Response Surface Modeling for Pb(II) Removal From Alcoholic Beverages Using Natural Clay: Process Optimization With Box–Behnken Experimental Design and Determination by Electrothermal AAS

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ABSTRACT

A three-level four-factor Box–Behnken experimental design (BBD) combined with response surface modeling (RSM) was used for the optimization and modeling of Pb(II) adsorption from alcoholic beverages onto natural clay. The BBD method was chosen as the statistical prediction method to reduce the experimental numbers which saves time and chemicals and reduce analysis cost. Various independent process variables including solution pH (X_1 : 3.0–7.0), contact time (X_2 : 2–60 min), adsorbent dosage (X_3 : 0.01–0.1 g), and agitation speed (X_4 : 50–150 rpm) were optimized. The optimal conditions used for Pb(II) removal were pH of 5.3, contact time 38.9 minutes, 0.071 g adsorbent dosage, and 98.7 rpm agitation speed, resulting in a maximum removal efficiency of 120 mg g⁻¹. Pb was determined by electrothermal AAS.

The significance of the independent variables and their interactions were tested by means of the analysis of variance (ANOVA) and are based on the ANOVA statistical value. The adsorption of Pb(II) onto clay was found to be highly significant with very low probability (p) values (<0.001). These results were justified by the relatively high correlation coefficients ($R^2 = 0.9965$, $R^2_{\text{adj}} = 0.9930$, and $R^2_{\text{Pred}} = 0.9819$) of the statistical prediction. FTIR analysis confirmed major participation of amide, amines, ketones, including the primary alcohol groups, during Pb(II) biosorption. Clay was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM), coupled with energy dispersive X-Ray (EDX). The proposed adsorption process efficiently removes Pb(II) present in various aqueous media and can be used for industrial wastewater or drinks.

goal is zero. In addition, the World Health Organization (WHO) has set a provisional limit of 0.05 mg L⁻¹ for Pb (11–15).

Removal of heavy metals, including Ni, Cd and Pb, from various matrices is necessary as these metals directly enter the human food chains, therefore presenting a high health risk to consumers. Recently, this problem has received considerable attention (16).

To remove the metal ions from aqueous solutions, a number of technologies have been developed and include membrane filtration systems, electrochemical technologies, evaporation, coagulation–flocculation, ion-exchange, membrane filtration, reverse osmosis, and adsorption. But all of these techniques have disadvantages and limitations in application. Moreover, some have high operating costs and produce sludges with high concentrations of Pb and other chemical substances. The desorption techniques are widely used as an alternative method for removing dissolved metal ions from liquid media because of simplicity, selectivity, and effectiveness for low metal concentrations (8–10, 17–19). In light of this information, the number of adsorption studies has grown significantly leading to research on the development and optimization of adsorbents, including metallic oxides, clay, biosorbents, zeolites, ion exchange resins, and various polymeric adsorbents, for Pb removal (19–23).

To minimize processing costs, the investigations have focused on

INTRODUCTION

The heavy metals Pb, Hg, Cd, Ni, Cr, and Cu persist in nature, bioaccumulate, and are considered toxic and hazardous to humans and other living organisms. In addition, due to rapid technological developments and the use of toxic metals in industry, environmental pollution has become a serious problem for the ecosystem (1–5). Lead is not essential for mammals, and about 800 mg

creates toxicity in humans (6–10). Various industries contribute to lead contamination such as electroplating, metal surface finishing, metallurgical, tannery, chemical catalysis, mining, and the manufacture of electrical goods. Bioaccumulation causes severe damage to the kidneys, the nervous and reproductive systems, including the liver and the brain resulting in reduced mental function and damage to blood composition. The U.S. Environmental Protection Agency (USEPA) mandates the maximum contaminant level for lead as 0.015 mg L⁻¹, while the maximum contaminant level

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the use of ecofriendly and inexpensive adsorbents, as well as using statistical methods, such as the Box-Behnken Design (BBD) with the response surface methodology (RSM) (24-26). BBD is the most commonly used combination design of the RSM model (27, 28) and has been adopted as an experimental design model to study the interactions of combinations of parameters such as solution pH, stirring time, and temperature (29, 30). Its greatest advantage is a reduction in the number of experiments required to interpret multiple parameters and their interactions. The RSM optimization process contains three steps: (a) appropriate experimental design selection, (b) estimation of all of the coefficients of the model using ANOVA, and (c) model validation based on prediction and experimental runs of the process response validation of the final model (31).

The present study is first to report Pb(II) determination in alcoholic beverages using natural locally available clay (Malatya, Turkey) for batch experiments. The RSM method in combination with the BBD was selected to determine and optimize the effects of the process conditions on the response surface analysis of the Pb(II) amount adsorbed on clay. The experimental conditions studied include solution pH, contact time, adsorbent dose, and agitation speed, along with their interactions in Pb(II) adsorption on clay.

EXPERIMENTAL

Instrumentation

A study involving thermal programs for the determination of Pb(II) in several beer and home-made wines by electrothermal atomic absorption (ETAAS) using the AAnalyst™ 800 (PerkinElmer, Inc., Shelton, CT, USA) is presented. The instrumental operating conditions are given in Table I. Because

of practicability, sensitivity, precision, and accuracy, ETAAS allows a higher throughput and can be a useful alternative when compared to FAAS, which inevitably requires either a sample pre-concentration or use of the standard additions method.

Chemicals

Lead, sodium hydroxide, hydrochloric acid, and nitric acid were obtained from Merck (Darmstadt, Germany). All chemicals used were of analytical reagent grade.

Preparation of Standard Solutions

A stock solution of 1000 mg L⁻¹ Pb(II) was prepared by dissolving an accurate quantity of Pb(NO₃)₂ in distilled water. Other concentrations varying from 10 µg L⁻¹ to 400 mg L⁻¹ were prepared from the stock solutions by dilution.

Box-Behnken Design and Optimization Procedure

A 3-level (low, medium, and high: coded as -1, 0, and +1) 4-factor BBD, combined with RSM, was used to determine the maximum Pb(II) biosorption on clay. The four critical parameters affecting Pb(II) adsorption, namely pH (X₁), contact time (X₂), adsorbent dosage (X₃), and agitation speed (X₄) were selected as independent variables,

and removal of biosorption (Y) was considered as the dependent variable (response). Table II lists the independent experimental variables and their levels for adsorption of Pb(II). The experimental results were analyzed using the Design Expert software program (Design Expert, Version 10, Stat-Ease, USA) and the regression model was proposed. Table II also lists the different parameters such as variable conditions, run order, experimental values, and predicted values. The final equation obtained from RSM in terms of actual factors was as follows:

$$Y (\mu\text{g Pb} / \text{mg clay}) = -549.03 - 169.93X_1 + 261.160.98X_2 + 3809.16X_3 + 1.42X_4 + 0.21X_1X_2 - 64.50X_1X_3 - 0.06X_1X_4 + 8.07X_2X_3 + 4.77X_2X_4 + 12.0X_3X_4 - 15.92X_1^2 - 0.04X_2^2 - 34905.33X_3^2 - 0.01X_4^2$$

In the optimization process, the responses can be simply related to the chosen factors by linear or quadratic models. In this study, 29 experiments were performed in randomized order. The adequacy of the proposed model is then revealed using the diagnostic tests provided by ANOVA. The property of the fit polynomial model is represented by the coefficient of determination R². The R² values assure a measure of how variability in the observed response values can be

TABLE I
Instrumental Operating Conditions of AAnalyst 800 ETAAS

Steps	Temp. (°C)	Ramp Time (s)	Hold Time (s)
Dry 1	110	1	30
Dry 2	130	15	30
Pyrolysis	850	10	20
Atomization	1600	0	5
Clean-out	2450	1	3
Wavelength (λ)		283.3 nm	
Hollow cathode lamp current		440.0 mA	
Background correction		Zeeman-effect	
Injection volume		20 µL	
Slit width		0.7 nm	

TABLE II
Box–Behnken Design and Observed Responses
of Pb(II) Levels on Clay (mg g⁻¹)

Run	pH X ₁	Contact Time X ₂ (min)	Adsorbent Dosage X ₃ (g)	Agitation Speed X ₄ (mL)	Pb(II) (q _e , mg g ⁻¹) Observed
1	3	31	0.075	50	8.2
2	5	60	0.05	100	85.6
3	5	31	0.1	50	49.4
4	5	2	0.075	50	45.8
5	5	2	0.1	100	27.5
6	5	31	0.075	100	121.2
7	7	31	0.075	50	47.4
8	7	31	0.05	100	54.8
9	5	60	0.075	150	80.1
10	5	31	0.05	150	61.2
11	5	31	0.075	100	120
12	5	60	0.075	50	69.8
13	5	31	0.075	100	116.9
14	5	31	0.075	100	117.2
15	5	31	0.075	100	115.9
16	3	60	0.075	100	12.1
17	7	60	0.075	100	62.6
18	5	2	0.075	150	28.4
19	5	31	0.1	150	75.5
20	3	31	0.05	100	22.7
21	5	2	0.05	100	54.3
22	7	31	0.075	150	33.2
23	5	31	0.05	50	95.1
24	3	2	0.075	100	6.7
25	3	31	0.075	150	17.5
26	5	60	0.1	100	82.2
27	7	2	0.075	100	8.3
28	3	31	0.1	100	15.1
29	7	31	0.1	100	34.3

clarified by experimental factors and their interactions (39). These analyses are performed by the agency of Fisher's 'F'-test and the P-value (probability). Based on the experimental data obtained, the levels of the three main parameters investigated in this study are listed in Table III.

RESULTS AND DISCUSSION

Characterization Method

The morphology of clay and the Pb(II)-loaded clay were characterized using a digital scanning electron microscope (SEM) coupled with an energy dispersive X-ray (EDX) (Hitachi SU3500, Japan). The spectra were recorded using a FTIR spectrophotometer (Thermo Nicolet iS10, Thermo Scientific, USA) in the frequency range from 4000 cm⁻¹ to 500 cm⁻¹. The sam-

ples were analyzed with attenuated total reflectance (ATR).

FTIR Spectroscopy

The FTIR measurements were used in order to confirm the formation of Pb(II) on the clay surface. The spectra were recorded in the frequency range of 4000-500 cm⁻¹. The instrumental operating conditions are given in the table below. The FTIR spectra of the unloaded Pb(II) and the loaded Pb(II) were performed for a better comprehension of the structure. An absorption band revealing the vibrational properties of skeletal vibration of the C-O bond was observed for around 960-1030 cm⁻¹. This band is mainly assigned to the stretching vibrations of Pb-O. The natural clay sample showed lower intensity peaks at 3600 cm⁻¹, 3400 cm⁻¹, 1370 cm⁻¹, and 1242 cm⁻¹ compared with the Pb(II)-loaded clay sample, suggesting a disruption of some of these groups during treatment. At around 3336 cm⁻¹ peak represents the -OH group, indicating existence of the hydroxyl groups on the surface of the clay. It can be explained by some atmospheric water adsorption appearing during the FTIR measurements. Also, the C-O stretching mode of the functional groups on the surface of the clay or arising from the absorption of atmospheric CO₂ on the surface of the clay can cause peaks between 1500 and 1650 cm⁻¹. The two peaks at 2919 and 2850 cm⁻¹ correspond to the C-H stretch vibration, originating from the surface of the clay, Figure 1(b), which are obviously weak in Figure 1(a), and sug-

Table of Instrumental Parameters for FTIR Analysis

Wavelength range	4000-500 cm ⁻¹
Sample to KBr mass ratio	1:100
Spectral resolution	4 cm ⁻¹
Crystal Type	Diamond

TABLE III
Analysis of Variance (ANOVA) for the Quadratic Polynomial Mode

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	39466.16	14	2819.01	283.46	< 0.0001	Significant
A-pH	2088.24	1	2088.24	209.98	< 0.0001	
B-Contact time	4084.83	1	4084.83	410.74	< 0.0001	
C-Adsorbent dosage	670.51	1	670.51	67.42	< 0.0001	
D-Agitation speed	32.67	1	32.67	3.29	0.0914	
AB	597.80	1	597.80	60.11	< 0.0001	
AC	41.60	1	41.60	4.18	0.0601	
AD	138.06	1	138.06	13.88	0.0023	
BC	136.89	1	136.89	13.76	0.0023	
BD	191.82	1	191.82	19.29	0.0006	
CD	900.00	1	900.00	90.50	< 0.0001	
A2	26291.92	1	26291.92	2643.74	< 0.0001	
B2	7324.44	1	7324.44	736.50	< 0.0001	
C2	3087.12	1	3087.12	310.42	< 0.0001	
D2	4933.39	1	4933.39	496.07	< 0.0001	
Residual	139.23	14	9.94			
Lack of Fit	119.02	10	11.90	2.36	0.2122	Not significant
Pure Error	20.21	4	5.05			
Cor Total	39605.39	28				
R-Squared	0.9965					
Adj R-Squared	0.9930					
Pred R-Squared	0.9819					

*p<0.01 highly significant; 0.01<p<0.05 significant; p>0.05 not significant.

Fig. 1. FTIR spectra of (a) clay and (b) Pb-loaded clay.

gests that the surface of the clay was covered with Pb(II).

Surface Morphology

The morphological differences between the clay and the Pb(II)-loaded clay were proved by using SEM. In Figure 2, the SEM images show the differences between the surface morphologies of the clay (Figure 2a) and the Pb(II) loaded (Figure 2b). After pretreatment with Pb(II), the surface of the clay is smoother which may be due to the Pb(II) adsorption onto clay. It can be stated that the nature of this clay is good for adsorption of Pb(II).

The mineralogical composition using EDX was determined as; 21.7% for SiO₂, 6.8% for Al₂O₃, 4.8%

Fig. 2. SEM image of clay: (left) before adsorption of Pb and (right) after adsorption of Pb.

Fig. 3. Actual predicted and residual values of the experimental design.

for Fe_2O_3 , 3.3% for MgO, 1.1% for K_2O , and 1.6% for CaO_2 .

Second-order Polynomial Model

The results of the Pb(II) adsorption onto clay conditions using BBD with RSM and ANOVA are shown in Tables II and III, respectively. The Model F-value of 283.46 indicates that the model is significant. There is only a 0.01% chance that an F-value this large could occur because of noise. Since the "Prob>F" values are less than 0.0500, this indicates that the model terms are significant. In this case, X_1 , X_2 , X_3 , X_1X_2 , X_1X_4 , X_2X_3 , X_2X_4 , X_3X_4 , X_1^2 , X_2^2 , X_3^2 , X_4^2 are statistically significant. On the other hand, the X_4 and X_1X_3 values greater than 0.1000 indicate that the model terms are not significant.

Because the model coefficient (R^2) was 0.9965, it can be said that 99.65% of the model-predicted values (Figure 3) matched the experimental adsorbed Pb(II) values on clay. In addition, Ince and Kaplan Ince (39) reported that a model is adequate at $R^2 > 0.75$ value. The "Pred R-Squared" value of 0.9819 is in reasonable agreement with the "Adj R-Squared" of 0.9930; i.e., the difference is less than 0.2. "Adeq Precision" measures the signal-to-noise ratio and where a value greater than 4 is desirable. Thus, this study ratio of 51.448 indicates an adequate signal. This study also revealed that the lack of fit that measures the fitness of the model was not significant ($p > 0.05$). The "Lack of Fit F-value" of 0.2122

implies that the Lack of Fit is not significant relative to the pure error. There is a 21.22% chance that a "Lack of Fit F-value" this large could occur because of noise. In addition, the number of experiments made was sufficient to determine the effects of the independent variables for Pb(II) adsorption on clay. The results verify that the statistical model was adequate in predicting the Pb(II) levels and was fitted to the second-order polynomial equation. Thus, while X_1 , X_2 , X_3 , X_4 , X_2X_3 , X_3X_4 , X_1^2 , X_2^2 , X_3^2 , X_4^2 are highly significant ($p < 0.01$) X_1X_2 , X_1X_3 , X_1X_4 , X_2X_4 , they are significant model terms for Pb(II) adsorption onto clay.

RSM Analysis

Two-dimensional (2D) contour plots and three-dimensional (3D) response surface graphs were made because they are useful in determining the maximum, minimum, and middle response points. Contour plots indicate the level of the variables and contribute to a desired response. Figure 4 shows the effect of contact time and pH on Pb(II) adsorption on clay. It was found that the adsorbed Pb(II) amount ($p < 0.01$) increased with an increase in pH and reached a plateau at 5 (see Figure 5) and also the quadratic variables had significant effects (pH, $p < 0.01$). The effects of agitation speed and pH on Pb(II) adsorption onto clay are shown in Figure 6. The adsorbed Pb(II) amount increased with increasing adsorbent dosage until reaching a plateau at 0.075 g along with contact time reaching a plateau at 38.9 minutes. Interaction of these two variables had a significant effect on Pb(II) adsorption and also the quadratic variables had significant effects ($p < 0.01$). Based on the agitation speed up to 100 rpm and contact time studies, these two variables have important effects for Pb(II) adsorption on clay, and also on the quadratic variables ($p < 0.01$).

Fig. 4. Response surface and contour plot for lead adsorption on clay as contact time and pH.

Fig. 5. Response surface and contour plot for lead adsorption on clay as adsorbent dosage and pH.

Fig. 6. Response surface and contour plot for lead adsorption on clay as agitation speed and pH.

Thus, the variables of agitation speed, pH, and dosage amount have significant effects on Pb(II) adsorption.

Confirmation Experiments

To support the optimized data given by numerical modeling, the experiments were conducted using pH 5.3, contact time 38.9 minutes, adsorbent dose 0.071 g, agitation speed 98.7 rpm, resulting in the removal of Pb(II) close to 100% (Table IV). A recent study by Ince et al. (40) reported the use of various adsorbents reported, using a 3-factor, 3-level BBD combined with RSM for maximizing Cu(II) removal from aqueous solution for adsorption of Cu(II) onto banana peel, chestnut shell, and tea leaf waste. The equilibrium data agreed well with the two isotherm models Freundlich and Langmuir. Based on the astragalus adsorption capacity results, their capacity was calculated as 1.94 mg g^{-1} , 2.25 mg g^{-1} , and 3.36 mg g^{-1} (pH 4-6), respectively. Srivastava et al. (41) removed the Cd^{2+} , Ni^{2+} , and Zn^{2+} ions from aqueous solutions of rice husk ash using Taguchi's optimization methodology. Some adsorption parameters including initial metal concentration, temperature, solution pH, adsorbent amount and stirring time were varied at three levels. The results revealed that Taguchi's method is suitable for optimizing the experiments for total metal ion removal. They obtained optimum adsorptive removal of metal ion conditions as $C_i = 0-100 \text{ mg L}^{-1}$, $T = 40^\circ \text{C}$, $\text{pH} = 6$, $m = 10 \text{ g L}^{-1}$ and $t = 60 \text{ min}$. Sardelle et al. (42) prepared various materials as adsorbent, including grape stalk and pomace to remove Pb and Cd. Adsorbents were characterized by BET and FTIR. They mentioned that the Langmuir and Freundlich models were fitted for Pb and Cd on these adsorbents. Optimum pH was obtained for Pb and Cd as 5.5 and 6, respectively. When grape

TABLE IV
Removal of Pb(II) Ions Using Clay From
Various Alcoholic Beverage Samples

Sample	SA	Pb(II) ($\mu\text{g L}^{-1}$)	
		Found	(%)Removal
Beer 1	0.0	8.3 $\pm$ 0.4	
	20	27.9 $\pm$ 0.4	99.0
Beer 2	0.0	6.5 $\pm$ 0.2	
	20	26.3 $\pm$ 0.6	99.0
Beer 3	0.0	7.6 $\pm$ 0.2	
	20	26.8 $\pm$ 0.3	97.0
Beer 4	0.0	7.2 $\pm$ 0.2	
	20	26.9 $\pm$ 0.3	99.0
Beer 5	0.0	8.1 $\pm$ 0.3	
	20	27.8 $\pm$ 0.3	96.0
Beer 6	0.0	9.2 $\pm$ 0.2	
	20	28.9 $\pm$ 0.5	97.0
Beer 7	0.0	8.8 $\pm$ 0.4	
	20	29.0 $\pm$ 0.6	100
Beer 8	0.0	8.7 $\pm$ 0.2	
	20	28.8 $\pm$ 0.5	100
Beer 9	0.0	7.7 $\pm$ 0.2	
	20	27.7 $\pm$ 0.2	100
Beer 10	0.0	7.7 $\pm$ 0.2	
	10	26.6 $\pm$ 0.4	96.0
Home-made red wine 1	0.0	17.7 $\pm$ 0.3	
	20	38.1 $\pm$ 2.1	100
Home-made red wine 2	0.0	21.2 $\pm$ 3.1	
	20	41.8 $\pm$ 2.5	100
Home-made white wine 1	0.0	28.4 $\pm$ 1.2	
	20	49.3 $\pm$ 2.2	100
Home-made white wine 2	0.0	23.4 $\pm$ 2.4	
	20	42.6 $\pm$ 2.2	100
Standard reference materials	100.0	98.0 $\pm$ 3	99.0

SA: Standard Addition.

pomace-activated carbons were used as adsorbent removal, the gain was around 98% (41). Mishra and Patel (15) used kaolin and bentonite clays as adsorbent with a particle size between 100 mesh and 200 mesh to remove the Pb and Zn ions from water. They investigated the effect of contact time, pH, and adsorbent dosage on Pb and Zn removal. While the equilibrium

time was found to be 3 hours for kaolin and bentonite, the most effective pH value for Pb and Zn removal was 6. According to experimental results, it was found that bentonite clay was an effective adsorbent for Pb and Zn removal. Potgieter et al. (43) removed Pb, Ni, Cr, and Cu from aqueous solution of palygorskite clay. Their study was carried out at room tem-

perature and metals adsorption onto clay was studied by using a batch method, and the adsorption results were fitted to both the Langmuir and Freundlich models. The adsorption capacity of the palygorskite clay was calculated according to the Langmuir isotherm with 62.1 mg g⁻¹ Pb(II), 33.4 mg g⁻¹ Ni(II) g⁻¹, 58.5 mg g⁻¹ Cr(VI), and 30.7 mg g⁻¹ Cu(II) at a pH of 7.0 at 25 °C (42). Ince et al. (44) studied a batch experimental system for removal of several heavy metals including Ni²⁺, Pb²⁺, and Cd²⁺ using banana peel food waste. After investigating the effects of various parameters, the maximum adsorbent amount was found to be Pb 0.1 g, for Cd and Ni 0.25 g. According to the results of another study (45) in an aqueous system, eggshell was used as adsorbent to remove Cd²⁺. In that study, the design experimental methodology and RSM were used to optimize the parameters such as pH and adsorbent dosage. The RSM indicated that the optimum adsorbent dosage of hydroxyapatite was 0.57 g for the adsorption of Cd²⁺.

Analytical Application to Real Samples

The Pb content was tested using real samples, such as beer and wine, purchased at different local markets in Tunceli city, Turkey. The Pb(II) ions were concentrated by using an adsorption technique on natural clay and determined by ETAAS. The developed analytical method of BBD combined with RSM and quadratic programming using natural clay was found to be an effective and eco-friendly adsorbent. Under optimum conditions, an approximate 50 mL of real samples was filtered and adjusted to pH 5.3. Additional 50 mL aliquots were spiked with Pb(II) at pH 5.3. The solutions were agitated with 0.071 g of clay for 38.9 minutes. The metal ions were then eluted with 4 mL of 1M HNO₃ and the Pb concentrations determined by ETAAS. The

results in Table IV show the efficiency of clay for the removal of Pb(II) ions. The results revealed that Pb concentration in the beer and wine samples were in the range of 6.5 ± 0.2 – 9.2 ± 0.2 ng mL⁻¹ and 17.7 ± 0.2 – 28.4 ± 1.2 ng mL⁻¹, respectively. Accuracy of the method was studied using standard addition for the standard reference material (SRM) SPS-SW1 Batch 113 Surface Waters (Spectrapure Standards AS-Oslo, Norway), resulting in 99%.

CONCLUSION

The present study revealed that the effects of solution pH, contact time, adsorption amount, and agitation speed were researched using RSM and BBD for the adsorption of Pb(II) from alcoholic beverages by clay. The application of the present technique to alcoholic beverages is unique in the literature. The result is that the environmentally friendly adsorbent, clay, can be efficiently and simply used to remove Pb(II). Also, the obtained data from this study revealed that the removal of Pb(II) using clay was influenced by the main and quadratic independent variables effects investigated. Based on the ANOVA, whole coefficients ($R^2 > 0.9965$) were of high value in the regression model. Hence, to describe and predict the variation of the response variables, an empirical point of view was developed. In this study, optimization with BBD has the advantages of being economical, saves analysis time, and is efficient.

Received February 1, 2018.

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