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Adsorptive desulfurization of oil derivatives using nanostructured Mg-Al layered double hydroxides: Experimental design and modeling

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ABSTRACT

This study focuses on the application of nanostructured Mg-Al layered double hydroxide as a promising adsorbent in desulfurization of dibenzothiophene, an aromatic sulfur bearing compound from gasoil model. The Mg-Al LDH was synthesized by a co-precipitation method and characterized by FT-IR, XRD, EDX and SEM. The XRD and FT-IR approved the layered structure and crystalline form of the adsorbent, the EDX showed the material content in synthesized adsorbent and SEM approved the nanostructure of the synthesized LDH. Four factors were selected as effective factors of desulfurization process. The optimum state of the factors, including calcination temperature of Mg-Al LDH, dibenzothiophene concentration, adsorbent amount and treatment times selected as the 600 °C, 50 ppm, 0.1 mg and 120 min, respectively and the highest desulfurization percentage reached to 73.24%.

Keywords: Layered double hydroxides, Design of experiment and modeling, Desulfurization, Nanostructure, Oil derivatives.

1. Introduction

In recent years desulfurization of Oil derivatives has attracted much attention due to the gradual reduction of the statutory sulfur content in most western countries [1]. One of the most applied methods for desulfurization in industrial scale is hydrodesulfurization (HDS) which is highly efficient in removing tiles, sulfides, and disulfides. Besides the useful application of the HDS, it has difficulty in reducing dibenzothiophene (DBT) and its derivatives as refractory sulfur-containing compounds, especially 4,6-dimethyldibenzothiophene (4,6-DMDBT), to a low level [2]. For example, the production of H_2S is one of the main inhibitors for deep HDS of unreactive species during the reaction of some thiophene derivatives [3].

Reduce of the sulfur-containing compounds of the diesel to ultra-low-sulfur diesel (ULSD) has become a major task of refineries all over the world. The presence of sulfur-bearing compounds in Oil derivatives has shown an adverse impact on the environment [4,5]. It is because of the transformation of the sulfur-bearing compounds to the SO_x in the combustion process in the cars engines.

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The most adverse function of Sulfuric oxides is that it poison the catalyst surface in catalytic converters used for reducing CO and NO_x emissions and this severely affects the environment. The acidic rain and contamination of the catalyst after the desulfurization process is because of the SO [6,7].

Besides the efficiency of the adsorption process, the authors used the oxidative method in order to maximize the efficiency of the process by using the H_2O_2 as an oxidative agent [8]. The sulfones can be readily separated from the diesel using an extractant, and desulfurization of the simulated fuel derivative can be achieved but because of the low activity of the oxidative agent, the benzothiophene (BT) and its derivatives, which are present largely in nonhydrotreated diesel, can't be oxidized efficiently, and achieving deep desulfurization of various actual fuel is difficult with this system [2,9].

The basic layer structure of LDHs is based on that of brucite [Mg (OH)$_2$] which is of the CdI$_2$ type, typically associated with small polarizing cations and polarizable anions. It consists of magnesium ions surrounded approximately octahedrally by hydroxide ions [10]. These octahedral units form infinite layers by edge-sharing, with the hydroxide ions sitting perpendicular to the plane of the layers [11]. The

chemical composition of LDHs are expressed by the general formula $[M^{II}_{1-x} M^{III}_{x} (OH)_2][A^{n-}_{xn}.mH_2O]$, where M^{II} and M^{III} represent di- and trivalent metal ions within the brucite-like layers, and A^{n-} is an interlayer anion [12].

The aim of this work is to develop a new system and process using Mg-Al layered double hydroxide as an adsorption agent with recoverable nature by heating to 300-500°C and to design the experiment and modeling in order to gain as much as efficiency the can be anticipated from the process and to analyze the effect of each factors in the process.

2. Experimental

The material used in this study as Magnesium nitrate,(Mg $(NO_3)_2$), aluminum nitrate (Al $(NO_3)_3$), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), n-Heptane and dibenzothiophene were purchased from Merck (Germany) with purity of 99%>.

2.1. Adsorbent preparation

The Mg-Al LDHs (molar ratios Mg/Al = 2) was prepared by co-precipitation of magnesium and aluminum salts from homogeneous solution. A typical synthetic procedure is as follows: 6.4 g Mg $(NO_3)_2 \cdot 6H_2O$ and 4.6 g Al $(NO_3)_3.9(H_2O)$ dissolved in 100 mL of deionized water under vigorous stirring. After 10 min, the solution B contains 1.125 g Na_2CO_3 and 4 g NaOH were added dropwise in the above homogeneous solution and kept the mixture solution under constant magnetic stirring for 3 min at room temperature. Then the solid was separated by vacuum filter and washed thoroughly with water and finally dried overnight at 70°C. After that, the synthesized layered double hydroxide was heated to distinct temperature according to designed limits and been calcined.

2.2. Adsorbent characterization

X-ray diffraction (XRD) studies were carried out on a Siemens D500 diffract meter working with K_α line of copper (λ=0.154 nm). Measurement of the samples was carried out in the range 2θ of 2.5-50°. The mean crystal sizes were estimated using the Scherer equation, D=Kλ/β cos θ, where K=0.89, λ =0.15418 nm, β is the half peak width of the X-ray reflection and θ is the diffraction angle. Infrared (IR) spectra were recorded with a Bruker 27 FT-IR spectrometer using the Universal ATR Accessory in the range from 3650 to 400 cm^{-1} with 4 cm^{-1} resolution. SEM images and EDX analyses were taken on a Hitachi S4800 Field-Emission Scanning Electron Microscope with

pre-coating samples with gold. Surface characterization of the material was carried out using a nitrogen gas adsorption-desorption technique at 77 K, with a Micromeritics ASAP 2000 instrument.

2.3. Evaluation of the procedure

In order to testify adsorption property, the batch mode selected for desulfurization of the sulfur-bearing compounds. The simulated fuel derivative in this experiment was n-heptane as fuel derivative with the addition of the experimentally designed amount of dibenzothiophene (DBT) as sulfur-bearing compounds. A sample of the adsorbent with amounts, designed by Minitab 17 was added to the solution at room temperature and vigorously stirring. After the distinct times according to the designed procedure, the adsorbed amount of the DBT by Mg-Al LDH was determined by UV/visible spectrophotometer (T+80,made in united kingdom). The amount of DBT removal (%) was calculated as:

$$\text{Amount of DBT removal (\%)} = \frac{c_0 - c_t}{c_0} \times 100 \quad (1)$$

Where Co is the initial concentration before adsorption (ppm) and Ct is the concentration of the DBT after a specified time.

As far as we know, RSM as an affordable method to study of experimental variables, reduces the number of designed experiments needed in a process. In general, a second-order polynomial model is used in RSM analysis. The behavior of the system is explained by the following empirical second-order polynomial model Eq. (2):

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i x_i + \sum_{1 \leq i \leq j}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

Where Y is the predicted response, x_i, x_j, . . ., x_k are the input variables, which affect the response Y, x^2_i, x^2_j, . . ., x^2_k are the square effects, $x_i x_j$, $x_i x_k$ and $x_j x_k$ are the interaction effects, β_0 is the intercept term, β_i (i=1, 2, . . ., k) is the linear effect, β_{ii} (i=1, 2, . . ., k) is the squared effect, β_{ij} (i=1, 2, . . ., k; j=1, 2, . . ., k) is the interaction effect and ε is a random error [13].

2.4. Experimental design and modeling by response surface methodology

One of the useful statistical methods for the optimization is response surface methodology (RSM) that can be used for optimization of the chemical reactions and/or industrial processes and widely used for experimental design [13-15]. This method of optimization is being used for modeling a curved quadratic surface to continuous factors. By application

of the RSM model, the minimum or maximum response can be determined, if one exists inside the factor region [16,17]. Three distinct values for each factor are necessary to fit a quadratic function, so the standard two-level designs cannot fit curved surfaces. The main objective of this method for modeling and optimization is simply to optimize the response surface that is influenced by process parameters [18]. Also, the relationship between the controllable input parameters and the obtained response surfaces can be quantified by RSM [19].

To find the optimum conditions for desulfurization process a Box-Behnken design (BBD) was adopted to evaluate the combined effect of four factors (variables), i.e. calcination temperature, the amount of adsorbent, reaction time and dibenzo thiophene (DBT) concentration as sulfur-bearing compounds. For four variables (n = 4) and two levels (high (+) and low (−)), the total number of experiments was 27 (shown in Table 1). By application of the Minitab 17 software, the statistical analysis was performed using and a regression model was proposed.

Table 1. The 4-factor Box Behnken design matrix (independent variables and their coded and actual levels; calcination temperature ($^\circ$C), DBT compounds concentration (ppm), adsorbent amount (mg) and treatment time (min) and the experimental results (desulfurization efficiency (%)).

Run	Calcination temperature ($^\circ$C)	DBT concentration (ppm)	Adsorbent amount (mg)	Treatment time (min)	Response	Predicted
1	300	150	0.075	75	59.854	60.76702
2	450	100	0.075	75	44.72	44.07726
3	450	50	0.075	30	31.524	29.36293
4	450	150	0.075	30	44.57	44.13932
5	450	100	0.1	30	39.975	37.97922
6	450	100	0.075	75	30.478	31.67367
7	300	100	0.1	75	32.451	33.17831
8	300	100	0.075	120	42.53	44.20218
9	450	100	0.05	120	62.352	62.80216
10	600	50	0.075	75	42.325	43.44381
11	450	50	0.075	120	53.96	53.82882
12	600	150	0.075	75	35.2514	35.31144
13	300	100	0.05	75	43.922	44.13932
14	450	150	0.1	75	45.807	45.19243
15	450	150	0.075	120	31.124	33.65981
16	450	100	0.1	120	61.325	60.43888
17	600	100	0.075	120	38.858	39.78038
18	450	100	0.075	75	52.67	50.89627
19	600	50	0.1	120	73.204	73.18717
20	450	50	0.1	75	24.954	26.07334
21	600	100	0.075	30	44.383	44.13932
22	450	100	0.05	30	36.18	35.10312
23	450	150	0.05	75	47.521	48.42476
24	300	100	0.075	30	28.902	29.00589
25	600	100	0.05	75	60.632	60.98477
26	300	50	0.075	75	36.645	36.16184
27	600	100	0.1	75	38.321	36.48495

The analysis of variance (ANOVA) based on the proposed model was carried out in order to analyze and evaluate the data of the experiment. The accuracy and applicability of the second order model obtained from RSM were evaluated by the correlation coefficients (R^2, R^2_{adj}). In the same program calculated F values (Fisher variation ratio), p values, and adequate precision were used to determine both the significance of the model and of the input variables. The selection and rejection of the model terms are based on the probability value with 95% confidence level (p-value > 0.05). Eventually, the three-dimensional response surface plots and contour plots were drawn for the visualization of the interaction effects of the independent variables on desulfurization process [20].

3. Results and Discussion

3.1. Adsorbent characterization

After synthesis of adsorbent, four detection methods were used to characterize Mg-Al layered double hydroxides. Fig. 1 shows the FT-IR spectrum of Mg-Al layered double hydroxides synthesized using co-precipitation method. The peaks under 1000 cm^{-1} are because of the M-O and M-O-M bond vibration and stretching. Naturally, peaks in 1377 and 3471 cm^{-1} are related to the existence of CO_3^{-2} and hydroxyls groups adsorbed to the layers, respectively. Fig. 2 represents XRD patterns of Mg–Al–CO_3 LDHs and CLDH. The XRD patterns of Mg–Al–CO_3 LDHs exhibit the characteristic reflections of the hydrotalcite structure and accordingly, the patterns can be indexed in a hexagonal lattice with an R3m rhombohedral space group symmetry, further indicating the successful formation of the LDHs structure. The XRD patterns of CLDH showed the disappearance of the peaks of hydrotalcite, due to the collapse of the structure of Mg–Al–CO_3 LDHs, and the appearance of broad peaks attributed to the formation of Mg–Al mixed oxides, indicating Mg–Al–CO_3 LDHs decomposes into magnesium and aluminum oxides when heated at 500°C. As LDH materials have a similar layered structure, they all share a similar characteristic XRD pattern. Crystalline impurities in the samples can be readily identified using powder XRD by simply comparing their characteristic diffraction pattern to a reference library of patterns. Additional information can be obtained by examining changes in the d $_{(003)}$ spacing of the LDH. The d $_{(003)}$ spacing of an LDH corresponds to the distance between the cation layers. When the interlayer anions in an LDH are changed, a corresponding change in the d $_{(003)}$ spacing should be observed. This change will indicate if the new anions have been successfully intercalated into the LDH or simply adsorbed onto the surface of the material. The particle morphology and chemical composition of the Mg–Al–CO_3 LDHs and CLDH can be seen in the SEM images and corresponding EDX spectrum presented in Fig. 3. The SEM image of Mg–Al–CO_3 LDHs showed a layered structure and particles aggregation with lateral size 50–100 nm and corresponding EDX spectrum showed the presence of Mg, Al, C, O, also indicating Mg–Al–CO_3 LDHs was successfully prepared. The SEM micrograph of the CLDH revealed the collapsed layer structure, which further indicated the Mg–Al–CO_3 LDHs transforms to mixed magnesium and aluminum oxides.

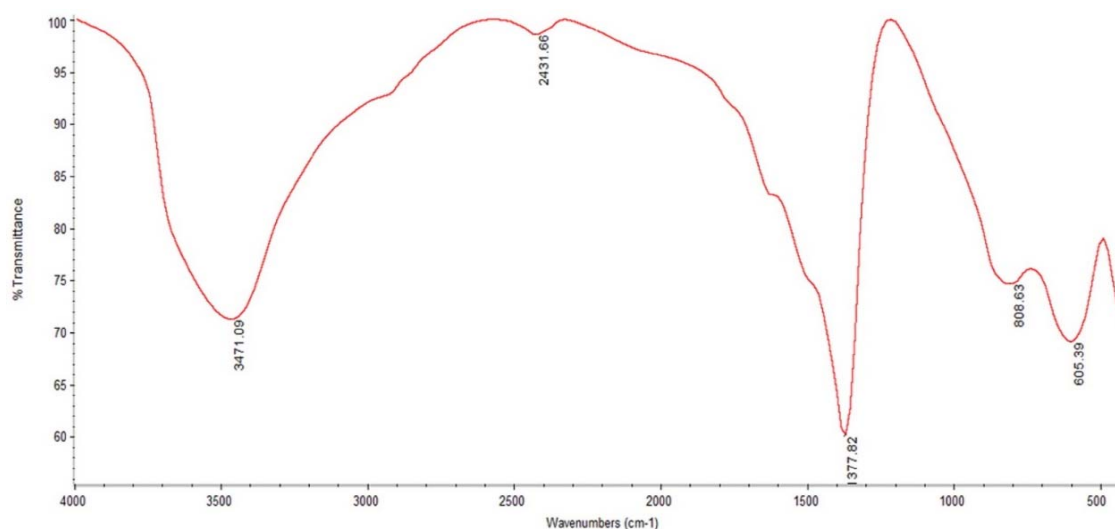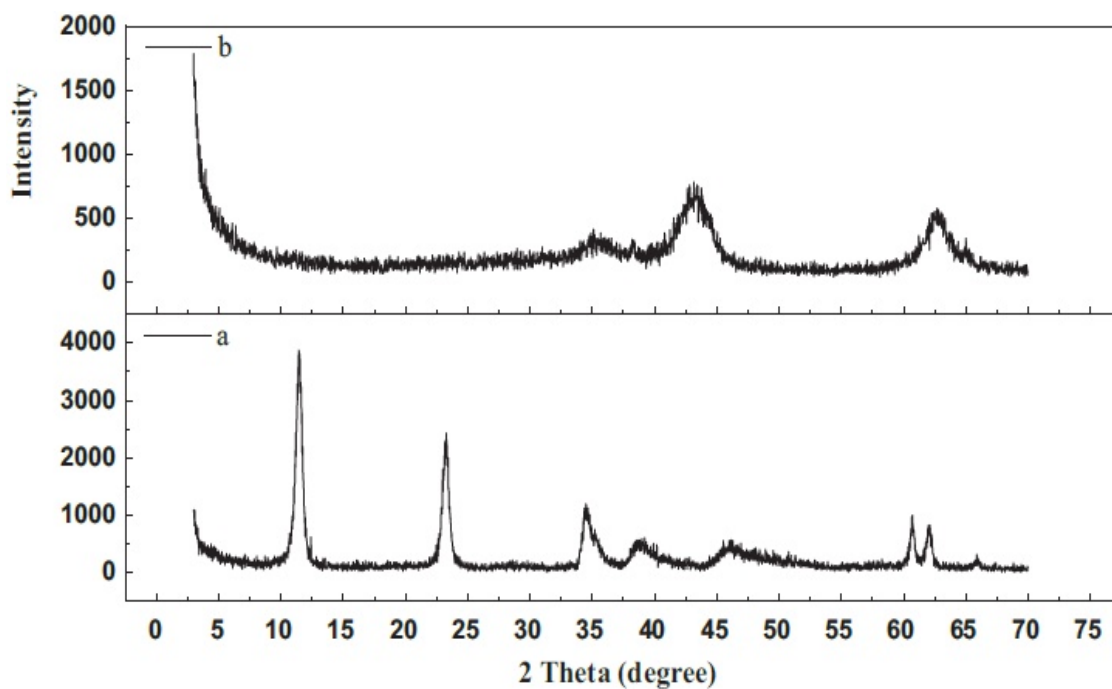**Fig. 1.** FT-IR spectra of Mg-Al layered double hydroxide (uncalcinated).

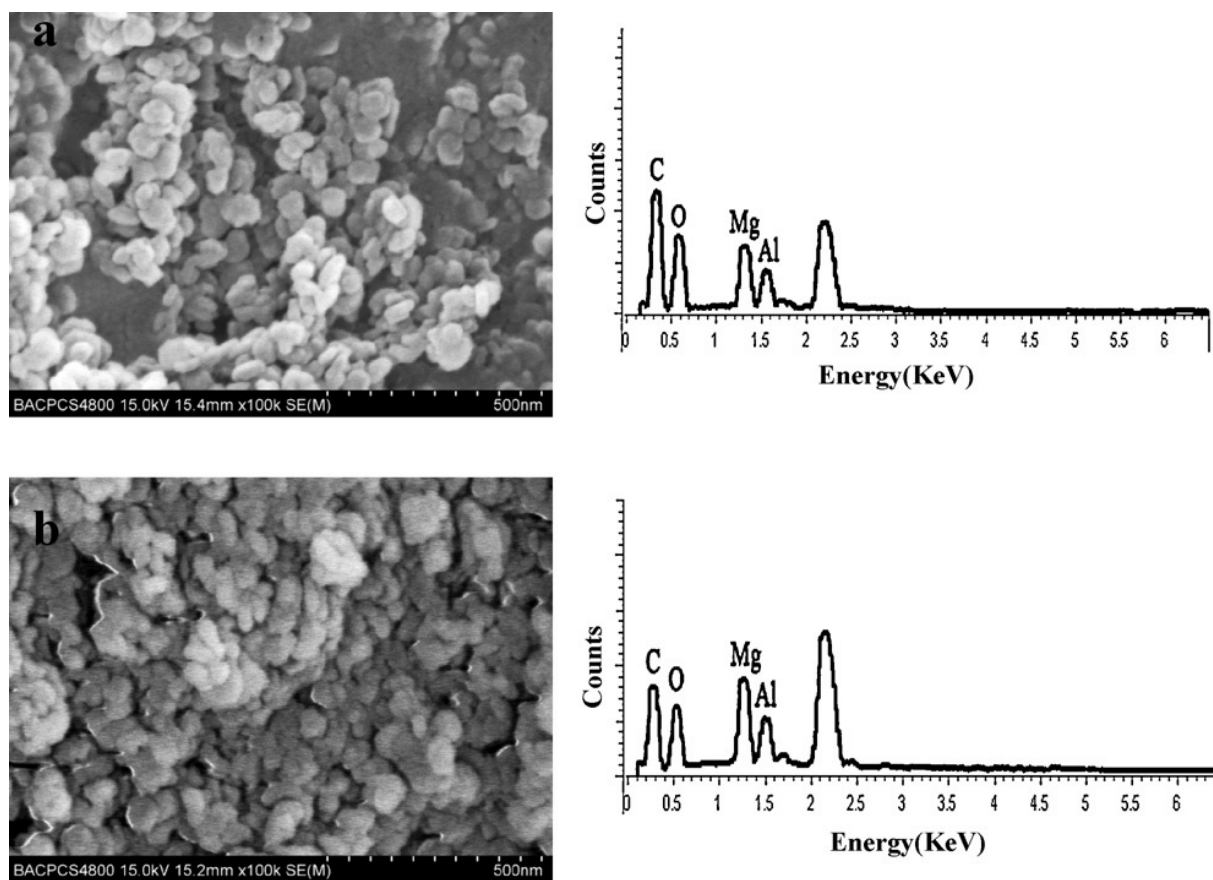**Fig. 2**. XRD patterns of (a) Mg–Al–CO$_3$ LDHs, (b) Mg–Al–CO$_3$ LDHs calcined at 500°C

Fig. 3. SEM images and corresponding EDX spectrum of (a) Mg–Al–CO$_3$ LDHs, (b) Mg–Al–CO$_3$ LDHs calcined at 500°C.

Moreover, corresponding EDX spectrum of CLDH still showed the presence of Mg, Al, C, O, although their contents are lower than those in Mg–Al–CO$_3$ LDHs, indicating that carbonate was not completely removed after calcined at 500°C. According to BET analysis the specific surface area of the LDH was 10.2 m^2/g.

3.2. Fitting data

In order to find the statistical significance of the quadratic model, the analysis of variance (ANOVA) was carried out as presented in Table 2. As it is shown in results, this regression was statistically significant at F-value of 168.01 and values of prob > F (<0.0001). Fitting the model was checked by the determination of the coefficient (R^2) [15]. In this case, the value of the determination coefficient (R^2 = 0.9906) indicated that only 0.94% of the total variable was not explained by the model. The closer the R^2 is to 1, the stronger the model and the better it predicts the response. The term adjusted R^2 = 0.9847 is also high as the value of the adjusted determination coefficient, showing a high significance of the model (Table 3). The value of predicted R^2 is also high to support for a high significance of the model. The regression equation after the analysis of variances (ANOVA) gave the level of DBT removal as a function of the calcination temperature (°C), the adsorbent amount (mg), DBT concentration (ppm) and time (min). The experimental results of the BBD design were fitted with a second-order full polynomial equation by applying multiple regression analysis on the experimental data (Eq. 3). The empirical relationship between desulfurization (Y) and the four test variables in coded units obtained by the application of RSM is given by:

Y = 44.139 + 12.411 X$_1$ + 5.044 X$_2$ - 4.487 X$_3$ + 8.345 X$_4$ + 1.765 X$_1$ *X$_1$ - 2.375 X$_2$*X$_2$ + 6.526 X$_1$*X$_4$ + 2.871 X$_2$*X$_3$ + 5.285 X$_2$*X$_4$ - 3.796 X$_3$*X$_4$ (3)

X$_1$ = Calcination temperature (°C)

X$_2$ = Adsorbent amount (mg)

X$_3$= DBT concentration (ppm)

X$_4$ = Time (min)

Where Y is a response variable of desulfurization efficiency. The model explained perfectly the experimental range studied, as can be seen from a comparison of the graphical representation of actual vs. predicted values (Fig. 4).

The Analysis of variance for regression, Lack of fit, residuals and total sources of variations are listed in Table 2. By application of F-value and p-value which are listed in Table 2, the significance of each coefficient can be determined [14]. The more amounts of the coefficients is the larger magnitude of the F-value and contrarily the small amount of the p-value. The p-values less than 0.0500 also indicate high significant regression at 95% confidence level. In this case, the first-order main effects, square effects and interaction effects of calcination temperature, adsorbent dosage, sulfur concentration and adsorption time were significant model terms [16].

The student t distribution and the corresponding values, along with the parameter estimate, are given in Table 4. In order to understand the pattern of mutual interactions between the test variables, it is necessary to check the p-value as a tool to indicate the significance of each coefficient. The optimum value the more significant corresponding coefficient is the larger amount of the t-value and contrarily the small p-value.

3.3. Response surface and contour plots for desulfurization process

Better understanding of the interactions between factors could be achieved by graphical representation of the resulted regression equation (Eq. (3)) via three-dimensional (3D) response surface plots. These helps to determine the optimum level of each factor for obtaining maximum process efficiency. Such plots of the dependent y-factor as a function of two independent factors, while other factors fixed at the corresponding levels, give worthy information about the main factors and the interactions of such two independent factors.

Table 2. Analysis of variance (ANOVA) for fit of desulfurization efficiency from Box-Behnken design.

Source of variations	Sum of square	Degree of freedom	Adjusted mean square	F-value	P-value
Regression	3673.39	10	367.34	168.01	0.000
Lack of fit	34.76	14	2.48	22.32	0.044
Residuals	0.22	2	0.11	-	-
Total	3708.37	26	-	-	-
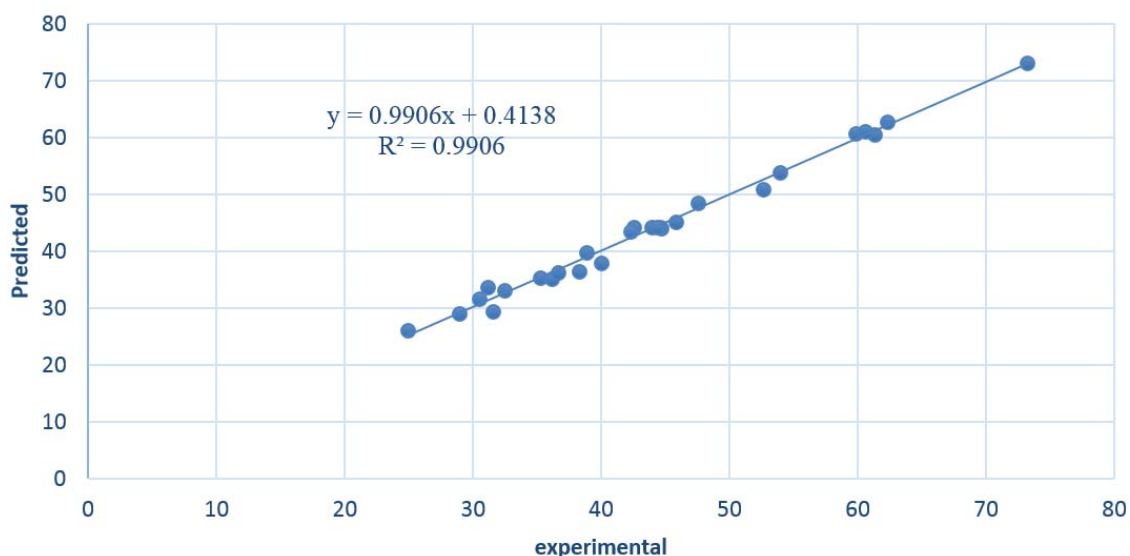
Fig. 4. Comparison of the experimental results of desulfurization efficiency with those calculated via Box-Behnken design resulted equation.

Alternatively, 2D contour plot is the projection of 3D surface plot on a two dimensional page. Three-dimensional response surface plots and counter plots computed by means of the response surface model for desulfurization of Oil derivatives are shown in Figs. 5 and 6, revealing the predicted effects of factors upon response.

As the figures represent the increasing in calcination temperature, reaction time and adsorbent amount enhance the efficiency of the desulfurization process and addition in a dosage of the DBT amount causes a decrease in desulfurization process. It is clearly obvious that the increase in calcination temperature causes more depletion in the holes of the layers because of carbonate and hydroxyl groups' emancipation and providing more anionic holes for adsorption of the DBT from the solution.

**Table 3**. Statistical measures and performance of the RSM using Analysis of variance (ANOVA).

S	R-sq	R-sq (adj)	R-sq (pred)
1.47863	99.06%	98.47%	96.48%

Table 4. Estimated regression coefficients and corresponding t and P-values from the data of Box-Behnken design experiments.

Coefficient	Parameter estimate	Standard Error	t-value	P-value
b0	44.139	0.493	89.55	0
b1	12.411	0.427	29.08	0
b2	5.044	0.427	11.82	0
b3	-4.487	0.427	-10.51	0
b4	8.345	0.427	19.55	0
b11	1.765	0.584	3.02	0.008
b22	-2.375	0.584	-4.06	0.001
b14	6.526	0.739	8.83	0
b23	2.871	0.739	3.88	0.001
b24	5.285	0.739	7.15	0
b34	-3.796	0.739	-5.13	0
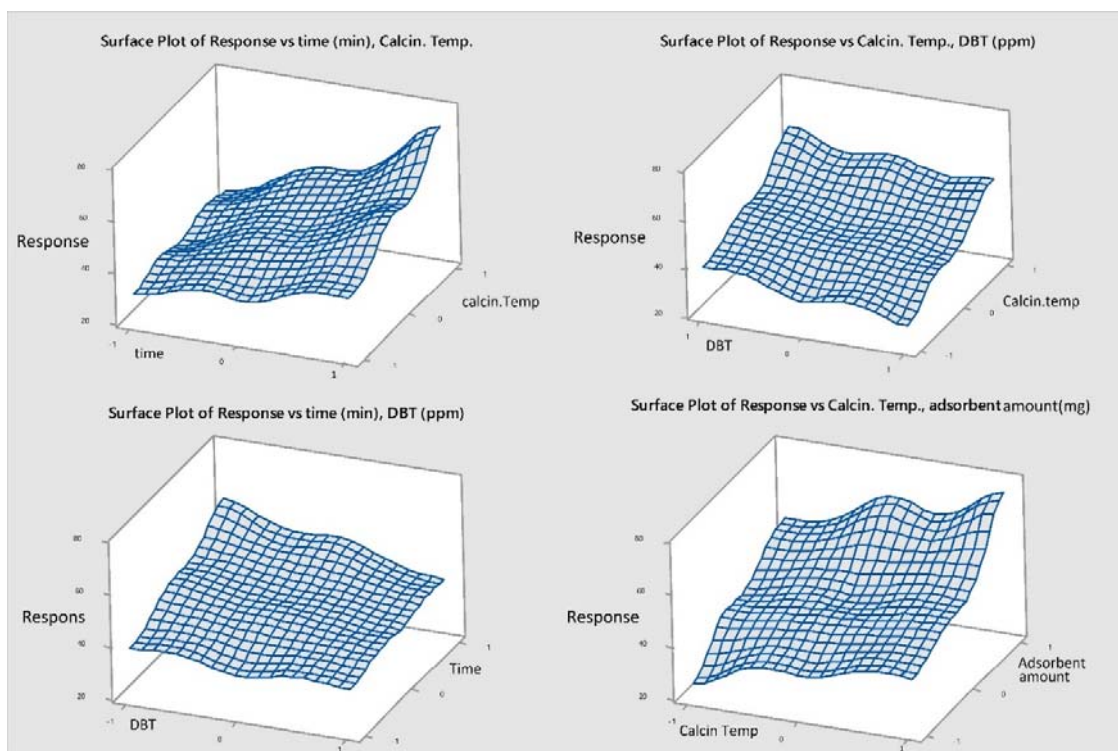
Fig. 5. The response surface plots for desulfurization efficiency as the function of: (a) Calcination temperature (℃) and treatment time (min), (b) Calcination temperature (℃) and DBT concentration (ppm), (c) Treatment time (min) and DBT concentration (ppm) and (d) Adsorbent amount (mg) and calcination temperature (min).
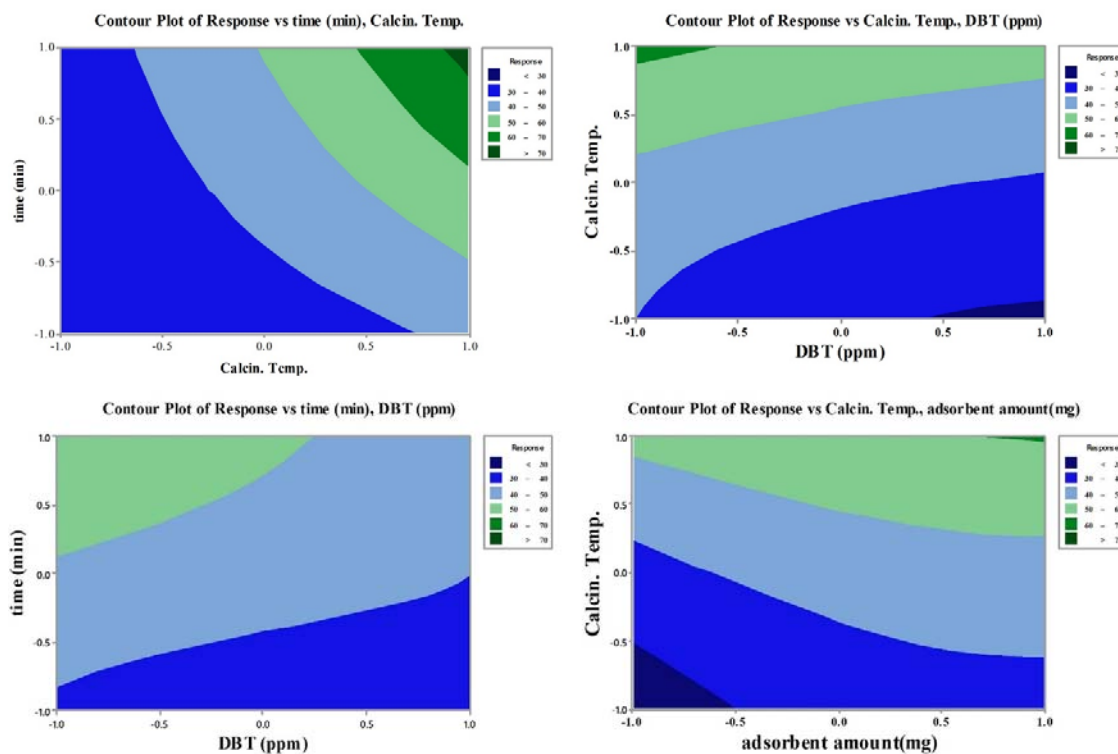
Fig. 6. The contour plots for desulfurization efficiency as the function of: (a) Calcination temperature (℃) and treatment time (min), (b) Calcination temperature (℃) and DBT concentration (ppm), (c) Treatment time (min) and DBT concentration (ppm) and (d) Adsorbent amount (mg) and calcination temperature (min).

Increase in reaction times is one of the most important factors in the process efficiency because of providing enough time for the layers to adsorb as much DBT as they can. After a Specified period of time, the efficiency of process decreases because of holes' repletion for adsorption of DBT.

More area and more anionic holes are provided by increasing the adsorbent amount and cause much more desulfurization anticipated from the process. But, because of the determined and limited capacity of the layers addition in a dosage of the DBT decreases adsorption efficiency. The best feature of the layered double hydroxides is that the ability of the adsorptive property can be easily returned by heating the layers after process till 500-600 °C to desorb the DBT. The relative importance of each term of the model was evaluated by Pareto analysis according to the following equation, which gives the percentage effect of each term on the response [21,22].

$$P_i = \left(\frac{b_i^2}{\sum b_i^2}\right) \times 100 \ (i \neq 0) \tag{4}$$

The collected results in Fig. 7 show the following sequence for relative importance of the terms containing singular factor: A (calcination temperature =17.262) > D (Time = 11.6072) > B (adsorbent amount =4.0159) > C (DBT =6.2403). The sequence of importance of quadratic terms is as follows: AD (5.2408) > BD (4.2439) > CD (3.0480) > BC (2.3050) > AB (0.7486) > AC (0.5382).

As it is obviously shown on the figure the most important factor playing a substantial role in enhancing the efficiency is calcination temperature. Preheating the layered double hydroxides in order to purify the layers from any anions or the water molecule seemed so necessary for removal process. Providing enough time for process and adsorbent amount are the second and third important factor for enhancing the efficiency of the removal the process by providing the enough time fill the all capacity of the adsorbent and increasing new layer for removal process; respectively. Minus sign of X_3 (DBT concentration) in Eq.3 confirms negative effect of the variable on the response and last important factor for the process but negatively reduces the efficiency of the process.

3.4. Determination of optimal conditions for desulfurization

In this experiment for desulfurization of DBT efficiency, the desired goal was defined as "maximize" to gain the highest desulfurization performance.
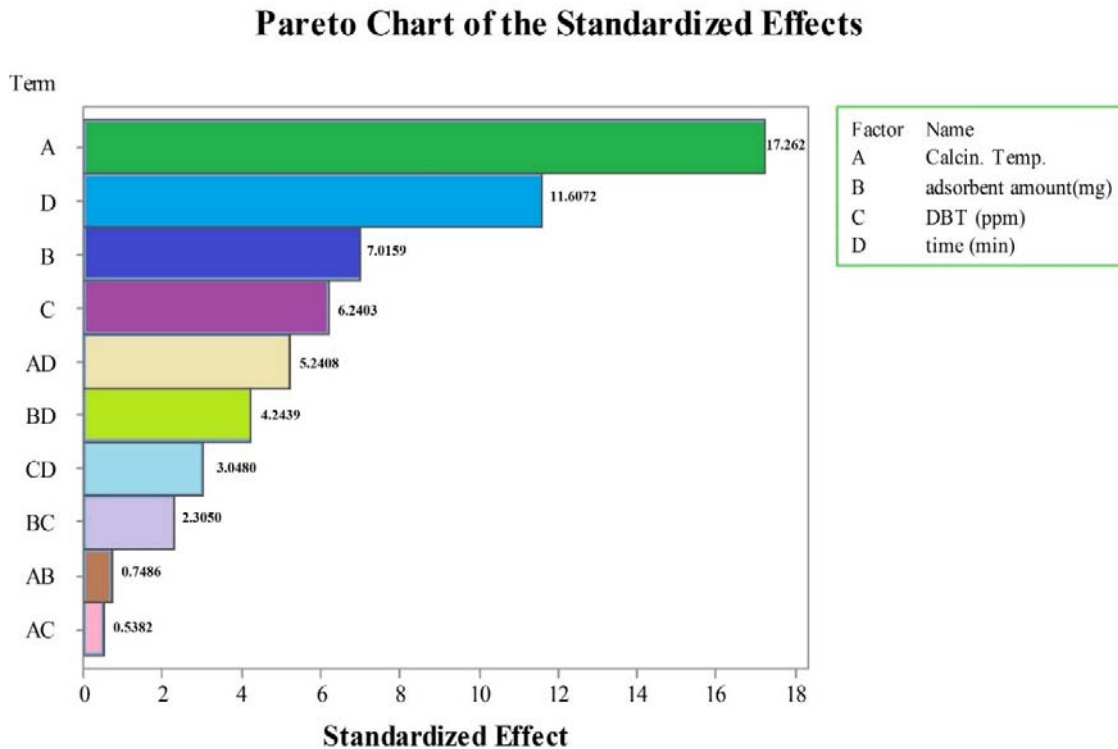

Fig. 7. The Pareto plot showing graphical importance of each 4 factors on the efficiency of the removal process.

The optimum values of the process variables in optimum conditions are 600 (℃), 50 (ppm), 0.1 (mg) and 120 (min) for calcination temperature, DBT concentration, adsorbent amount and reaction time, respectively. After a further experimental test with the predicted values for verification, the result indicates that the maximum desulfurization efficiency was obtained when the values of each parameter were set as the optimum values. Optimizing of the adsorption conditions and achieving to the maximum removal efficiency by RSM for the desulfurization process from oil derivative using Mg-Al LDH was effective. It seems that there is some specific interactions including polar interaction and acid-base interaction may exist between the surface functionalities of LDH and the sulfur atom of DBT. Consequently, DBT adsorption onto LDH in this work is mainly through the dispersive interaction, which is a kind of physisorption. In other words, physisorption is still the dominant mechanism in this situation although more types of interactions exist now. The presence of hydroxyl groups on the surface of LDH increases the adsorption rate.

3.5. Discussion: Optimization using the desirability function

For optimization of the process, we choose the desired goal for each factor and response from the menu. The possible goals are: maximize, minimize, target, within range, none (for responses only) and set to an exact value. For each parameter, a minimum and a maximum level must be provided. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. The study seeks to maximize this function. The goal seeking begins at a random starting point and proceeds up the steepest slope to a maximum. Because of curvature in the response surfaces and their combination into the desirability function, there may be two or more maximums. Chances improve for finding the "best" local maximum by starting from several points in the design space. The numerical optimization found a point that maximizes the desirability function. A minimum level of DBT dosage (50 ppm), the maximum level of initial layered double hydroxide amount was (0.1 mg) and sulfur removal was (73.24%). The level of initial time within range of 75-120 and calcination temperature in the range of 450-600 ˚C with the excellence of 600 ˚C in some of the experiments, were set for maximum desirability. The importance of each goal was changed in relation to the other goals. The obtained value of desirability (0.9906) shows that the estimated function may represent the experimental model and desired conditions.

4. Conclusions

The results of present study showed the good adsorptive performance of Mg-Al layered double hydroxides in removal of dibenzothiophene from gasoil model. The experiments were performed as a function of initial calcination temperature, adsorbent dosage, DBT concentration in pure n-heptane and reaction time. The obtained results showed that Mg-Al LDH is a good adsorbing medium for sulfur-bearing compounds and had high adsorption yields for the treatment of oil derivative containing sulfur as a harmful and detrimental material for both industry and environmental. After optimization of the desulfurization process with response surface methodology, the final experiment was carried out with the optimized amount of the factors and resulted in 73.24% DBT removal. Mg-Al LDH (SEM) shows the surface of the adsorbent seems to have multi-layered walls available for the sulfur bearing compounds and anions.

Acknowledgements

References

[1] A. Bösmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz, P. Wasserscheid, Chem. Commun. (2001) 2494-2495.

[2] H. Lü, J. Gao, Z. Jiang, F. Jing, Y. Yang, G. Wang, J. Catal. 239 (2006) 369-375.

[3] A.J. Hernández-Maldonado, R.T. Yang, AIChE. J. 50 (2004) 791-801.

[4] P.S. Kulkarni, C.A.M. Afonso, Green Chem. 12 (2010) 1139-1149.

[5] K.G. Knudsen, B.H. Cooper, H. Topsøe, Appl. Catal. A 189 (1999) 205-215.

[6] A. Stanislaus, A. Marafi, M.S. Rana, Catal. Today 153 (2010) 1-68.

[7] H. Mei, B. Mei, T.F. Yen, Fuel 82 (2003) 405-414.

[8] D. Wang, E.W. Qian, H. Amano, K. Okata, A. Ishihara, T. Kabe, Appl. Catal. A 253 (2003) 91-99.

[9] K. Yazu, Y. Yamamoto, T. Furuya, K. Miki, K. Ukegawa, Energy Fuels 15 (2001) 1535-1536.

[10] Y.L. Yun Zhi, Q. Zhang, H. Wang, Langmuir 26 (2010), 15546–15553.

[11] D.G. Evans, R.C. Slade, Structural Aspects of Layered Double Hydroxides, 1st Ed., Springer, Berlin, 2006.

[12] Z. Liu, R. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada, T. Sasaki, J. Am. Chem. Soc. 128 (2006) 4872-4880.

[13] H. Derikvandi, A. Nezamzadeh-Ejhieh, J. Colloid Interface Sci. 490 (2017) 652-664.

[14] R.H. Myers, D.C. Montgomery, C.M. Anderson-Cook, Response Surface Methodology, 3rd Ed., John Wiley & Sons, New Jersey, 2016.

[15] N.S. El-Gendy, H.N. Nassar, S.S. Abu Amr, J. Pet. Sci. Technol. 32 (2014) 1669-1679.

[16] V. Gunaraj, N. Murugan, J. Mater. Process Technol. 88 (1999) 266-275.

[17] B.S. Zakaria, H.N. Nassar, S.S.A. Amr, N.S. El-Gendy, Pet. Sci. Technol. 33 (2015) 880-892.

[18] C.A. Basha, R. Saravanathamizhan, P. Manokaran, T. Kannadasan, C.W. Lee, Ind. Eng. Chem. Res 51 (2012) 2846-2854.

[19] M.B. Kasiri, H. Aleboyeh, A. Aleboyeh, Environ. Sci. Tech. 42 (2008) 7970-7975.

[20] O. Kempthorne, The Design and Analysis of Experiments, 1st Ed., John Wiley & Sons, New Jersey (1952).

[21] H. Derikvandi, A. Nezamzadeh-Ejhieh, J. Colloid Interface Sci. 490 (2017) 628-641.

[22] M. Nosuhi, A. Nezamzadeh-Ejhieh, Electrochim. Acta 223 (2017) 47-62.