degrees of freedom	Sum of Squares	Mean Square (Variance)	F-ratio	p-value	Standard Deviation
Total	22	13.9077	0.63217			
Constant	1	12.8246	12.8246			
Regression	14	1.0678	0.07623	34.9544[a]	0.000	0.276176
Residual	7	0.0153	0.00218			0.046713
Lack of Fit (model error)	5	0.0151	0.00303	50.3777[b]	0.020	0.055053
Pure Error (replicate error)	2	0.0001	0.00006			0.007756
Total corrected	21	1.0831	0.05158			0.227104

*R^2 = 0.9859; R^2_{adj} = 0.9577; Q^2 = 0.8254.
[a] F-ratio (regression/residual); $F_{(0.1, 14, 7)}$ = 2.64; $F_{(0.05, 14, 7)}$ = 3.53; $F_{(0.01, 14, 7)}$ = 6.36;
[b] F-ratio (lack of fit/pure error); $F_{(0.1, 5, 2)}$ = 9.29; $F_{(0.05, 5, 2)}$ = 19.3; $F_{(0.01, 5, 2)}$ = 99.3.

In the ANOVA test, the *F*-ratio value obtained for the response is higher than the Fisher's *F*-value corresponding to a probability of 99% ($F_{(0.01,\ 14,\ 7)} = 6.36$), and so one can conclude that the variations that occur in the responses are associated to the model, not to random errors. *F*-ratio value obtained for the lack of fit is lower only than the Fisher's *F*-value at 99% probability ($F_{(0.01,\ 15,\ 2)} = 99.3$), which emphasize a poor model adequacy. The value of R^2 indicates that 98.59% of the response variability is explained by the model.

After the analysis of the second order model correlation and adequacy, the statistically significant variables and/or interactions were identified by means of p-value (< *0.1*). From *p*-values reported for each MLR equation factors, parameters and interactions are considered influent or not. Moreover, for one given parameter, the smallest the *p*-value is, more influent is this parameter onto the model. The scaled and centered coefficients of model fitted are resumed in Table 3. It can be seen that the process variables and interactions that are statistically significant are the flow rate (x_1), its interactions with temperature (x_1*x_2) and time (x_1*x_4), temperature (x_2), its interactions with time (x_2*x_4), time (x_4) and quadratic term of relative humidity (x_3^2) due to these parameters present p-values lower than *0.1* (for *90 %* of statistical meaning).

Table 3. Estimates of the screening model regression for packed-bed adsorption efficiency.

Real variables	Term	Estimate	p-value
Constant	Intercept	0.766762	$1.01464 \cdot 10^{-6}$
Flow rate (M_v)	x_1	-0.061249	$1.31372 \cdot 10^{-3}$
Temperature (T)	x_2	-0.128828	$1.63306 \cdot 10^{-5}$
Relative humidity (u)	x_3	-0.016199	***0.2204*** **(!)**
Time (t)	x_4	-0.116779	$1.98756 \cdot 10^{-5}$
M_v * M_v	x_1^2	0.019252	***0.5106*** **(!)**
T * T	x_2^2	-0.025020	***0.4286*** **(!)**
u * u	x_3^2	0.064716	$6.31456 \cdot 10^{-2}$
t * t	x_4^2	-0.030894	***0.3827*** **(!)**
M_v * T	$x_1 * x_2$	-0.039980	$1.81612 \cdot 10^{-2}$
M_v * u	$x_1 * x_3$	0.011961	***0.3866*** **(!)**
M_v * t	$x_1 * x_4$	-0.040362	$1.61997 \cdot 10^{-2}$
T * u	$x_2 * x_3$	-0.013064	***0.3593*** **(!)**
T * t	$x_2 * x_4$	-0.039177	$1.74276 \cdot 10^{-2}$
u * t	$x_3 * x_4$	0.005222	***0.7027*** **(!)**

In Figure 2 is shown the normal probability plot of effects (double of the absolute values of coefficients) emphasizing the amplitude of the effects influence over the objective function. As can be noticed, all of the insignificant effects, disposed on the linear fit, belong to the insignificant coefficients having p-values higher than *0.1*.

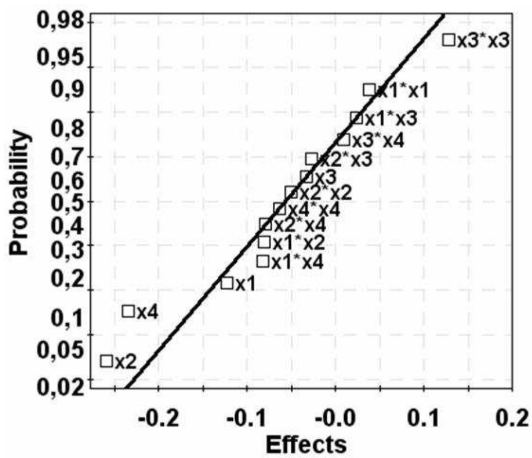

Figure 2. Normal probability plot of effects.

However, removing one by one the terms of the screening model in order of their insignificance it was found that the relative humidity (x_3) becomes significant as listed in Table 4. All the terms left in the model are significant at 99% confidence level excepting the interaction between temperature and time (x_2*x_4) that is significant at 95% confidence level.

After removing the insignificant terms of the screening model, runs number 1 and 18 were also removed due to their high residual values. Thus, the p-values of the remained coefficients became lower stressing their statistical significance, and goodness of fit was much improved as shown in Table 5.

Table 4. Estimates (95% confidence level) of the RSM model regression for packed-bed adsorption efficiency.

Real variables	Term	Estimate	Standard Error	p-value	Confidence interval (±)
Constant	Intercept	0.733285	0.014807	$2.79499 \cdot 10^{-14}$	0.03259
Flow rate (M_v)	x_1	-0.068246	0.006995	$9.45817 \cdot 10^{-7}$	0.01539
Temperature (T)	x_2	-0.131912	0.007338	$1.67252 \cdot 10^{-9}$	0.01615
Relative humidity (u)	x_3	-0.030803	0.007207	$1.31195 \cdot 10^{-3}$	0.01586
Time (t)	x_4	-0.126896	0.007004	$1.53964 \cdot 10^{-9}$	0.01541
u * u	x_3^2	0.068263	0.016960	$1.99944 \cdot 10^{-3}$	0.03733
M_v * T	$x_1 * x_2$	-0.032883	0.007888	$1.56534 \cdot 10^{-3}$	0.01736
M_v * t	$x_1 * x_4$	-0.043390	0.007690	$1.50559 \cdot 10^{-4}$	0.01693
T * t	$x_2 * x_4$	-0.023773	0.008272	$1.51367 \cdot 10^{-2}$	0.01821

The final regression model in terms of coded factors is presented as follows:

$$\hat{Y} = 0.733285 - 0.068246 \cdot x_1 - 0.131912 \cdot x_2 - 0.030803 \cdot x_3 - \\ - 0.126896 \cdot x_4 - 0.032883 \cdot x_1 \cdot x_2 - 0.04339 \cdot x_1 \cdot x_4 - \\ - 0.023773 \cdot x_2 \cdot x_4 + 0.068263 \cdot x_3^2 \quad (3)$$

In terms of actual factors, the packed-bed adsorption efficiency is expressed by the following regression equation:

$$\hat{Y} = 1.56311 + 0.296634 \cdot M_v - 0.00057486 \cdot T - 0.0182241 \cdot u + \\ + 0.00145229 \cdot t - 0.0121791 \cdot M_v \cdot T - 0.00262967 \cdot M_v \cdot t - \\ - 0.000048 \cdot T \cdot t + 0.000134841 \cdot u^2 \quad (4)$$

subjected to $0.6 \le M_v \le 1.2$ [m^3 h^{-1}]; $20 \le T \le 38$ [°C]; $40 \le u \le 85$ [%] and $10 \le t \le 120$ [min.].

Table 5. Analysis of variance (ANOVA) for the response surface modeling.*

Source of variation	Degrees of freedom	Sum of Squares	Mean Square (Variance)	F-ratio	p-value	Standard Deviation
Total	20	12.2473	0.61236			
Constant	1	11.2176	11.21760			
Regression	8	1.0214	0.12768	169.19[a]	0.000	0.3573
Residual	11	0.0083	0.00075			0.0275
Lack of Fit (model error)	9	0.0082	0.00091	15.1085[b]	0.064	0.0301
Pure Error (replicate error)	2	0.0001	0.00006			0.0776
Total corrected	19	1.0297	0.05419			0.2328

* R^2 = 0.9919; R^2_{adj} = 0.9861; Q^2 = 0.9645.
[a] F-ratio (regression/residual); $F_{(0.1, 8, 11)}$ = 2.295; $F_{(0.05, 8, 11)}$ = 2.935; $F_{(0.01, 8, 11)}$ = 4.275;
[b] F-ratio (lack of fit/pure error); $F_{(0.1, 9, 2)}$ = 59.9; $F_{(0.05, 9, 2)}$ = 241; $F_{(0.01, 9, 2)}$ = 6022.

After performing the screening step and removing the insignificant coefficients, the determination coefficient (R^2), adjusted-R^2 and especially goodness of prediction (Q^2) underwent an obvious improvement. Considering that R^2 gives overestimation and Q^2 gives underestimation of the goodness of fit and for a model to be acceptable both values should be as close to *1* as possible and ideally not separated by more than 0.3 (R^2-Q^2<0.3) [16]. The *F*-test revealed that RSM regression is statistically significant at a confidence level of 99%. According to the analysis of variance the *F*-value of the model (regression) (*Fmodel = 169.19*) was much higher than the tabular *F*-value with the same number of degrees of freedom of two sources of variance ($F_{(0.01,8,11)} = 4.275$), indicating that the differences are highly significant. The *P*-value for lack of fit was *0.064*, indicating that the probability of error for the lack of fit was higher than *0.05* and the model represents the actual relationships of parameters well within the range selected. This is also evident from the fact that the observed and predicted values of the response are very close to each other (Figure 3), clearly indicating that the prediction of experimental data is extremely accurate.

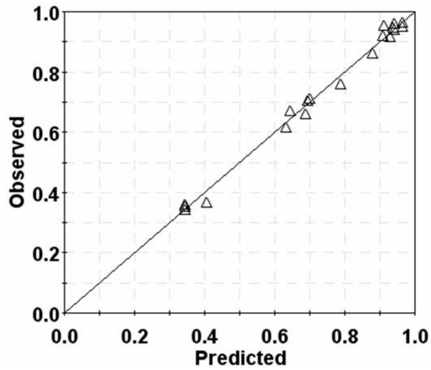

Figure 3. Observed vs. predicted values of the response.

Response surfaces were plotted using MODDE software to emphasize the effects of the significant parameters and their interactions on gas drying. Contour plots, as presented in Figure 4, are very useful to see interaction effects of the significant factors on the responses. These types of plots show effects of two factors on the response at a time. In all the presented figures, the other one factor was kept at the intermediary level.

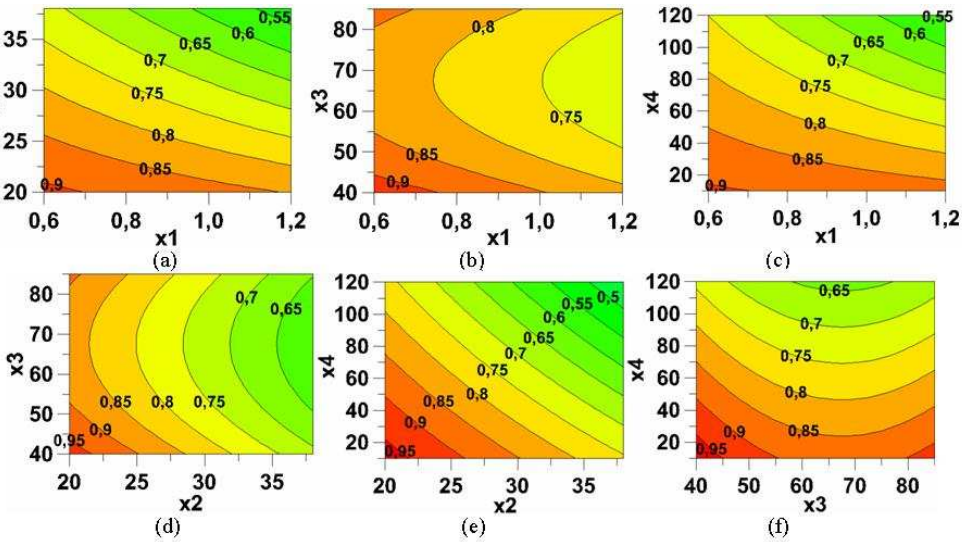

Figure 4. Contour plots of the packed-bed adsorption efficiency as function of (a) flow rate and temperature at an air relative humidity of 60% and 60 min.; (b) flow rate and drying time at 27 °C and 60 min; (c) flow rate and drying time at 27 °C and 60% air relative humidity; (d) temperature and relative humidity at 0.9 $m^3 \cdot h^{-1}$ and 60 min.; (e) temperature and drying time at 0.9 $m^3 \cdot h^{-1}$ and 60% air relative humidity; (f) air relative humidity and drying time at 0.9 $m^3 \cdot h^{-1}$ and 27 °C.

As can be seen an increase of the flow rate and/or temperature leads to a diminishing of the fixed-bed adsorption efficiency. Figs. 4c and 4e emphasize the stronger effect of temperature as a function of time compared to the effect of air flow rate. Though the combined effects of air relative humidity and any of the other effects seem to pinpoint a minimum point near the investigated range, one should take into consideration that these interactions have no statistical significance.

To validate the suggested model, confirmatory experiments were carried out. Verification experiments indicate the validity and adequacy of the predicted models (Figure 5).

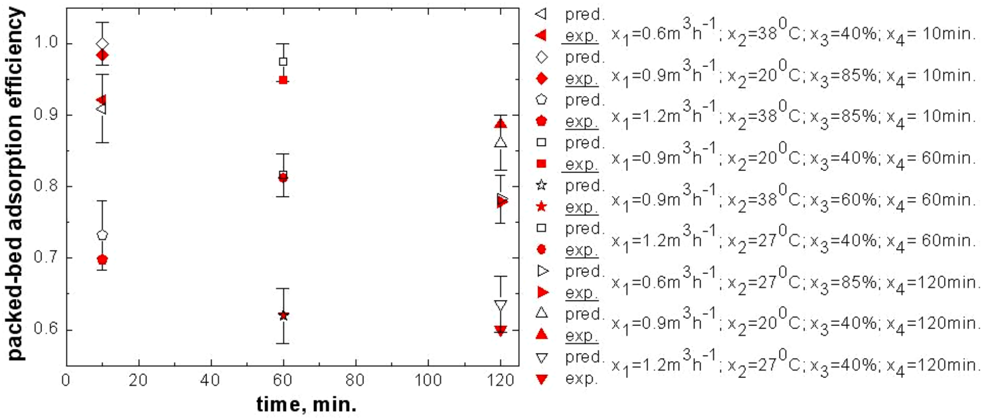

Figure 5. Model validation.

As can be seen, all the considered verification experiments (filled symbols) are placed within the confidence interval of the values predicted (open symbols) by the suggested model.

MODDE software allows one to minimize or maximize the objective function within the investigated ranges of the considered factors. Nevertheless, it was of interest to find the maximum value (Table 6) of packed-bed adsorption efficiency at the longest investigated drying time (120 min.). Beside the predicted value, the experimental one is presented in the table.

Table 6. Optimal conditions of the packed-bed adsorption efficiency at 120 min.*

x_1^*	M_v^*, $m^3 \cdot h^{-1}$	x_2^*	T^*, °C	x_3^*	u^*, %	Y*, Experimental	Y*, Predicted
-1	0.6	-1	20	-1	40	0,9405	0.9399

* Maximum predicted value within the investigated ranges of the considered factors, at the longest drying time.

CONCLUSIONS

In this work is presented the screening and response surface modeling of gas drying by adsorption in packed bed of silica gel using D-optimal design at three levels for four factors.

The use of an experimental design permitted the rapid screening of a large experimental domain for gas drying by adsorption in fixed bed of silica gel. Thus, it was emphasized the order of influence of the four factors considered pinpointing the strong influence over the packed-bed adsorption efficiency of the temperature factor.

The experimental and the predicted values were very close which reflected the correctness and the applicability of RSM. In this case, the value of the determination coefficient (R^2 = 0.9919) indicated that near about negligible of total variations were not explained by the model. The value of the adjusted determination coefficient (adjusted R^2 = 0.9861) was near to 1, showing a high significance of the model.

EXPERIMENTAL SECTION

Experimental Technique

In the experimental investigations was used a laboratory installation consisting in an adsorption column, a wetting air column, a ventilating fan and devices for measuring and controlling temperature and air flow rate. A full description of the experimental installation employed to obtain the data needed in this study can be found in our previous work [15].

The investigations were carried out using as adsorbent material purchased-spherical silica gel grains having a diameter of $2.57 \cdot 10^{-3}$ *m*. Experimental investigations were performed under atmospheric pressure at three initial values of air temperature (*20*, *27* and *38°C*), using wet air as gaseous phase at three values of the air relative humidity (*40*, *60* and *85 %*), and at three values of air flow rate: *0.6*, *0.9* and $1.2\ m^3 \cdot h^{-1}$. Air relative humidity was measured at the input and output of the fixed bed by using a Testo 625 psyhrometer.

The adsorption process was achieved in fixed granular bed of composite materials under dynamic regime and non-isothermal and non-adiabatic conditions. The geometrical parameters of the fixed adsorbent bed were *0.15 m* in height and $2.95 \cdot 10^{-2}$ *m* in diameter.

Experimental Design

A D-optimal experimental design at three levels for four factors was used for screening and response surface modeling (RSM) of gas drying by adsorption in fixed bed of ordered silica gel grains. Screening and RSM were employed to analyze the operating conditions of air flow rate, temperature, relative humidity and drying time. The software of MODDE (Unimetrics, Demo Version 8.02) [16] was used to design and regress the experimental data.

The operating ranges and the levels of the independent variables considered in this study are given in Table 7. For the statistical calculations, the natural variables (denoted as z_i) are converted into dimensionless codified values (x_i) to allow comparison of factors of different natures with different units and to decrease the error in the polynomial fit. This is done using the following relationship:

$$x_i = \frac{z_i - z_i^0}{\Delta z_i};\ i = 1, 2, 3, 4 \quad (5)$$

where z_i^0 refers to the value of variable *i* in the centre of the domain (i.e., it corresponds to $x_i = 0$) and Δz_i corresponds to the difference of that variable between the maximum level and the centre of the domain.

Table 7. Predictor variables and their coded levels and actual values used in the experimental design.

Source of variation	Symbol	Inferior level	Intermediary level	Superior level
Flow rate, m^3/h	x_1	-1	0	+1
	z_1	0.6	0.9	1.2
Temperature, K	x_2	-1	-0.222	+1
	z_2	20	27	38
Air relative humidity, %	x_3	-1	-0.111	+1
	z_3	40	60	85
Drying time, min.	x_4	-1	-0.0909	+1
	z_4	10	60	120

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