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# Study of cadmium adsorption onto calcite using full factorial experiment design

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## ABSTRACT

Full factorial experimental design technical was used to study the main effects and interactions between operational parameters in batch adsorption of cadmium using calcite as adsorbent. The significant parameters which affect cadmium removal efficiency and adsorption amount, such as initial concentration, adsorbent dose, temperature and contact time, were investigated. Parameters that influence the cadmium removal efficiency from water were evaluated statistically by using factorial plots: the Pareto chart, main effect, interaction effect, contour plot, surface plot and the cube plot. Analysis of variance and p-value significant levels were used to check the significance of the effect on percentage removal. The statistical analysis was allowed to verify that the four studied parameters have an influence on the cadmium elimination (p-values $\leq 0.05$ and $R^2 = 0.9652$). It was found that the most effective parameters of adsorbed cadmium amount were initial concentration and adsorbent dose. The interaction between initial concentration and adsorbent dose was the most important factor.

*Keywords:* Cadmium removal; Adsorption; Water treatment; Calcite; ANOVA; Full factorial design

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## 1. Introduction

Pollution of water resources is an important environmental problem in the modern societies, arise from unsustainable social development. Ions of metal elements including copper, lead, cadmium, nickel and chromium, mainly present in industrial and domestic wastes, may cause serious intoxications in water and soil media and also cause dangerous effects on human health [1]. Investigation of cadmium effects on human health indicated that long-term contact with the cadmium compounds will cause kidneys disorders (Fanconi's syndrome), cancers, skeletal decays (itai-itai syndrome), high blood pressure, mental disorders, pulmonary disorder, weight loss, hepatic and blood disorders [2–4]. The World Health Organization has set a guidance value of 0.003 mg/L for cadmium in drinking water. Treatment and remediation of water contaminated with heavy metals, as a main concern of many researchers in the world, are exceedingly important. Several methods have been developed in wastewater treatment technology to remove heavy metals from wastewater, such as chemical precipitation [5], ion exchange [6], membrane filtration [7] and electrochemical processes [8,9]. Among them, adsorption technique is found to be the most effective treatment process with selection of a proper adsorbent [10,11]. The significant advantages of the adsorption technique are; high efficiency in removing very low levels of heavy metals from dilute solutions, easy handling, high selectivity, lower operating cost, minimization of chemical or biological

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sludge, and regeneration of adsorbent [12]. A wide range of adsorbents including activated carbon [13], waste mud [14] montmorillonite, kaolin, tobermorite, magnetite, silica gel and alumina [15] lime mud and boiler cash generated from a pulp and paper factory [16], and bacteria [17] have been tested for their heavy metal adsorption capacity.

Geological calcium carbonate ($CaCO_3$) is among the most abundant minerals and usually exists in two polymorphs: calcite (CAL, trigonal) and aragonite (ARA, orthorhombic). Calcite is the crystalline form of $CaCO_3$, highly stable and insoluble in water. Calcite-water systems supplied carbonate ions to solutions, producing insoluble metal species. This mechanism involves the formation of metallic carbonates which remain at bottom or fixed on the surface of soil particles. pH control is essential in this process, because soluble bicarbonate species are produced under pH = 8.

Calcite is one of the important cheapest and harmless biomaterials and had already been studied for heavy metal ions removal [18]. $CaCO_3$ has been utilized in the immobilization of a wide variety of cadmium by many investigators [19–21].

Several factors influencing the adsorption of cadmium onto calcite such as adsorbent dose, contact time, initial concentration of cadmium, and temperature have been considerably studied and reported. Previous researchers use the traditional one variable at a time experiments to determine the individual effect of various factors on adsorption processes [22–24]. However, factorial design technique can be employed to provide a large amount of information and reduce the number of experiments, time, and overall research cost. The most important advantages of this technique are that the effects of individual parameters as well as their relative importance are obtained and that the interactional effects of two or more variables can be known [25]. Recently, a number of investigations have been conducted using this technique to model pollutant adsorption process [26–30]. One of the goals of this study is to apply a two-level design of experiment in order to determine the influence of these parameters and their interactions on the removal efficiency of cadmium.

Preliminary tests of cadmium adsorption were carried out with calcite to assess the different factors influencing the cadmium sorption.

## 2. Materials and methods

### 2.1. Adsorbent

In this study, natural calcite used as an adsorbent in the experiments was received from mountain Borj Cedria, located in the southern of Tunisian suburb, the capital city of Tunisia. It was used directly in the natural state.

The chemical composition of natural calcite samples was obtained by X-ray diffration (XRD) using a Bruker D8 Advance diffractometer equipped with $CuK_\alpha$ ($\lambda$ = 1.541) X-rays. Moreover, the functional groups present in the solid sample were identified using Fourier transform-infrared spectrometry (FTIR) with the KBr disk method (Perkin, Elmer, UK). The particle size distribution of the calcite was determined using a Malvern Mastersizer STD06 laser granulometer. The $pH_{zpc}$ (pH isoelectric point) of the sample was determined by the procedure described by Wan Ngah and Hanafiah [31], using 0.2 g of adsorbent in 100 mL aqueous solution of NaCl (0.1 M) at different values of initial pH of 2, 4, 6, 8, 10, and 12.

### 2.2. Adsorbate

Cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) with purity of 95% (Merck) was used for preparing solution in various concentrations. A stock cadmium solution of 1.000 mg/L was prepared with distilled water and used throughout this study. The analysis of cadmium concentrations at the outlet of the batch was performed using an atomic absorption spectrometer analytik novAA 350. During the assays, the pH values were adjusted with 0.1 M HCl or 0.1 M NaOH. The pH measurements were performed using a pH meter 692 pH/ion meters, Metrohm.

### 2.3. Batch adsorption experiments

All batch cadmium sorption studies were carried out in a high-density polyethylene bottles which were kept in an orbital shaker with thermostatic control (Grant OLS 200).

The required concentrations of metal ion solution were prepared by appropriate dilutions of the stock solution. The applicability of natural calcite for elimination of cadmium was conducted by adding 0.5 g of adsorbent in 500 mL of a solution with initial cadmium concentration varying between 5–50 mg/L at 25°C and pH between 2 and 8. The mixtures were agitated at a speed of 400 rpm for 120 min to reach equilibrium. Samples were withdrawn behind a definite time interval and filtered through 0.45 µm whatman filter paper. After equilibrium, the adsorbent was separated from the metal ion solutions by centrifugation and the filtrates were analyzed for the cadmium levels by a flame atomic absorption spectrometer.

The amount of adsorption at equilibrium ($q_e$, mg/g) were calculated according to Eq. (1)

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{1}$$

The removal percentage of cadmium was calculated using Eq. (2):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where $C_0$ and $C_e$ are the initial and equilibrium concentrations (mg/L), $V$ is the volume of solution (L), and $m$ is the weight of calcite (g). In all figures, the error bars represent the standard deviation of three identical experimental points.

### 2.4. Statistical design

Factorial design was employed to reduce the total number of experiments in order to achieve the best overall optimization of operating conditions. For the $2^4$ experimental designs, the four independent variables were coded as $X_1$, $X_2$, $X_3$ and $X_4$ at two levels. The higher level was designated as +1 and the lower level as −1.The coded values of process parameters were determined by Eq. (3):

$$X_{ij} = \frac{x_{ij} - x_j^0}{\text{step}} \quad (3)$$

where $X_{ij}$ is the jth coded variable of the ith experimentation, $x_{ij}$ is the jth uncoded variable of the ith test, $x_j^0$ is the uncoded value of the ith test variable at the center point, and the step is the variation of the uncoded variable j.

## 3. Results and discussion

### 3.1. Adsorbent characterization

#### 3.1.1. Laser granulometer

The particle size distribution of the used calcite was determined using a Malvern Mastersizer STD06 laser granulometer. The particle diameter of the natural calcite was illustrated in Fig.1. In fact, the studied sample was found to contain 10% particles with diameters smaller than 2.8 µm, 50% particles with diameters smaller than 10.1 µm, and 95% particles with diameters smaller than 32.1 µm. The mean particle diameter is 10.1 µm.

#### 3.1.2. Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy, which could provide some useful information on the structure and conformation of molecules, were employed to investigate the existing state of our adsorbent. From the FTIR spectrum of the used adsorbent illustrated in Fig. 2, it can be seen that the adsorbent has adsorption bands at 2924–2872 cm$^{-1}$, corresponding to the vibration mode of C–H of stearic acid, and also 718, 875 and 1425 cm$^{-1}$ corresponding out plane bending and asymmetrical stretching vibration peaks of O–C–O, respectively. IR spectra of the adsorbent are in agreement with the calcite characteristic vibrations [32].

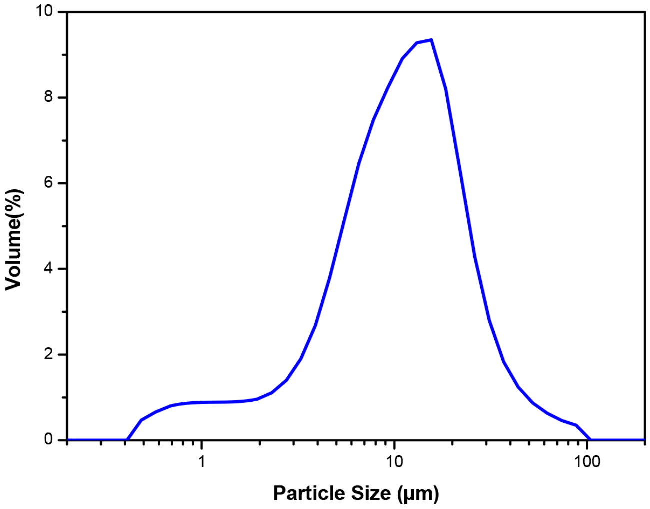

Fig. 1. Granulometric range curve of calcite.

#### 3.1.3. X-ray diffraction

The XRD pattern of the calcite sample is shown in Fig. 3 before and after cadmium adsorption: (a) sample of calcite pure and (b) after cadmium adsorption. The adsorption product of the reaction is carried out 0.01 g of calcite and 40 mg/L of initial cadmium concentration, at 18°C and pH 3.5 for 1 h. The studied sample diffractions exhibit three characteristic peaks of calcite crystals which become localized in 2θ angles of 29.39, 47.50 and 48.49°, corresponding to d-spacing of 3.03, 1.91 and 1.87 respectively. Other peaks from the calcite crystal plane can be observed in minor intensity. The synthesized calcite belongs to the calcite structural type (PDF # 5–586 and 85–1108), and it was of pure calcite phase, they are composed of pure calcite phase. The sample is pure phase without other mineral impurity. Additionally, d-spacing of the (1 0 4) plane increases after cadmium adsorption.

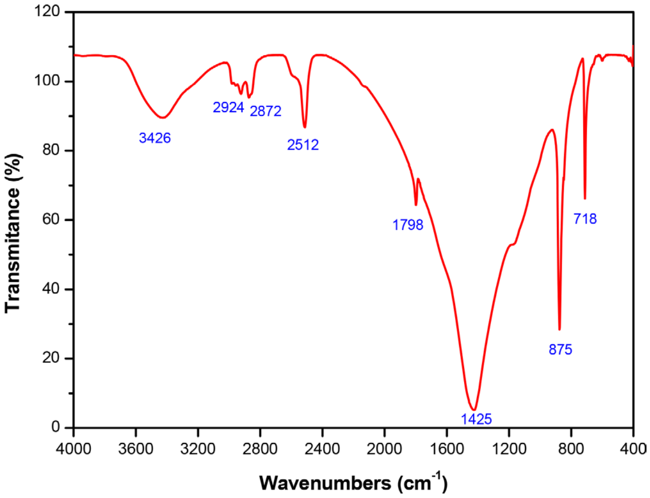

Fig. 2. FTIR-Spectra of calcite.

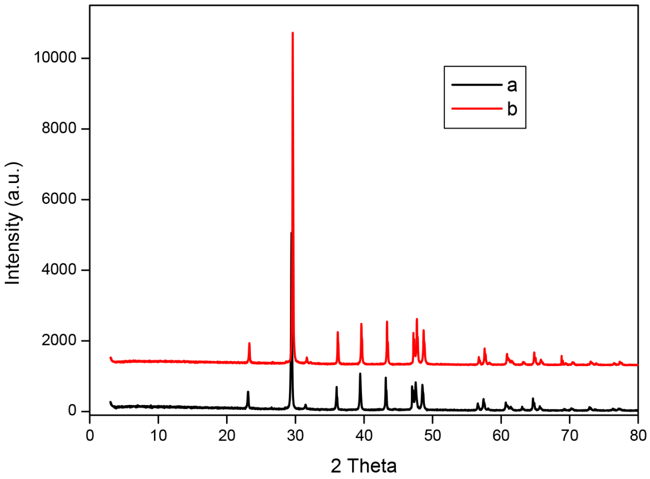

Fig. 3. XRD patterns of the calcite sample before and after cadmium adsorption: (a) before, (b) after cadmium adsorption (Adsorbent dose = 0.4 g/L, Cadmium concentration = 40 mg/L, pH = 3.5 and T = 18°C).

### *3.2. Parameters affecting the adsorption*

Adsorption processes were affected by several factors, such as contact time, initial concentration of cadmium, adsorbent dose, and temperature. The main purpose of this study is to establish the optimal conditions, of the adsorbent capacity.

#### *3.2.1. Effect of initial pH of solution*

The removal of cadmium from aqueous solution is highly dependent on the pH. It influences the strength of cadmium adsorption mechanism as it determines the degree and sign of the charge on these ions. For aqueous pH lower than 4, the dominant species is free $Cd^{2+}$.

For pH higher than 6, cadmium is mainly present as $CdHO_3^+$, $CdCO_{3(aq)}$ and $Cd(CO3)_3^{4+}$ [18]. In this step, only pH of the solution changes under fixed conditions for other parameters. The pH values of 2, 3, 4, 5, 6, 7 and 8 are tested. It shall be noted that at pH values more than 8, cadmium ions precipitated in the form of hydroxide compound .The effect of pH was determined by studying adsorption at an initial cadmium concentration of 5 mg/L with adsorbent dose of 0.5 g/500 mL of calcite, contact time of 90 min and using shaker at 400 rpm over a pH range of 2–8, keeping the other parameters constant at 25°C. The pH adjustments were made either with 0.1 M HCl or 0.1 M NaOH. Fig. 4 shows that the percentage removal of metal ion increase with increase of pH, to reach a maximum at pH = 3.5, reaching a maximum removal value of 100%. At higher pH acid values the surface of the adsorbents was associated with $H_3O^+$ ions and the competition between the cadmium ions and $H_3O^+$ ions for the active adsorption sites on the surface of the adsorbent cadmium to decrease in uptake of metal ions. Indeed, equilibrium pH value was evaluated to 7.4 for initial pH of 3.5. These outcomes indicate that cadmium precipitation should be negligible. This trend has been also pointed out by Rangel-Porras [18], when they studied cadmium removal using calcite materials. Consequently, the experiments carried out hereafter were conducted at an initial aqueous pH of3.5. The effect of pH can also be explained in terms of adsorbent $pH_{zpc}$ which is found around 8.3 for natural calcite. The $pH_{zpc}$ of shown that natural calcite exhibits a negative charge at pH > 8.3 and yields a positive charge at pH < 8.3. The cadmium is a cationic. Therefore, pH value was increased, the surface of the natural calcite became more negatively charged and hence electrostatic repulsion between the cadmium and adsorbent surface sites and competing effect of $H_3O^+$ ions decreased which increased the adsorption amount of metal ions onto calcite.

#### *3.2.2. Effect of initial concentration of cadmium*

The effect of initial cadmium concentration was studied by varying the initial concentration of cadmium from 5 mg/L to 50 mg/L. Other fixed conditions considered in experiments of this step are: optimized pH obtained from the first step (pH = 3.5), optimized contact time obtained from the second step (90 min), adsorbent dose 0.5 g, volume 500 mL of solution and shaking samples at 400 rpm. Fig. 5 illustrates the effect of initial cadmium concentration on the removal of cadmium using the calcite. In general, cadmium exhibited higher sorption percentages at lower starting concentrations. This evolution has been reported by quite a number of adsorption studies in literature [33–35]. Therefore, the percentage removal gradually decreased since relatively fewer active sites were available as a result of increasing the initial concentration of cadmium for the same dose of the calcite. At higher concentration the amount of cadmium ions are quite higher compared to available adsorption sites. Thus, the percentage removal of heavy metal ions mainly depends on the initial ions concentration. In effect, when the initial concentration of cadmium increase from 5 to 50 mg/L, the percentage removal of cadmium decrease from 92.8% to 37.3%.

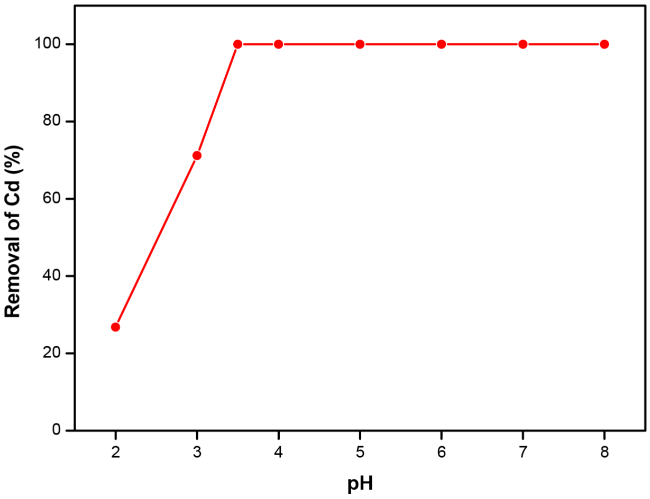

Fig. 4. Effect of initial pH of solution on efficiency of cadmium adsorption capacity by calcite (adsorbent dose = 0.5 g/L, Cadmium concentration = 5 mg/L, and contact time = 90 min).

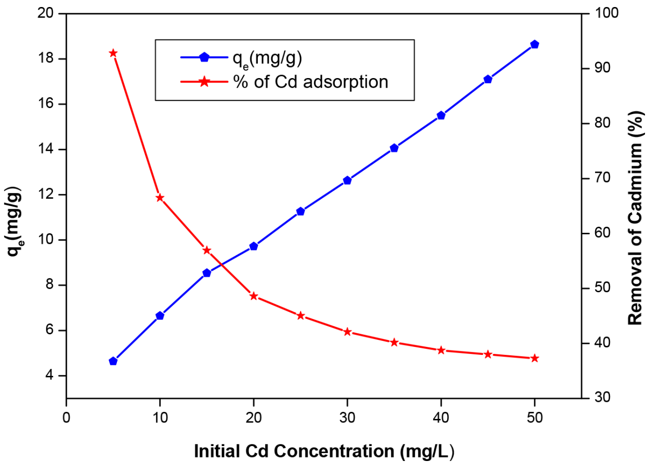

Fig. 5. Effect of initial concentration of cadmium ions in aqueous solution on efficiency of cadmium adsorption capacity by calcite (contact time = 90 min, adsorbent dose = 0.5 g/L, pH = 3.5).

### 3.2.3. Effect of contact time

A kinetics modeling is very important for the efficiency of the adsorption process. In the present study, the kinetic of cadmium removal is used to understand the adsorption behavior of natural calcite (Fig. 6). The effect of contact time on the cadmium removal was studied at pH of 3.5 with an initial cadmium concentration of 5 mg/L and an adsorbent dose 0.5 g. Initially, adsorption of the cadmium ions was fast and about 92.8% of total uptake capacity was achieved in first 90 min. It was due to high initial concentration of cadmium ions and empty metal binding sites of adsorbents [36]. After 120 min, there was no significant increase of cadmium removal. Hence the equilibrium time for the adsorption of cadmium ions using calcite was taken as 120 min. This result is important because it took calcite absorbent a lesser time to reach equilibrium when compared to most adsorption studies reported in literature [37].

## 3.3. Statistical analysis

A $2^4$ full factorial design was applied to evaluate the effects of all four factors ($X_i$) on the removal of cadmium. The experimental conditions obtained for each reaction set by the full factorial design are shown in Table 2 (experiments 1–16), together with the four central point repetitions (reactions 17–20). The high and low levels defined for the $2^4$ factorial designs are listed in Table 1. The higher level was designated as (+1) and the lower value was designated as (−1). In Table 1, $X_1$, $X_2$, $X_3$ and $X_4$represent the levels of temperature, adsorbent dose, initial concentration of cadmium and contact time respectively. The results were analyzed using the means of statistical analysis software Minitab 16 and along with the main effects the interactions of different factors were determined. The coded mathematical model for $2^4$ factorial designs can be given by the following expression Eq. (4):

$$Y = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_4 + A_{12}X_1X_2 + A_{13}X_1X_3 + A_{14}X_1X_4 + A_{23}X_2X_3 + A_{24}X_2X_4 + A_{34}X_3X_4 \ldots \quad (4)$$

where $Y$ is the percentage removal of cadmium (% R), $X_i$ is the coded variable (−1 or +1), $A_i$ represents the estimation of the principal effect of the factor i for the response % R, where as $A_{ij}$ represents the estimation of interaction effect between factor i and j for the response. The coefficient $A_0$ is the global mean of the response of 20 assays. By substituting the coefficients $A_i$ in Eq. (4) by their coded values from Table 3 we get.

$$\begin{aligned}Y &= 33{,}936 + 5{,}437X_1 + 9{,}900X_2 - 5{,}850X_3 + 6{,}100X_4 +\\&2{,}863X_1X_2 - 3{,}712X_1X_3 + 1{,}863X_1X_4 - 8{,}250X_2X_3 +\\&5{,}125X_2X_4 - 4{,}050X_3X_4 - 1{,}837X_1X_2X_3 + 2.513X_1X_2X_4\\&-1{,}737X_1X_3X_4\\&-3{,}575X_2X_3X_4 - 1.638X_1X_2X_3X_4\end{aligned} \quad (5)$$

The experimental design matrix for cadmium removal by adsorption from aqueous solutions is given in Table 2. According to the results, cadmium removal was varied between 16.8% and 100%. Higher value of cadmium removal was obtained under elevated temperature with minimum initial concentration (experiment 12).

The results of the experimental design were analyzed using Minitab 16 statistical software to assess the effects as well as the statistical parameters and the statistical plots. The coded values of variables with the responses were illustrated in Table 4 for cadmium removal. The mains effect is the difference between the responses of two levels (high and low level) of factors. The regression model coefficients are obtained by dividing the effects by two, the standardized effects are obtained by dividing the regression coefficients by standard error coefficient [38]. The p-values are used as a tool to check the significance of each coefficient, which in turn may indicate the pattern of the interactions between the independent variables. If the p-value is below 0.05, then the model is significant at the 95% confidence interval [39]. The Pareto plot represents the absolute values of the effects of main factors and the effects of interactions factors.

$R^2 = 0.9652$, $R^2_{(adj)} = 0.8349$

### 3.3.1. Student's t-test

Pareto's charts were used to evaluate the meaning and type of effects. Pareto analysis indicates the relative

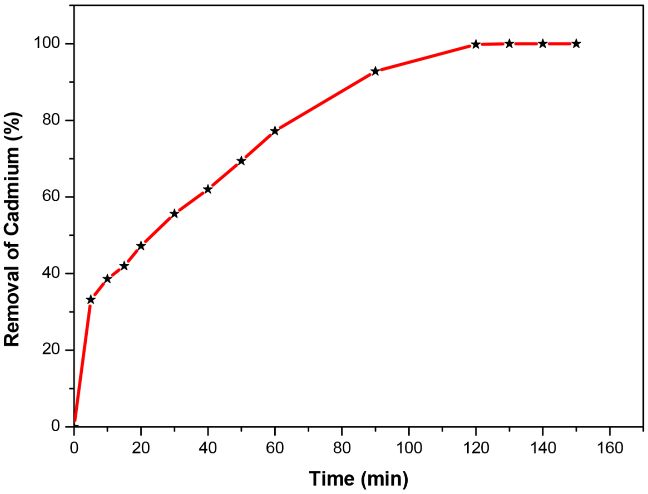

Fig. 6. Effect of contact time on efficiency of cadmium adsorption capacity by calcite (adsorbent dose = 0.5 g/L, cadmium concentration = 5 mg/L, pH = 3.5 and T= 25°C).

Table 1
Factors and levels used in $2^4$ factorial design

| Variables | Factors | Unit | Experimental region | |
|---|---|---|---|---|
| | | | Minimum value (−1) | Maximum value (+1) |
| $X_1$ | Temperature (A) | °C | 10 | 40 |
| $X_2$ | Adsorbent dose (B) | G | 0.1 | 0.5 |
| $X_3$ | Initial concentration of cadmium (C) | mg/L | 5 | 50 |
| $X_4$ | Contact time (D) | Min | 10 | 90 |

Table 2
Experimental design matrix with the results of 2^4 full factorial design

| Experiment | A (°C) | $X_1$ | B(g) | $X_2$ | C (mg/L) | $X_3$ | D (min) | $X_4$ | R(%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 10 | –1 | 0.1 | –1 | 5 | –1 | 10 | –1 | 16.80 |
| 2 | 40 | 1 | 0.1 | –1 | 5 | –1 | 10 | –1 | 26.80 |
| 3 | 10 | –1 | 0.5 | 1 | 5 | –1 | 10 | –1 | 34.60 |
| 4 | 40 | 1 | 0.5 | 1 | 5 | –1 | 10 | –1 | 46.80 |
| 5 | 10 | –1 | 0.1 | –1 | 50 | 1 | 10 | –1 | 26.10 |
| 6 | 40 | 1 | 0.1 | –1 | 50 | 1 | 10 | –1 | 29.00 |
| 7 | 10 | –1 | 0.5 | 1 | 50 | 1 | 10 | –1 | 26.00 |
| 8 | 40 | 1 | 0.5 | 1 | 50 | 1 | 10 | –1 | 29.50 |
| 9 | 10 | –1 | 0.1 | –1 | 5 | –1 | 90 | 1 | 20.80 |
| 10 | 40 | 1 | 0.1 | –1 | 5 | –1 | 90 | 1 | 28.60 |
| 11 | 10 | –1 | 0.5 | 1 | 5 | –1 | 90 | 1 | 56.80 |
| 12 | 40 | 1 | 0.5 | 1 | 5 | –1 | 90 | 1 | 100 |
| 13 | 10 | –1 | 0.1 | –1 | 50 | 1 | 90 | 1 | 28.60 |
| 14 | 40 | 1 | 0.1 | –1 | 50 | 1 | 90 | 1 | 28.50 |
| 15 | 10 | –1 | 0.5 | 1 | 50 | 1 | 90 | 1 | 31.20 |
| 16 | 40 | 1 | 0.5 | 1 | 50 | 1 | 90 | 1 | 38.70 |
| 17 | 25 | 0 | 0.3 | 0 | 27.5 | 0 | 50 | 0 | 27.78 |
| 18 | 25 | 0 | 0.3 | 0 | 27.5 | 0 | 50 | 0 | 26.69 |
| 19 | 25 | 0 | 0.3 | 0 | 27.5 | 0 | 50 | 0 | 27.45 |
| 20 | 25 | 0 | 0.3 | 0 | 27.5 | 0 | 50 | 0 | 28.00 |

importance of each independent model's parameter and their interactions on the removal of cadmium. Bar lengths are proportional to the absolute value of the estimated effects, allowing comparing relative importance of the effects. If an effect is much as the experimental error, it will be meaningless. But if it is more than the experimental error, it will be meaningful. The vertical line indicates minimum statistically significant effect magnitude for a 95% confidence level. The values displayed in the horizontal columns are Student's t-test values for each effect. According to the data presented in Table 3 and graphical Pareto chart showed in Fig. 7, the final first-order model for cadmium removal (%R) in term of coded parameters is given by Eq. (5):

$$Y = 33{,}936 + 5{,}437X_1 + 9{,}900X_2 - 5{,}850X_3 + 6{,}100X_4 + 2{,}863X_1X_2 - 8{,}250X_2X_3 + 5{,}125\,X_2X_4 \quad (6)$$

Moreover, by analyzing the values in Table 3, it can be concluded that the adsorbent dose (B) was the most important parameter of the overall adsorption procedure. The positive value of its coefficient indicates that the amount of cadmium adsorbed by calcite was favored at high adsorbent dose (0.5 g). The second important factor for overall optimization of the adsorption process was contact time (D). According to Table 3, the interaction of two factors (BD) was more significant than the main factor (AB). The positive value of the coefficient of this interaction indicated an increase in the adsorbent dose and the contact time which provide an increase in the response (Y).

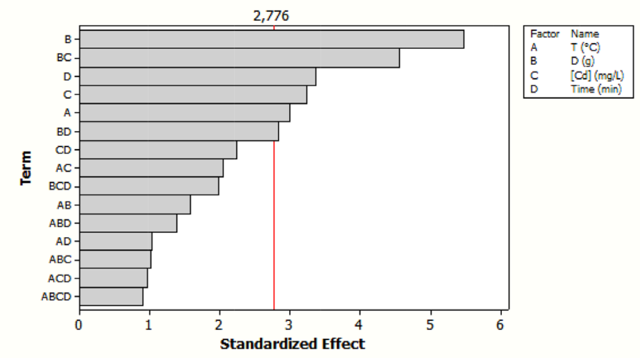

Fig. 7. Pareto chart for standardized effects.

### 3.3.2. Model term verification by ANOVA

After estimating the main effects, the interacting factors affecting the removal of cadmium were determined by performing the analysis of variance ANOVA. This is a method based on the p-value, t-value, sum of squares (SS) and mean square (MS) of each factor. The importance of the data is judged by its p-value, with values closer to zero denoting greater significance. To consider statistically significant for 95% confidence level, the p-value should be less than or equal to 0.05. The statistical validation of the model was performed by means of ANOVA which is presented in Table 4. Moreover, there are various statistical parameters like coefficient of determination ($R^2$) adjusted $R^2$ and predicted $R^2$ values are adequate for selection of the model. The coefficient of determination ($R^2$) known as the proportion of variation in the response attributed for the regression model should be close to 1. In our case, the obtained value of $R^2$ is equal to 0.9652, meaning that more than 96.52% of the data deviation can be explained by an empirical model indicating in his turn that the regression model is statistically significant. Moreover, it is preferred to use the adjusted $R^2_{adj}$ values in order to evaluate the model adequacy since it is adjusted for the number of terms in the model [40].The $R^2_{adj}$ value is 83.49%, indicating a high degree of correlation between the experimental and predicted responses. To clarify the goodness of the proposed model, Fig. 8 presents the plot of observed data as a function of those obtained from the model equation (Eq. (4)). From this figure, it was found that the points marked by open circles are concentrated near the diagonal line, which confirms that there is a very good agreement between the experimental data and the model prediction.

### 3.3.3. Main and interaction effects

Moreover, the main effect is used to confirm the results of the ANOVA table. The main effect is the mean of all of the responses produced by changing the level of a factor. A main effect plot could be used to determine which factors influence the response and to compare the relative strength of the effects. According to this notion, the larger the vertical line in main effect plots is the larger the change in removal efficiency of cadmium when it is changing from level 1 to level 3. The main effects of four factors (A, B, C and D) on cadmium removal were presented in Fig. 9.

From the analysis of the graphs and the coefficients of Eq. (5), it can be concluded that adsorbent dose is the most important variable on the cadmium removal since its coefficient is the largest (19.8). The positive sign of this coefficient means that the intensification of this parameter increased the removal of cadmium. On the other hand, the removal of cadmium increased with increasing the adsorbent dose and reached a maximum at 0.5 g/L. Thus, the adsorption of cadmium increased with increasing adsorbent dose. As can be seen from Fig. 9, the plot indicates that the temperature and contact time have a positive effect on the removal of cadmium. However, the effect initial cadmium concentration factor is negative since a decrease in %R. It was observed when this factor changes from low to high. Also, one can conclude a comparison of the slopes of the lines can be used for deter-

Table 3
Estimated effects and coefficients for cadmium removal efficiency (coded units)

| Term | Effect | Coefficient | S.E coef | T-value | p-value |
|---|---|---|---|---|---|
| Constant | | 33,936 | 1,618 | 20,98 | 0,000 |
| A | 10,875 | 5,437 | 1,809 | 3,01 | 0,040 |
| B | 19,800 | 9,900 | 1,809 | 5,47 | 0,005 |
| C | –11,700 | –5,850 | 1,809 | –3,23 | 0,032 |
| D | 12,200 | 6,100 | 1,809 | 3,37 | 0,028 |
| A*B | 5,725 | 2,863 | 1,809 | 1,58 | 0,189 |
| A*C | –7,425 | –3,712 | 1,809 | –2,05 | 0,109 |
| A*D | 3,725 | 1,863 | 1,809 | 1,03 | 0,361 |
| B*C | –16,500 | –8,250 | 1,809 | –4,56 | 0,010 |
| B*D | 10,250 | 5,125 | 1,809 | 2,83 | 0,047 |
| C*D | –8,100 | –4,050 | 1,809 | –2,24 | 0,089 |
| A*B*C | –3,675 | –1,837 | 1,809 | –1,02 | 0,367 |
| A*B*D | 5,025 | 1,837 | 1,809 | 1,39 | 0,237 |
| A*C*D | –3,475 | –1,737 | 1,809 | –0,96 | 0,391 |
| B*C*D | –7,150 | –3,575 | 1,809 | –1,98 | 0,119 |
| A*B*C*D | –3,275 | –1.638 | 1,809 | –0,91 | 0,416 |

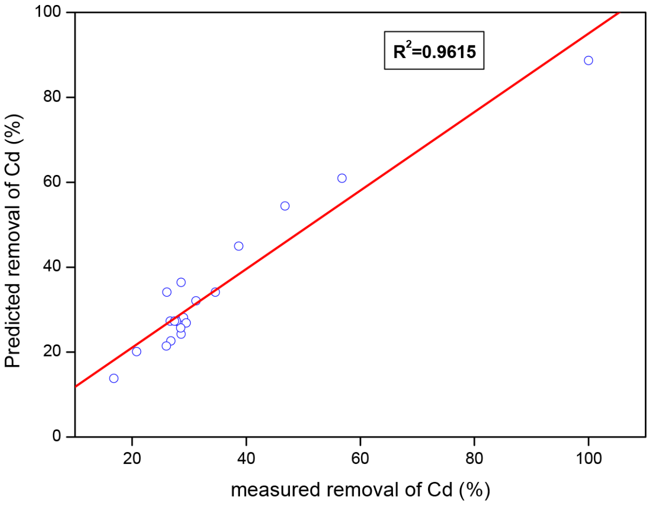

Fig. 8. Comparison between experimental and calculated values of removal of cadmium (%).

Table 4
Analysis of variance for cadmium removal by calcite using batch technique

| Source | Degrees of freedom | Sum of squares | Mean of squares | F–ratio | p–value |
|---|---|---|---|---|---|
| Main effects | 4 | 3184,14 | 796,04 | 15,21 | 0.011 |
| 2-way interactions | 6 | 2178,82 | 363,14 | 6,94 | 0.041 |
| 3-way interactions | 4 | 407,82 | 101,95 | 1,95 | 0.267 |
| 4- way interactions | 1 | 42,90 | 42,90 | 0,82 | 0.416 |
| Residual error | 4 | 209,39 | 52,35 | | 0.000 |
| Total | 19 | 6023,07 | | | |

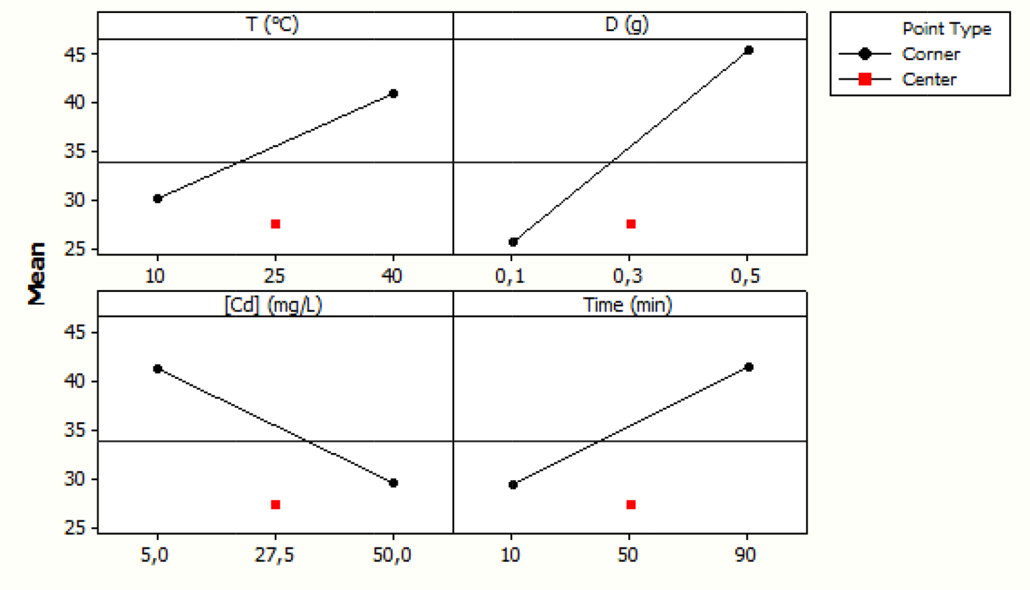

Fig. 9. Main effects plot for cadmium removal.

mination of the relative magnitudes of the factors effects which demonstrates the relative order of importance of the factors is adsorbent dose > contact time = temperature = initial concentration.

Although to confirm the results of the ANOVA table, one can use an interaction plots, the interaction between those two parameters would promote a better statement of the process.

Fig. 10 illustrates the possible positive and negative two-variable interactions among the variables A, B, C and D for % removal of cadmium. When the lines are parallel indicate that there is no interaction between the two factors. However, the non parallel lines indicate that there is a significant interaction between these two factors. Fig.10 reflects that for removal of cadmium, there was a relatively strong interaction between AB, BC, and CD, since the removal of cadmium increased with higher adsorbent dose at the lower initial concentration. Also, a positive interaction effect was observed between temperature and cadmium concentration. More, the interaction between contact time and temperature were very low and neglected as the lines lied in nearly parallel direction toward each other. The other two-factor interactions were not noticeable on the removal of cadmium because the lines on the plots were approximately parallel to each other for different levels of two factors, which indicated the lack of interaction between these factors.

In addition,for an evaluation of models and the relationship between factors and a response, a cube plot as shown in Fig. 11. The cube plot indicates that increasing adsorbent dose from 0.1 to 0.5 g enhances significantly the cadmium removal efficiency by 71.4% (from 28.60 to 100%) at higher temperature 40°C and contact time 90 min. Moreover, increasing initial cadmium concentration from 5 to 50 mg/L, at higher adsorbent dose 0.5 g and contact time 90 min, diminishes the response from 56.8% to 31.2% which means a decrease of 25.6% at low temperature 10°C. A variance of only 7.5% is observed at higher temperature. This means that both the effect of adsorbent dose and initial cadmium concentration are higher when the temperature is low. Other interactions showed important features for discussion. Besides, the maximum adsorption of cadmium was 100%. This high percentage was obtained by using the optimal conditions, namely higher temperature 40°C, adsorbent dose of 0.5 g, contact time 90 min and the initial concentration of cadmium is 5 mg/L.

### *3.3.4. Response surface plots*

A three-dimensional surface plot and a two-dimensional contour plot are illustrated in Fig. 12. They are useful for establishing desirable response values and operating conditions [38]. The response surface is considered as a two-dimensional plane where all points that have the same response are related to produce contour lines of constant responses. A surface plot generally indicated a 3D view that may provide a clear picture of the response. These representations display the relative effects of any two variables when the remaining variables are kept constant. The effects and interactions of adsorbent dose and temperature on the removal of cadmium are illustrated in Fig. 12a. It can be seen that the adsorbent dose has a positive effect for the cadmium removal all the time. Increasing the adsorbent dose a significant variation of responses was observed. Since, the maximum cadmium removal was achieved at the highest adsorbent dose and a temperature more than 30°C. Fig.12b shows the initial concentration of cadmium and temperature. The removal of cadmium increases with increase the initial cadmium concentration and temperature, which is in correlation with the experimental result match 29% (the removal of cadmium experiment number 6). The maximum removal is obtained when the initial concentration value exceeds

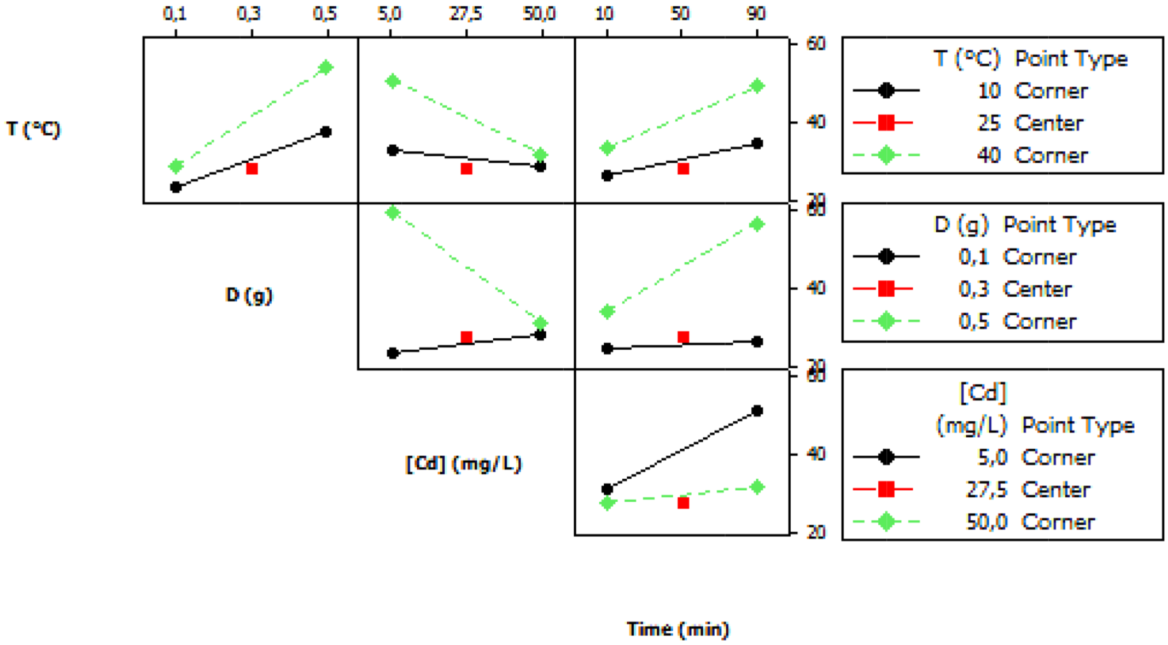

Fig. 10. Interaction effects plot for cadmium removal.

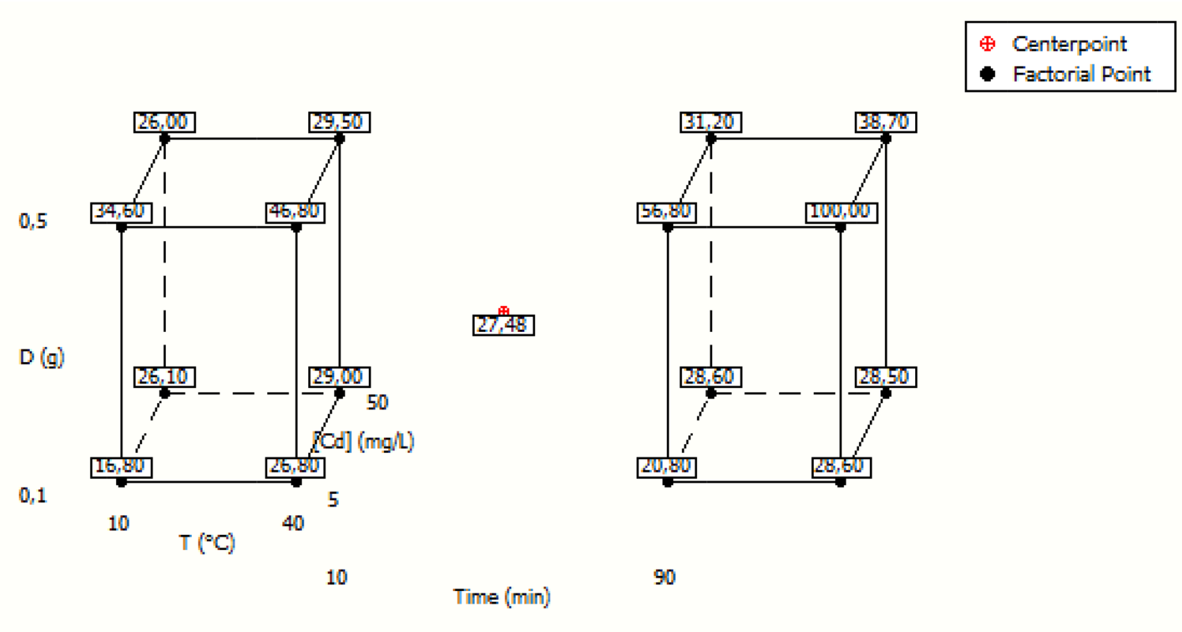

Fig. 11. Cube plot for cadmium removal.

20 mg/L and a temperature higher than 25°C. It can be observed from response surfaces that removal of cadmium increases with the increase of both contact time and temperature .When temperature increases from 10°C to 40°C and contact time increases from 10 min to 90 min, the removal of cadmium could reach to the highest value ( Y > 26%) in Fig.12c .

The contour lines plots for yield removal of cadmium (Fig. 12d) show that, for the experimental conditions used in this research study, an increase of temperature was significant with higher time contact. It can be observed from response surfaces that the removal of cadmium increases with the increase of adsorbent dose and decreases initial concentration.

As revealed formerly, the higher removal of cadmium was produced when the adsorbent dose and contact time were increased simultaneously. Fig. 12e indicates the interaction between the adsorbent dose and contact time at the temperature is equal to 10°C and the initial concentration is equal to 5 mg/L in a 3D response surface plot of regression.

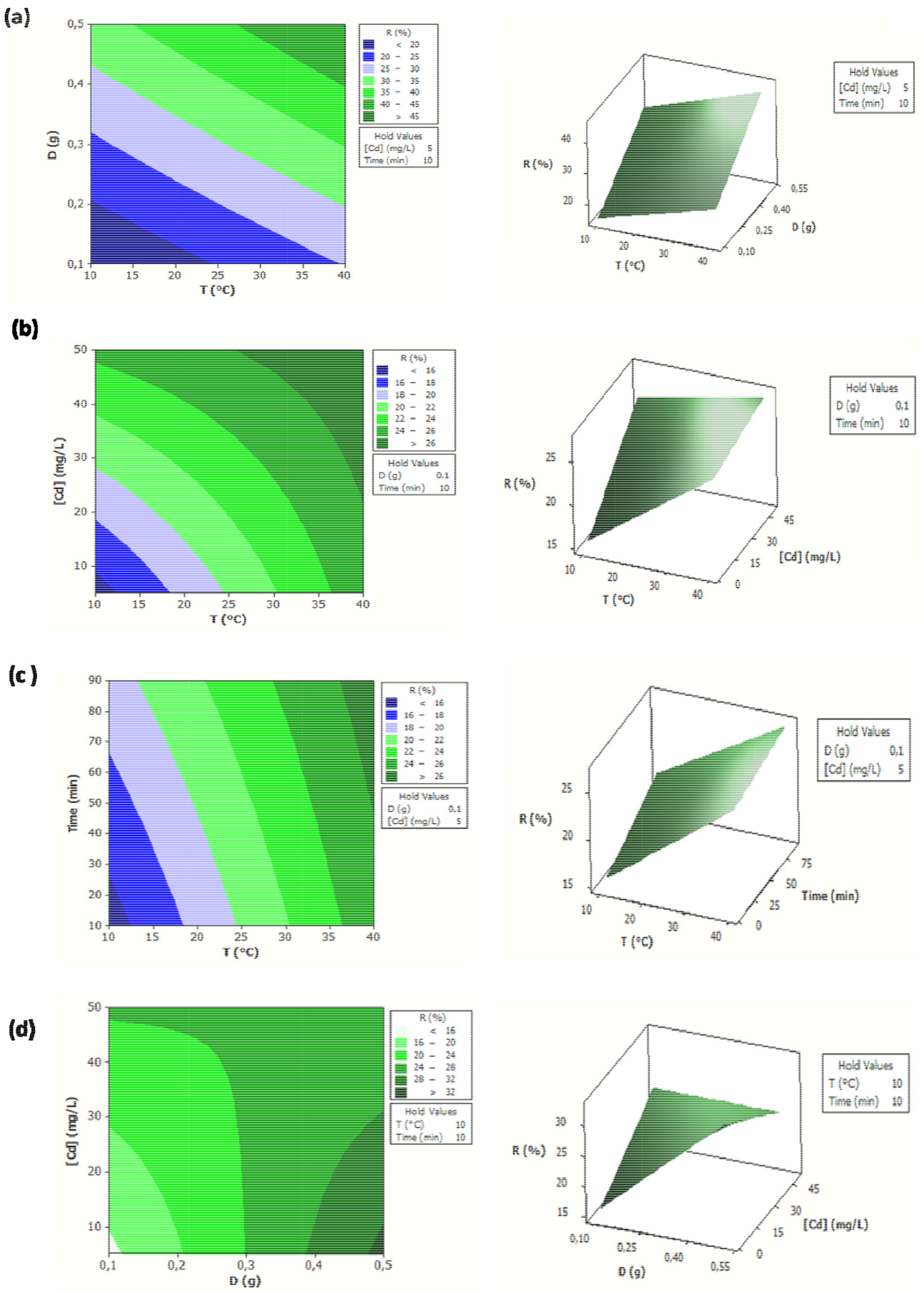

Fig. 12. 3D surface plot and two-dimensional contour plot for removal of cadmium in aqueous solution by adsorption as functions of operating factors. (a) R(%) vs adsorbent dose and temperature; (b) R(%) vs initial cadmium concentration and temperature; (c) R(%) vs time and temperature; (d) R(%) initial cadmium concentration and adsorbent dose.

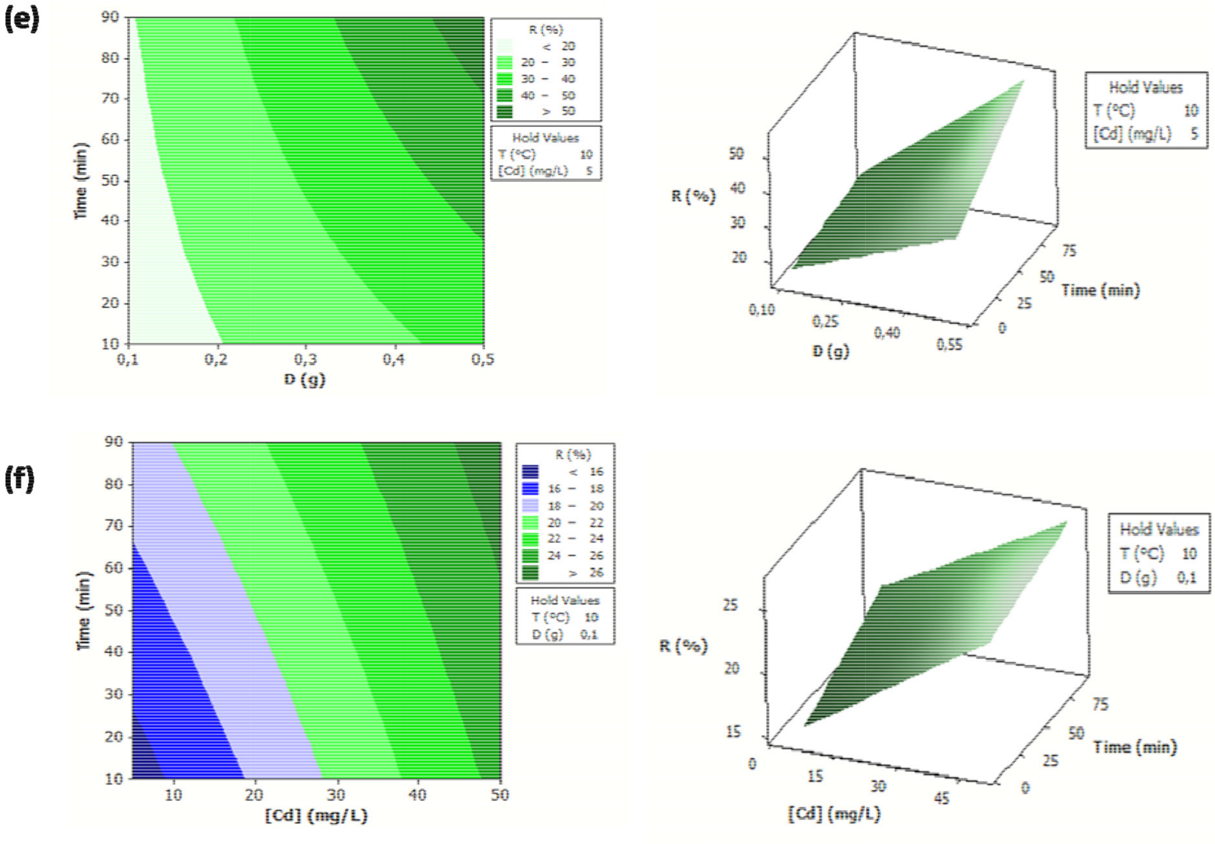

Fig. 12. (Continued) 3D surface plot and two-dimensional contour plot for removal of cadmium in aqueous solution by adsorption as functions of operating factors. (e) R(%) vs time and adsorbent dose; (f) R(%) vs time and initial cadmium concentration.

## 4. Conclusion

A method of cadmium removal adsorbed into calcite was optimized and validated by using full factorial experimental design. Effects and interactions between operational parameters have been studied. The full factorial design for the removal of cadmium was statistical validated by ANOVA and provided good quality to predict the response of which $R^2 = 0.9652$ and $R^2_{adj} = 0.8349$. Statistical analysis shows that all the studied parameters are highly influent and significant, with t-values greater than 2.776.

The ANOVA results show that at 95% confidence level, the adsorbent dose, temperature and contact time significantly affect the removal of cadmium. However, the negative effect factor of initial cadmium concentration is explained by the decrease of %R. The main significant factor was found for the adsorbent dose followed by the interaction between the adsorbent dose and the initial cadmium concentration. The increasing of initial cadmium concentration shows a negative effect. But the increasing of contact time, adsorbent dose and temperature has a positive effect on cadmium removal onto natural calcite. The maximum removal of cadmium was obtained by using the optimal conditions (Temperature = 40°C, adsorbent dose = 0.5 g, initial cadmium concentration = 50 mg/L and contact time = 90 min),which confirmed experimentally with a percentage deviation of 1.654%.

## Symbols

| | | |
|---|---|---|
| $C$ | — | Concentration (mg/L) |
| $q_e$ | — | Amount of adsorption at equilibrium (mg/g) |
| $C_0$ | — | Initial concentration (mg/L) |
| $C_e$ | — | Equilibrium concentration (mg/L) |
| $b_i$ | — | Estimation of the effect of the factor *i* |
| $b_{ij}$ | — | Estimation of the interaction effect between factor *i* and *j* for the response |
| $R^2$ | — | Correlation coefficient |
| step | — | The variation of the uncoded variable j |
| $t$ | — | Student value |
| $X_1$ | — | Temperature |
| $X_2$ | — | Adsorbent dose |
| $X_3$ | — | Initial cadmium concentration |
| $X_4$ | — | Contact time |
| $X_{ij}$ | — | The j coded variable of the ith experimentation |
| $x_{ij}$ | — | The j uncoded variable of the ith test |
| $x^0_j$ | — | The uncoded value of the ith test variable at center point |
| Y | — | Response (%) |

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