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Optimization of Adsorption Parameters for Ultra-Fine Calcite Using a Box-Behnken Experimental Design

Abstract: Removal of heavy metals from wastewater is a significant issue because it prevents environmental-based concerns and impacts a large number of diseases and disorders. Many low-cost natural materials have been offered recently as possible precursors to commercial synthetic adsorbents. Ultra-fine calcite, one of these natural materials, has been investigated as a potential commercial adsorbent. Response surface designs are effective experimental techniques to investigate the heavy metal adsorption capacity of ultra-fine calcite. In the present study, one such response surface design, Box-Behnken, is used in order to optimize adsorption factors, such as pH level, initial metal concentration, stirring rate and adsorption time, and to determine the heavy metal capacity of this adsorbent. Our results show that the proposed methodology is an effective approach to optimizing the adsorption process and to maximize the heavy metal capacity.

Keywords: Adsorption process; ultra-fine calcite; heavy metal removal; Box-Behnken experimental design; optimization.

1 Introduction

Heavy metal-based pollution is a significant concern these days because of hazardous effects on the environment [1]. For many life forms, some metal ions represent a significant danger due to their toxicity. Heavy metal ions dissolve to produce harmful outcomes, rivalled only by the toxicity of organic pollutants. In addition, the abundance of metals such as cadmium, chromium, iron, manganese, and zinc make them especially important environmental concerns [2]. In recent times, arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, and zinc have become increasingly important heavy metal-based environmental concerns; therefore, process improvement methodologies play key roles in the alleviation of these concerns.

In practice, familiar methods, including reverse osmosis, chemical precipitation, ion exchange, chemical precipitation, solvent extraction, and adsorption, are performed in order to remove heavy metals from environmental matrices. There are no perfect solutions, however. First of all, even though reverse osmosis is a powerful method, it is a costly process due to the need to replace membranes. Second, chemical precipitation is not a viable method when industrial wastes are present in trace amounts, and the precipitation process causes sludge to be formed. Third, ion exchange can be expensive, complicated, and inefficient. Fourth, solvent extraction and electrolytic processes require specialized solvents and other materials that can be expensive and can, themselves, cause environmental concerns. Finally, the adsorption process is widely used to remove toxic contaminants from water; this process has the potential to be effective, economical, versatile, and uncomplicated [3]. In addition, the adsorption process may be applied to very low concentrations in batch and continuous processes while generating a minimal amount of sludge [4].

It is important to remove heavy metals from wastewater in order to prevent significant environmental-based problems and to mitigate many diseases and disorders [5]. For this purpose, adsorption processes have been widely applied to remove pollutants from water [6]. Liquid-phase adsorption processes are efficient techniques for removing pollutants from industrial waste. Granular or powdered activated carbon is a popular adsorbent for this method; however, they see limited usage because they are not cost-

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effective. Therefore, many researchers and practitioners look for inexpensive adsorption substitutes, many involving natural materials and clays [7,8]. Adsorption techniques have therefore been paid a lot of attention in many research areas recently, and many studies are focused on identification of low-cost adsorbents. A large number of natural compounds have some adsorption capabilities as defined by porosity and ion exchange capacity [9]. Materials studied include carbon fibres, coconut waste, leaf mould, and other natural substances, for example by Sharma and Forster, Raji and Anirudhan, Bailey et al., Selvi et al., Park and Jung, and Gupta et al. [10,11,12,8,13,14,15]. Economical sorbents with high efficiencies are desired for use in removing pollutants [16].

Studies of calcite in particular have been performed frequently by researchers, who are especially interested in the uptake behaviour of toxic elements in industrial waste [17]. Solid solution formations are modelled as effective methods [18,19,20]. In addition to these research studies, calcite has been shown to be an effective scavenger, including activity against heavy metals [21].

One particularly interesting recent study was conducted by Dong and Wasylenki [22]. They studied zinc isotope fractionation during the process of adsorption to calcite at high and low levels of ionic strength. Furthermore, Tahervand and Jalali conducted sorption and desorption studies of toxic metals from amended soil using three sorbents, including bentonite, calcite and zeolite, within a pH range of 2 to 9 [23]. Along the same lines, Zhang et al. determined the adsorption mechanism by investigating the Ca^{+2} released upon removal of toxic heavy metal ions from aqueous solutions [24].

The goal of the present research is to optimize an experimental study of the adsorption process. The particular goal is to develop methods to study zinc ion sorption capacity of ultra-fine calcite, because calcite is a typical sorbent for removal of zinc from aqueous solutions. For this purpose, the Box-Behnken design, which is an effective technique for process improvement, was selected over other response surface designs because all quadratic effects of the experiment can be analyzed efficiently, and the number of experimental design runs is fewer, and the process more cost-effective, when assuming a constant variance over the experimental design region. In addition, Box-Behnken design-based methodology was developed in order optimize adsorption factors, such as pH level, initial metal concentration, stirring rate and adsorption time, in order to maximize micronized calcite heavy metal capacity. Furthermore, it is also believed that this study represents the first attempt to analyze the effects of micronized calcite heavy metal adsorption capacity with the Box-Behnken design.

2 Development of the Proposed Methodology

The development of the proposed experimental design consisted of a modelling phase, an analyzing phase and an optimization phase. The first phase dealt with the selection of an appropriate experimental design and the building of a second-order polynomial model. Then, the second phase was associated with developing data analysis tools in order to interpret experimental results. Finally, optimum operating conditions were obtained using the proposed optimization model.

2.1 Modeling Phase

The Box-Behnken design was chosen over other response surface designs. This design has some important advantages, such as a fewer number of design runs and a rotatable (or nearly rotatable) design. For example, the central composite design requires twenty design runs for three factors while the Box-Behnken design requires fifteen design runs. Optimal experimental designs are not good choices because these designs are not rotatable. Note that a design without rotatability may provide poor prediction quality over the experimental design region, especially when analyzing effects of pure quadratic terms.

A second-order polynomial model is used in order to analyze main, interaction, and quadratic effects of the experiment using the following formula [25]:

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

where k is the number of factors, β_i is the coefficient of the regression model, ε is the observed error, and x_i represents factors of the experiment.

The estimated mean response is found as follows:

$$\hat{\mu}(\mathbf{x}) = \hat{\alpha}_0 + \mathbf{x}'\mathbf{a} + \mathbf{x}'\mathbf{A}\mathbf{x}$$

where $\mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_k \end{bmatrix}$, $\mathbf{a} = \begin{bmatrix} \hat{\alpha}_1 \\ \hat{\alpha}_2 \\ \vdots \\ \hat{\alpha}_k \end{bmatrix}$, and $\mathbf{A} = \begin{pmatrix} \hat{\alpha}_{11} & \hat{\alpha}_{12}/2 & \cdots & \hat{\alpha}_{1k}/2 \\ & \vdots & \ddots & \vdots \\ \hat{\alpha}_{k1}/2 & \hat{\alpha}_{k2}/2 & \cdots & \hat{\alpha}_{kk} \end{pmatrix}$ (2)

where α_i is the regression coefficients, and $\mathbf{a}$ and $\mathbf{A}$ represent the vector and the matrix of the regression coefficients related to the estimated mean response, respectively.

2.2 Analyzing Phase

For the analyzing phase, a normal probability plot, a residual plot, a residual histogram plot, and a residual versus order plot were drawn to check the fundamental assumptions for the experiment. Furthermore, the regression and variance analyses were performed. In addition, an *F*-test was conducted and the determination coefficient, *R*, determined in order to check the adequacy of the model. The estimated regression coefficients of the mean response were also determined along with the relevant *p*-values. Therefore, the significance of every regression coefficient was checked in order to interpret the results. Surface plots were also drawn in order to investigate how the adsorption factor levels change during the response.

2.3 Optimization Phase

The aim of the experiment is to maximize the heavy metal capacity of micronized calcite. Therefore, the objective of the proposed nonlinear programming model is to maximize the estimated mean function subject to the boundary constraints over the experimental region. The proposed optimization model is as follows:

$$\text{maximize } \hat{\alpha}_0 + \mathbf{x'a} + \mathbf{x'Ax}$$
$$\text{subject to } \mathbf{x} \in X$$
$$\text{where } X \in R = \left\{ \mathbf{x} \in R^k \, \middle| \, -1 \leq x_i \leq +1 \text{ and } i = 1, 2, ..., k \right\}$$
$$\mathbf{a} = \left[\hat{\alpha}_1, \ \hat{\alpha}_2, \ ..., \ \hat{\alpha}_k \right]' \text{ and } \mathbf{A} = \begin{pmatrix} \hat{\alpha}_{11} & \hat{\alpha}_{12}/2 & \cdots & \hat{\alpha}_{1k}/2 \\ & \vdots & \ddots & \vdots \\ \hat{\alpha}_{k1}/2 & \hat{\alpha}_{k2}/2 & \cdots & \hat{\alpha}_{kk} \end{pmatrix} \quad (3)$$

Two different approaches, without and then with the *p*-value, are presented in order to obtain the estimated mean response in Equation (2) for the proposed optimization model in Equation (3). The first approach is to consider the quadratic model regardless of the significance levels. On the other hand, the second approach is based on the significance levels of the model using the concept of the *p*-value. Both of the methods were used here in order to obtain the optimum operating conditions for the experiment. Then, a study was conducted to compare the two strategies.
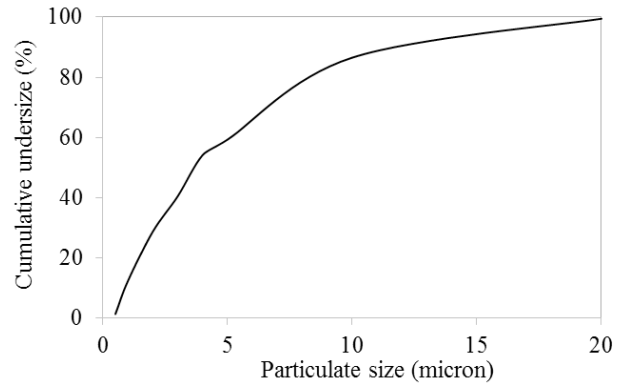

Figure 1: Cumulative undersize values of the ultra-fine calcite sample.

2.4 Material

The key material in the experiment is ultra-fine calcite. High purity ore, 99.5% $CaCO_3$ content, was obtained from Niğde, Turkey. The particle size distribution of the sample was determined with a Malvern Mastersizer 3000, and its cumulative undersize values are shown in Figure 1. The sizes of d_{10}, d_{50} and d_{90} values were 0.89 μm, 3.88 μm and 11.13 μm, respectively.

A batch technique was used for the sorption of the metal on the ultra-fine calcite sample. All solutions were prepared in deionized water. Then, a 1000 ppm Zn (II) solution was made by dissolving $Zn(NO_3)_2$ (Merck Company). Next, the pH level of each metal stock solution was set by titration with HNO_3 and NaOH. In each case, 1.0 g of adsorbent (dry wt.) was added to 100 ml of Zn metal stock solution at room temperature. Subsequently, the solution was continually stirred with a mechanical stirrer. The aqueous phase was isolated from the sample using filtration after the noted incubation time. Finally, Zn determination in the initial and the leftover solutions was executed with atomic absorption spectrophotometry (AAS).

The mass of metal ions adsorbed (MIA) per unit mass of adsorbent was expressed in units of mg metal ions/g as follows:

$$\text{MIA} = \frac{\left[(C_o - C) \times V \right]}{\left[m \times 1000 \right]} \quad (4)$$

where C_o and C represent metal ion concentrations (ppm) before and after the incubation period, respectively, V denotes the aqueous step volume (ml), and m represents the mass of adsorbent used (g).

Ethical approval: The conducted research is not related to either human or animal use.

3 Results of the Experiment

A Box-Behnken design with 27 runs was used while specifying four factors with three levels for the adsorption experiment and including three center points. The center points were added to ensure stability and to identify any potential variability. The coded factors and their levels for the adsorption experiment are shown in Table 1, and the experimental results are shown in Table 2.

Using Minitab software, the fundamental assumptions, normality and constant variance, were checked with a normal probability plot, a residual plot, a

residual histogram plot, and a residual versus order plot as displayed in Figure 2 (a)-(d), respectively.
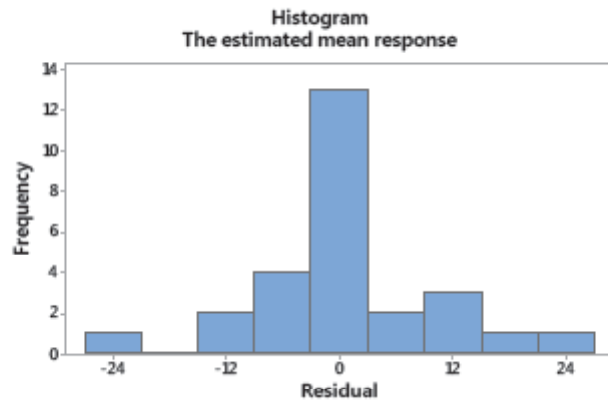
As shown in Figure 2, the normality assumption held true according to normality and histogram plots and the constant variance assumption was also satisfied

Table 1: Coded factors and their levels.

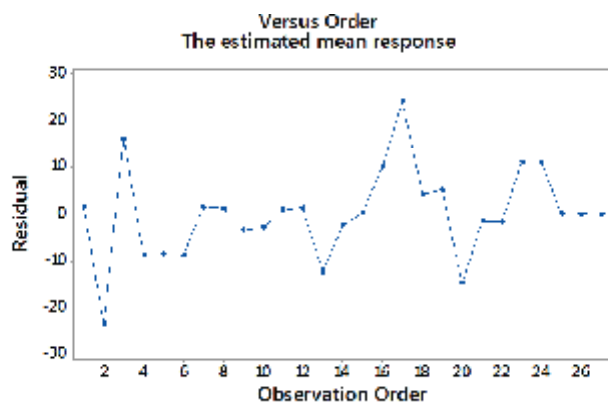| Factor	Notation	Coded levels		
		-1	0	1
pH level	x_1	5	7	9
Initial metal concentration (ppm)	x_2	200	400	600
String rate (rpm)	x_3	500	750	1000
Adsorption time (minutes)	x_4	20	40	60
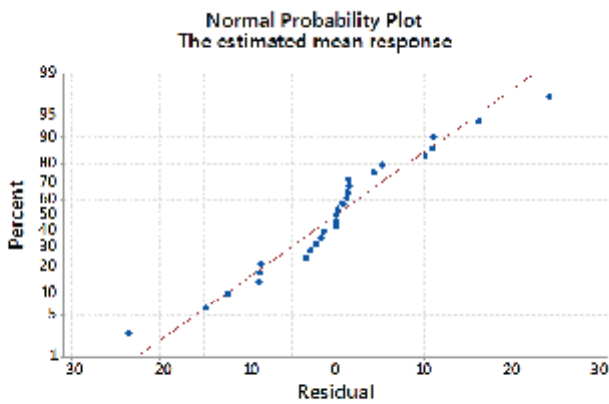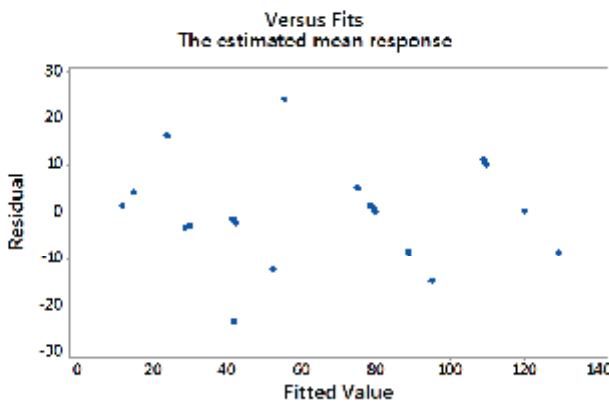
Figure 2: (a) Normal probability plot; **(b)** residual plot; **(c)** residual histogram plot; **(d)** residual versus order plot.

Table 2: Box-Behnken design and values of micronized calcite heavy metal capacity.

Run	x_1	x_2	x_3	x_4	Actual value (y)	Predicted value ($\hat{y}$)	Residual
1	-1	-1	0	0	13.20	11.74	1.46
2	-1	1	0	0	18.15	41.70	-23.55
3	1	-1	0	0	39.99	23.79	16.20
4	1	1	0	0	119.99	128.79	-8.80
5	0	0	-1	-1	79.98	88.48	-8.50
6	0	0	-1	1	79.96	88.78	-8.82
7	0	0	1	-1	79.74	78.27	1.47
8	0	0	1	1	79.89	78.73	1.16
9	-1	0	0	-1	25.25	28.69	-3.44
10	-1	0	0	1	27.10	29.99	-2.89
11	1	0	0	-1	79.99	79.19	0.80
12	1	0	0	1	79.99	78.64	1.35
13	0	-1	-1	0	39.96	52.23	-12.27
14	0	-1	1	0	39.90	42.17	-2.27
15	0	1	-1	0	119.95	119.78	0.17
16	0	1	1	0	119.76	109.58	10.18
17	-1	0	-1	0	79.51	55.31	24.20
18	-1	0	1	0	19.30	15.08	4.22
19	1	0	-1	0	79.99	74.78	5.21
20	1	0	1	0	79.99	94.75	-14.76
21	0	-1	0	-1	39.65	41.10	-1.45
22	0	-1	0	1	39.92	41.60	-1.68
23	0	1	0	-1	119.81	108.70	11.11
24	0	1	0	1	119.84	108.96	10.88
25	0	0	0	0	79.73	79.74	-0.01
26	0	0	0	0	79.76	79.74	0.02
27	0	0	0	0	79.73	79.74	-0.01

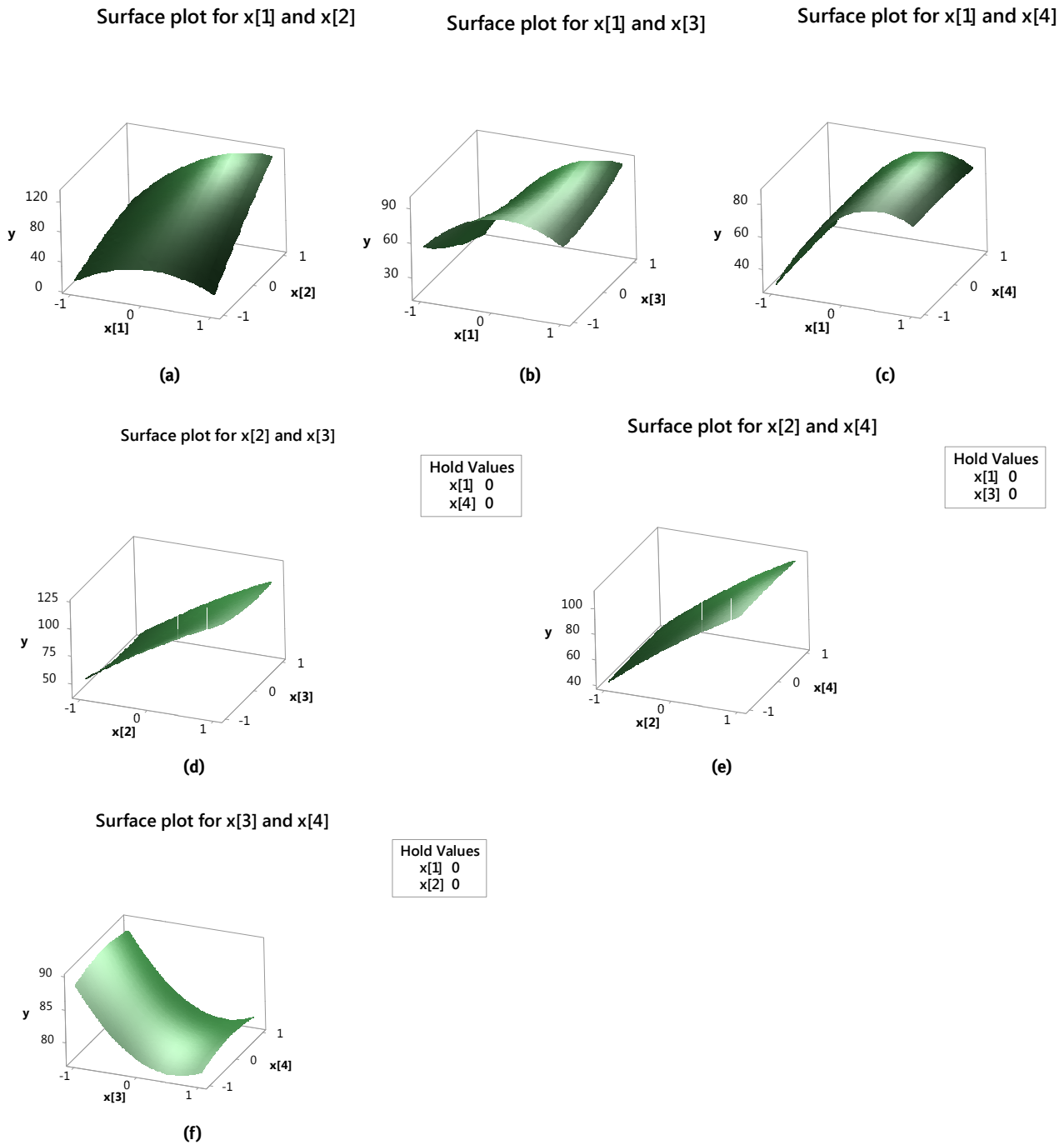**Table 3:** ANOVA results for optimization of heavy metal adsorption capacity of micronized calcite.

Source of variations	Degree of freedom	Sum of square	Mean square	F-value
Model	14	28003.2	2000.2	9.89
Linear	4	21340.9	5335.2	26.37
Square	4	4347.0	1086.8	5.37
Two-way interaction	6	2315.3	385.9	1.91
Error	12	2427.4	202.3	
Lack-of fit	10	2427.4	242.7	809139.2
Pure Error	2	0.0	0.0	
Total	26	30430.6		

Table 4: Regression analysis of a second-order model for optimization of the heavy metal adsorption capacity of micronized calcite.

Terms	Coefficient	Standard error	p-value
Intercept	79.74	8.21	**0.000**
x_1	24.79	4.11	**0.000**
x_2	33.74	4.11	**0.000**
x_3	-5.06	4.11	0.241
x_4	0.19	4.11	0.964
x_1^2	-24.60	6.16	**0.002**
x_2^2	-3.64	6.16	0.566
x_3^2	4.84	6.16	0.447
x_4^2	-1.01	6.16	0.872
$x_1 x_2$	18.76	7.11	**0.022**
$x_1 x_3$	15.05	7.11	0.056
$x_1 x_4$	-0.46	7.11	0.949
$x_2 x_3$	-0.03	7.11	0.996
$x_2 x_4$	-0.06	7.11	0.993
$x_3 x_4$	0.04	7.11	0.995

according to residual plots. Furthermore, the value of the determination coefficient, R^2, was calculated to be 0.9202. Therefore, it is concluded that the model may predict 92.02% of the variability for the response. The analysis of variance (ANOVA) is shown in Table 3, and the value of an F-test is 9.89 where the p-value is 0.0002. Thus, the regression model is highly significant. Along the same lines, the value of lack of fit was 809139.17, implying that it is not important comparing to the pure error.

The coefficients of the regression model of the heavy metal capacity of micronized calcite with related p-values are shown in Table 4. The significance of every regression coefficient was checked using the p-values. As shown in Table 4, the intercept and the linear coefficients of x_1 and x_2 were significant. In addition, the quadratic coefficient

Surface plot for x[1] and x[2]

Surface plot for x[1] and x[3]

Surface plot for x[1] and x[4]

(a)

(b)

(c)

Surface plot for x[2] and x[3]

Surface plot for x[2] and x[4]

Hold Values
x[1] 0
x[4] 0

Hold Values
x[1] 0
x[3] 0

(d)

(e)

Surface plot for x[3] and x[4]

Hold Values
x[1] 0
x[2] 0

(f)

Figure 3: (a) Surface plot for X_1 and X_2 ; (b) surface plot for X_1 and X_3 ; (c) surface plot for X_1 and X_4 ; (d) surface plot for X_2 and X_3 ; (e) surface plot for X_2 and X_4 ; (f) surface plot for X_3 and X_4 .

of x_1^2 and the interaction coefficient of x_1x_2 were also significant.

Surface plots were created to investigate the impact of altering factor levels on adsorption. These plots are depicted in Figure 3.

The full second-order model without the significance levels of the model fitting is given as follows:

$$y_{full} = 79.74 + 24.79x_1 + 33.74x_2 - 5.06x_3 + 0.19x_4 - 24.60x_1^2$$
$$- 3.64x_2^2 + 4.84x_3^2 - 1.01x_4^2 + 18.76x_1x_2 + 15.05x_1x_3 \quad (5)$$
$$- 0.46x_1x_4 - 0.03x_2x_3 - 0.06x_2x_4 + 0.04x_3x_4$$

The optimization model is given as follows:

$$\text{maximize } 79.74 + 24.79x_1 + 33.74x_2 - 5.06x_3 + 0.19x_4 - 24.60x_1^2$$
$$- 3.64x_2^2 + 4.84x_3^2 - 1.01x_4^2 + 18.76x_1x_2 + 15.05x_1x_3$$
$$- 0.46x_1x_4 - 0.03x_2x_3 - 0.06x_2x_4 + 0.04x_3x_4 \quad (6)$$
$$\text{subject to } -1 \le x_i \le 1 \text{ and } x_i \in R^k$$
$$\text{where } i = 1, 2, 3, 4$$

The optimum adsorption solution as derived from optimization model in Equation (6) is shown in Table 5. Note that the Mathematica NLP solver was applied to obtain the optimum adsorption conditions from the optimization models.

As shown in Table 5, the estimated mean response is 143.606 while maximizing the heavy metal capacity. On the other hand, the polynomial second-order model for heavy metal capacity is found with the significance levels of the model fitting as follows:

$$y_{significance} = 79.74 + 24.79x_1 + 33.74x_2 - 24.60x_1^2 + 18.76x_1x_2 \quad (7)$$

The optimization model is given as follows:

$$\text{maximize } 79.74 + 24.79x_1 + 33.74x_2 - 24.60x_1^2 + 18.76x_1x_2$$
$$\text{subject to } -1 \le x_i \le 1 \text{ and } x_i \in R^k \quad (8)$$
$$\text{where } i = 1, 2, 3, 4$$

The optimum solution of the model in Equation (8) is given in Table 6. Notice that both the necessary and sufficient conditions are met for the optimization model in Equation (8).

4 Discussion

Conventional experimental design methods, such as factorial designs, are not able to detect interaction and

Table 5: Optimum adsorption solution of the optimization model in Equation (6).

Factor	Optimum adsorption condition	
	Coded value	Actual value
x_1	1.000	9.00
x_2	1.000	600.00
x_3	1.000	1000.00
x_4	-0.152	36.96
Objective function		143.606

Table 6: Optimum adsorption solution of the optimization model in Equation (8).

Factor	Optimum adsorption condition	
	Coded value	Actual value
x_1	0.885	8.80
x_2	1.000	600.00
x_3	0.713	928.25
x_4	0.522	50.44
Objective function		132.954

quadratic effects of experiments. In addition, it is not possible to fit a regression equation in order to place optimum adsorption conditions through an entire experimental region. However, response surface designs are effective methods for the optimization of design factors to estimate the optimum operating conditions from the results of a lower number of experiments. In this study, a Box-Behnken design, one of the response surface designs, was conducted and the optimum adsorption conditions were determined through minimal number of experiments as compared with other response designs.

As shown in Table 3, the ANOVA of the regression model confirmed that the accuracy of the second-order model was very good, according to the p-value. As shown in Table 4, the regression coefficients were calculated and each coefficient was analyzed while considering significance levels. In addition, confirmatory experiments were performed in order to validate the model that had been based on predictions. As shown in Table 1, the actual and predicted values were in good agreement, except for the second and seventh runs. Therefore, the suitability of the design and method was confirmed. Further, the proposed optimization models were applied to determine each factor level while maximizing the heavy metal adsorption capacity. For the proposed optimization model

considering the full second-order model, a mean value of 143.606 mg metal ions/g of micronized calcite heavy metal adsorption capacity was obtained. For the optimization model with the p-value concept, a mean value of 132.954 mg metal ions/g of heavy metal capacity was obtained.

In this study, removal of Zn^{2+} using ultra-fine calcite was investigated. The results of the experiments demonstrated that the optimal conditions for adsorption are pH 8.80, initial metal concentration 600 ppm, stirring rate 928.25 rpm, and adsorption time 50.44 min. The pH of the solution plays an important factor on the capacity for the uptake of metal ions, since it determines the surface charge of the adsorbent [26]. The dependence of heavy metal ion adsorption on pH was different for the metal ions studied. Metal ion adsorption on oxide surfaces is related to the hydrolysis reaction that it will undergo in solution [27]. At low pH values, low metal adsorption is caused by the competition of metal ions with hydrogen ions for available adsorption sites as well as the positive charge density on the metal binding sites; therefore, high concentrations of protons are expected to inhibit adsorbent-mediated removal of metal ions from solution. In contrast, a negative charge density on the adsorbent surface increases as pH increases due to deprotonation of metal binding sites, thus enhancing adsorption efficiency [28]. At high pH levels, hydroxyl ions bind with zinc, forming complexes such as $ZnOH^+$ and $Zn(OH)_2$. At higher pH values, these zinc hydroxyl species may participate in the adsorption by precipitating onto the adsorbent structure [29]. Because of these factors, the optimal removal efficiency for zinc is achieved at pH levels greater than 7. Thus, the main mechanisms influencing the adsorption characteristics of adsorbents can be explained by dissolution, ion exchange/adsorption, and precipitation [30].

5 Concluding Remarks

In this research, a Box-Behnken design was conducted to analyze four important factors -- pH, initial metal concentration, stirring rate, and adsorption time -- in order to optimize these parameters and the heavy metal adsorption capacity of micronized calcite. For the modelling phase, this paper considered a second-order polynomial model for the mean response to have the highest predictive ability. Under optimal conditions, a maximum heavy metal capacity of 143.606 mg metal ions/g was predicted while using the proposed optimization model applying the full second-order model. With another model that used the p-value concept, a maximum heavy metal capacity 132.954 mg metal ions/g was predicted.

This report has three potential contributions. First, a Box-Behnken design-based methodology was developed in order to analyze the factors that affect the heavy metal adsorption capacity of micronized calcite. Second, optimization models were proposed in order to obtain optimum adsorption conditions; therefore, the results of the experiment might improve the removal of heavy metals from wastewater. This experimental study demonstrated specific factors that would optimize the removal of Zn^{2+} with ultra-fine calcite: pH of 8.80, initial metal concentrations of 600 ppm, stirring rates of 928.25 rpm and adsorption times of 50.44 min. Finally, this research might suggest general ways to attack many engineering problems and ultimately might lead to continuous process improvement.

Conflict of interest: Authors state no conflict of interest.

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