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Preparation and characterization of calcite for tannic acid adsorption: Optimization by response surface methodology coupled by Box-Cox transformation procedure

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Abstract: Calcite depression is the most effective physicochemical process to valorize fluorine mineral. This process is achieved by adsorption of tannic acid, as the commonly used reagent, onto calcite. Adsorption investigation is very important in mineral processing. The present work focuses on optimization of physicochemical parameters of tannic acid adsorption onto calcite. Experimental study is carried out by a response surface methodology based on Box-Behnken design. Obtained results are exploited to develop a statistical model. Analysis of variance and residuals are performed to check the significance of tested models. Among these models, Cox-Box model predicts very well the obtained experimental data. This model shows that initial tannic acid concentration and solution pH as well as their interactions are the most significant parameters. Optimal conditions are achieved using the obtained statistical model. The present investigation is an important preliminary step to better understand calcite flotation behavior using tannic acid as a depressant.

Keywords: calcite, tannic acid, adsorption parameters, optimization, Response Surface Methodology, Box-Cox transformation.

1. Introduction

Calcite is an important mineral of sedimentary rocks (Morse and Mackenzie, 1990). However, it can be intergrown, as a major gangue mineral, with valuable minerals in the ore deposits, such as fluorine (Albuquerque et al., 2012; Antti and Forssberg, 1989; Gao et al., 2018; Hiçyìlmaz et al., 1993; Schubert et al., 1990). Thus, calcite is known as the least one and must be separated from fluorine mineral. Because of their similar surface properties, their separation is difficult.

Calcite depression by flotation is the most effective physicochemical process to separate calcium minerals (Ayhan et al., 2006; Gao et al., 2018; Li and Gao, 2017; Zhu et al., 2018). This process is mainly achieved by adsorption of molecules, generally organics, on mineral surfaces. The widely used organic molecules contain starch, guar and sodium lignosulfonate (Chen et al., 2017; Somasundaran, 1969) and tannic acid is the most commonly used one (Rutledge and Anderson, 2015).

Tannic acid is a polyphenolic component that can be extracted from different parts of plants and trees, such as seeds, fruits, roots and bark (Bacelo et al., 2016; Martinez de Yuso et al., 2014). It is characterized by the presence of multiple adjacent hydroxyl groups that exhibit a specific affinity to calcium carbonate (Hoch et al., 2000).

According to Zhang et al literature, separation performance of calcite and fluorite by tannic acid has been evaluated and indicated that this reagent may effectively depress calcite surface (Zhang et al., 2018). Furthermore, preferential adsorption sites of calcite were easily occupied by tannic acid. Recently,

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it was shown that acidic conditions can significantly improve depression effect of tannic acid onto calcite (Gao et al., 2019). While, calcite dissolution in acidic medium (Somasundaran, 1969) may undergo a significant desorption of tannic acid onto calcite. Mohammadkhani et al (Mohammadkhani et al., 2011) examined that the reverse flotation of carbonate minerals using tannic acid as a depressant is not an efficient method to separate phosphate from carbonates.

Unfortunately, all above mentioned studies have been focused only on the depression performance of calcite using tannic acid as a depressant and didn't scrutinized the adsorption process. Whereas, the investigation of tannic acid adsorption onto calcite is very important to better understand the physico-chemical reactivity of tannic acid via calcite in mineral processing.

In our previous work, a detailed and profound experimental investigation of many physico-chemical parameters effect on tannic acid adsorption onto calcite, using a conventional optimization method, has been carried out (Tangarfa et al., 2019). This exhaustive method consists in varying one factor and keeping the others constant. On the other hand, a response surface methodology is an efficient procedure to design and optimize experiments by varying several factors at the same time. To our knowledge, optimization of tannic acid adsorption onto calcite by response surface methodology has not been studied in scientific literature.

Therefore, the aim of the present paper is to optimize tannic acid adsorption onto calcite using Box-Behnken design of response surface methodology, to determine significant physico-chemical parameters and their combined effect. The statistical model obtained is exploited in order to achieve optimal conditions. To reach data normality and enhance model significance of the adsorption process, a cox-box transformation procedure is performed. Based on scientific articles, this procedure has not been employed in this investigated adsorption process.

2. Materials and methods

2.1. Material and reagent

2.1.1. Adsorbent preparation

Calcite sample used in the experiment was derived from El hammam mine of Meknes in Morocco. Firstly, it was crushed by a jaw and cylindrical crusher to obtain less than 0.54 mm particle sizes. Secondly, several grinding steps were performed in a mechanical grounder. Then, a wet sieving in various fractions in order to collect +40-80 µm particle sizes for further investigation.

2.2.1. Adsorbate preparation

A commercial tannic acid reagent of a high purity greater than 95% and a molecular weight of 1701.20 Dalton was used in this work as an adsorbate, supplied from Sigma Aldrich. Stock solution was prepared by dissolving 1 g of dried tannic acid powder in 100 mL of distilled water. The intermediate solutions of desired concentrations were then obtained by stock solution dilution.

2.2. Adsorption procedure

In order to investigate the effect of initial tannic acid concentration, solution pH and ionic strength on tannic acid adsorption onto calcite, all performed experiments were carried out in a pyrex beaker of 250 mL. For each experiment, different amount of potassium chloride, as an electrolyte, was added to 100 mL of distilled water to investigate ionic strength effect. Knowing that this parameter is one of the parameters affecting the ion activity in aqueous solution. Then, 1 g of calcite and a required concentration of tannic acid solution were added to each beaker. The solution pH was adjusted by hydrochloric acid or sodium hydroxide solutions. The adsorbent-adsorbate mixture was shaken at 250 rpm for 30 minutes. After equilibrium, the obtained mixture was decanted, filtered and then analysed by Ultra Violet Visible spectrophotometer at 278 nm to determine the equilibrium tannic acid concentration. The resulting adsorption capacity of tannic acid was calculated as follow:

$$Q = \frac{(C_i - C_e)}{m} * V \quad (1)$$

where, Ci and Ce (mg/L) are the initial and equilibrium tannic acid concentration, respectively. V (L) is the solution volume, and m (g) is the adsorbent mass.

2.3. Response Surface Methodology: Box-Behnken experimental design

Response surface methodology was used to reduce experiments number, to evaluate the effect of different factors and their interactions on the response and hence to determine optimal conditions (Cho and Zoh, 2007; Ghaedi et al., 2015; Wang et al., 2007). Box-Behnken design is the most frequently used one of response surface methodology that has been applied in several studies especially to analyse and validate adsorption data (Aslani et al., 2018; Bilgin Simsek et al., 2015; Khatoon et al., 2018; Shah et al., 2017; Subramaniam et al., 2015). In the present work, experimental study of tannic acid adsorption onto calcite was performed according to Box-Behnken design. The operating parameters including initial tannic acid concentration, solution pH and ionic strength were selected in order to evaluate their influence on the adsorption capacity. The experimental range of each independent parameter was chosen on the basis of preliminary tests. It should be mentioned that this choice was based also on obtained results from our previous experimental study focused on the effect of physico-chemical parameters of tannic acid adsorption onto calcite using an optimization conventional method (Tangarfa et al., 2019). Real factor values were coded as -1 (low), 0 (centre point) and 1 (high) (Evans, 2003). The experimental range, real and coded values of these factors are presented in Table 1.

Table 1. Experimental range, real and coded independent variables

Variables	Levels and ranges		
	-1	0	1
X1: Initial tannic acid concentration (mg/L)	25	100	175
X2: pH	6	8	10
X3: Ionic strength (Mol/L)	0	0.05	0.1

The number of Box-Behnken Design experiments was calculated by the following formula:

$$N = 2k(k-1) + N_0 \tag{2}$$

where k is the factor number and N_0 is the replicate number of the central point of the design (Macedo et al., 2009). This point was replicated three times for estimating the experimental error and data reproducibility. In this case, a total of 15 experiments (including three centre points) was obtained. Box-Behnken design and its experimental results is summarized in Table 2. The experimental design was performed by using Statgraphics Centurium 18.

Table 2. Box–Behnken design and experimental results

Row	X1	X2	X3	Q (mg/g)
1	25	6	0.05	1.63
2	175	6	0.05	6.94
3	25	10	0.05	0.94
4	175	10	0.05	8.73
5	25	8	0.00	1.11
6	175	8	0.00	14.38
7	25	8	0.10	1.50
8	175	8	0.10	13.23
9	100	6	0.00	4.95
10	100	10	0.00	2.10
11	100	6	0.10	3.57
12	100	10	0.10	6.35
13	100	8	0.05	7.36
14	100	8	0.05	7.05
15	100	8	0.05	7.16

3. Results and discussion

3.1. Statistical modelling

2.3.1. Analysis of variance

To predict experimental adsorption capacity, three analysis option of multiple regression with and without constant were explored. These procedures are Ordinary Least Square (OLS), Forward Stepwise Selection (FSS) and Backward Stepwise Selection (BSS). Indeed, OLS fits a model containing all independent variables. While, FSS starts with only a constant and then adding significant variables. Whereas, BSS starts firstly with a model involving all variables and secondly removing non-significant variables. Thus, six different statistical models with and without constant are obtained and predicted by quadratic equation as followed:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j + e_i \quad (3)$$

where Y is the dependent variable, X_i and X_j are independent variables, β0, βi, βii and βij are the constant, linear, quadratic and interaction coefficients, respectively, and e_i is the random error (Chattoraj et al., 2014). In order to evaluate factors significance and their interactions as well as regression model adequacy, analysis of variance at 95% confidence level was performed (Liu et al., n.d.). Based on this analysis, comparison of all obtained six statistical models was performed. This allows to select the best models predicting our experimental data. Obtained results of the satisfactory models are summarized in Table 3. They correspond to FSS and BSS without constant, respectively.

Table 3. Analysis of variance results

Models	Parameter	Estimate	Standard Error	P-Value
FSS without constant	X1	0.0592664	0.00489038	< 0.0001
BSS without constant	X1* X2	0.00721715	0.000660901	< 0.0001

Models	Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value	R-squared (%)	Mean absolute error
FSS without constant	Model	684.938	1	684.938	146.87	< 0.0001	91.30	1.63
	Residual	65.2903	14	4.66359				
	Total	750.228	15					
BSS without constant	Model	671.405	1	671.405	119.25	< 0.0001	89.49	1.70
	Residual	78.8232	14	5.63023				
	Total	750.228	15					

From these results, it's so clear that P-Value is low than 0.0001. Furthermore, satisfactory correlation coefficient (between 89 and 91 %) and Mean Absolute Error values (between 1.60 and 1.70) are obtained. Furthermore, the initial tannic acid concentration (X1) and its interaction with solution pH (X1* X2) are the significant terms (P-Value < 0.05). While, the other parameters such as solution pH (X2) and ionic strength (X3) and their interaction as well as the interaction between X1 and X3 were not considered by the obtained models because they are not significant (P-Value > 0.05). Based on literature, solution pH is the main factor in adsorption process. Effectively, our previous study revealed that phenolic groups adsorption capacity was significantly dependent on solution pH (Tangarfa et al., 2019). The same result was also obtained by Richa Sharan et al (Sharan et al., 2009). Therefore, FSS and BSS without constant models require an improvement.

2.4.1. Residual analysis

Furthermore, the model significance can be checked by residual analysis. This allow to examine the residual between observed and predicted values of response (Bezerra et al., 2008). Residual plots versus row number for the two selected models are shown in Fig. 3 a) and b).

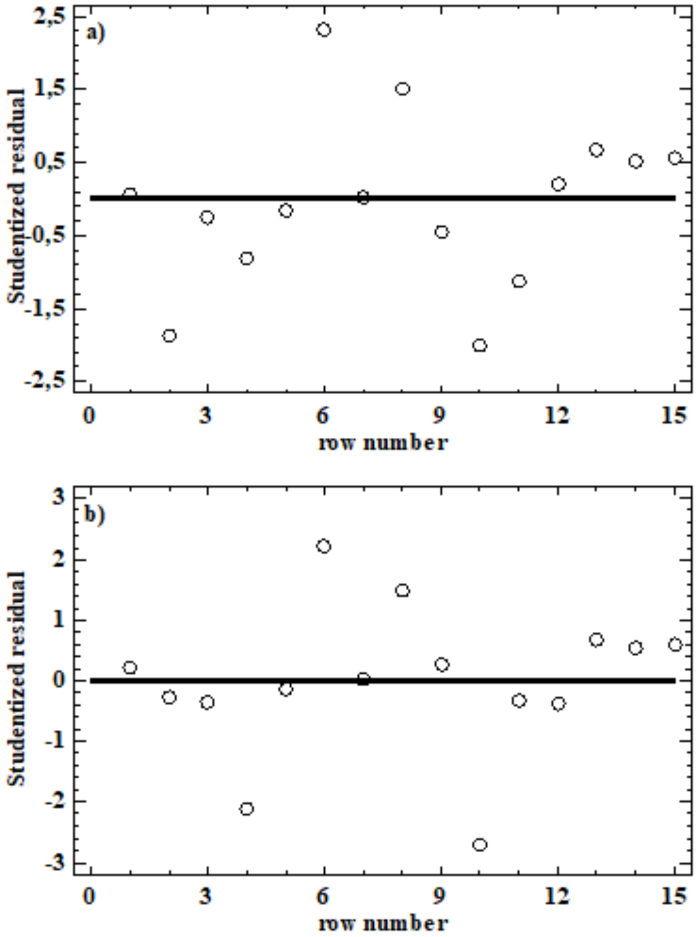

Fig. 3. Residual plots for a) FSS without constant and b) BSS without constant

From this Figure, we can observe that there are many points far from the straight line for the two models. Moreover, a variance systematic change is shown indicating a non normal distribution. These results confirm that the selected models according to FSS and BSS without constant need to be improved. This can be performed by Box-Cox transformation.

3.2. Box-Cox transformation

This transformation procedure permits, as described by Box and Cox, to ensure data distribution normality and to enhance model significance (Box P, 1964). This procedure was carried out by Statgraphics Centurium 18 according to the following expression:

$$Y' = -Y^{\lambda} \quad (4)$$

where Y and Y' are the response variable before and after transformation, respectively and λ is the parameter transformation estimated by Statgraphics Centurium 18. The transformed dependent variable was analysed by Analysis of variance as well as residual methods.

2.5.1. Analysis of variance

Analysis of variance was performed at 95 % confidence level. Table 4 indicate Box-Cox procedure results with and without constant, respectively.

Compared to previously obtained models by FSS and BSS without constant, Box-Cox model with and without constant show a high correlation coefficient (of approximately 99 %) and a low Mean Absolute Error (between 0.20 and 0.30). Moreover, these two models show that all factors and their interaction are significant, except ionic strength.

Table 4. Analysis of variance of Box-Cox transformation

Models	Parameter	Estimate	Standard Error	P-Value
Box-Cox transformation with constant (λ = -0.59)	CONSTANT	-12.9317	4.51808	0.0353
	Ci	0.113652	0.0168681	0.0011
	pH	4.80498	1.07366	0.0065
	I	-67.1762	23.9655	0.0379
	Ci*Ci	-0.000543462	0.0000466288	0.0001
	Ci*pH	0.00932962	0.00167998	0.0026
	Ci*I	-0.189598	0.0671993	0.0370
	pH*I	16.5414	2.51997	0.0012
	pH*pH	-0.434872	0.0655718	0.0012
	I*I	-303.974	104.915	0.0339
Box-Cox transformation without constant (λ = -0.78)	Ci	0.112674	0.0220964	0.0022
	pH	2.00888	0.359355	0.0014
	I	-79.3914	32.2256	0.0489
	Ci*Ci	-0.000630305	0.000064243	0.0001
	Ci*pH	0.0125145	0.0022329	0.0014
	Ci*I	-0.219657	0.0932917	0.0567
	pH*I	18.406	3.41973	0.0017
	pH*pH	-0.294363	0.0387317	0.0003
	I*I	-281.531	145.299	0.1008

Models	Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value	R-squared (%)	Mean absolute error
Box-Cox transformation (λ = -0.59)	Model	295.531	9	32.8368	129.27	< 0.0001	99.57	0.22
	Residual	1.27005	5	0.254011				
	Total (Corr.)	296.801	14					
Box-Cox transformation (λ = -0.78)	Model	2137.29	9	237.477	482.40	< 0.0001	99.86	0.35
	Residual	2.95371	6	0.492286				
	Total (Corr.)	2140.25	15					

2.6.1. Residual analysis

Residual plots of Box-Cox transformation models with and without constant are presented in Fig. 4, respectively.

This Figure shows that the most data points are close to straight line in Box-Cox transformation without constant (Fig.4 b)) satisfying a normal distribution. Thus, it is the best obtained model predicting experimental data as expressed in the following regression:

$$Cox - Box(Q) = 0.11\, X_1 + 2\, X_2 - 6 \times 10^{-4} X_1 \times X_1 + 0.01\, X_1 \times X_2 - 0{,}29\, X_2 \times X_2 \tag{5}$$

where:

$$Cox - Box(Q) = 1 + \frac{Q^{\lambda-1}}{\lambda * 4.24^{\lambda-1}} \tag{6}$$

According to Box-Cox transformation results, we can conclude that tannic acid adsorption capacity predicted by Box-Cox model without constant depends on the linear and second order term of both initial tannic acid concentration (X1 and X1* X1) and solution pH (X2 and X2* X2) as well as their interaction (X1* X2).

4. Optimization of tannic acid adsorption capacity

Optimization of tannic acid adsorption onto calcite was examined by three-dimensional (3D) contour desirability plot. Obtained results are illustrated in Fig. 5.

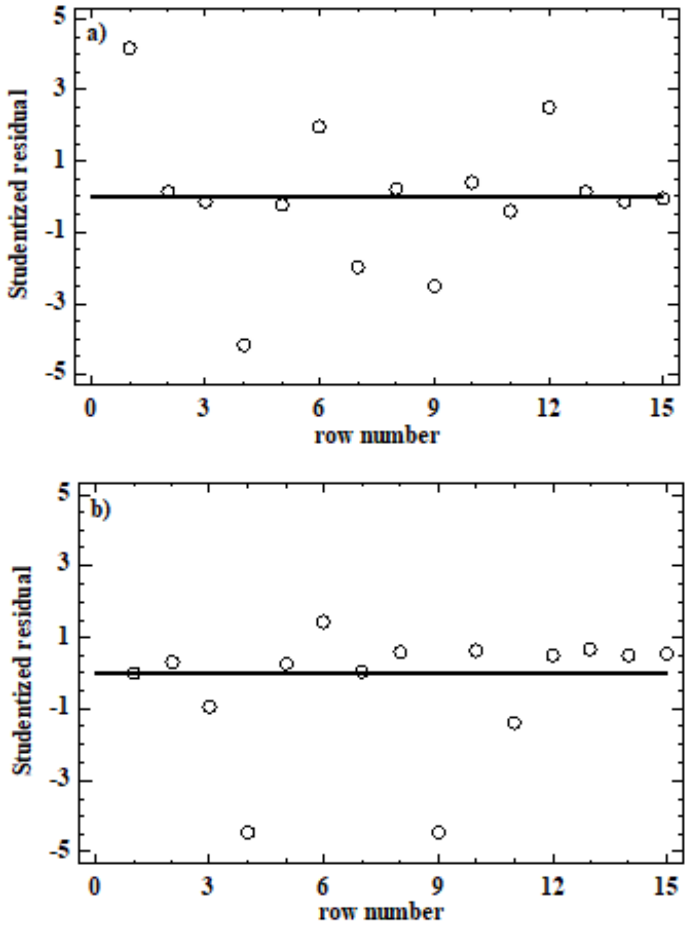

Fig. 4. Residual plots of Box-Cox transformation a) with constant and b) without constant

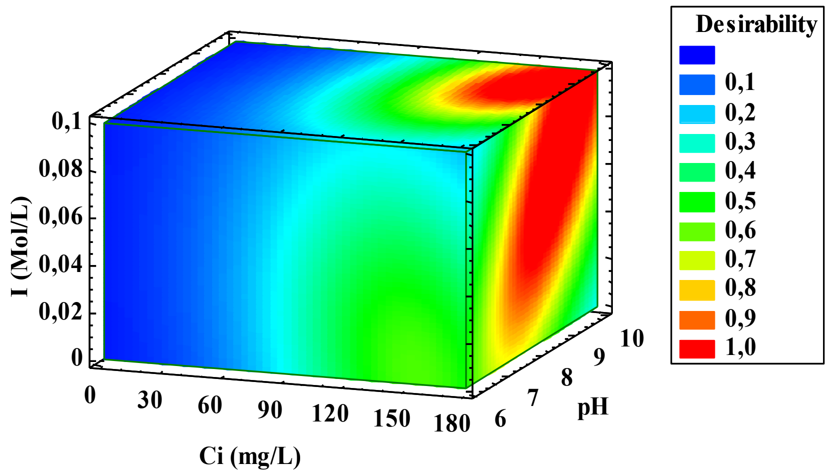

Fig. 5. 3D contour desirability plot of the effect of initial tannic acid concentration, pH and ionic strength

It is clear that tannic acid adsorption onto calcite is highly dependent on initial tannic acid concentration (X1) as well as solution pH (X2). The desirability increases with initial tannic acid concentration increasing. Furthermore, an optimum of solution pH is obtained that is maximized the desirability. Whereas, ionic strength (X3) doesn't strongly influence the studied adsorption. Therefore, optimal condition results of tannic acid adsorption onto calcite are presented in Table 5 and revel that maximum adsorption capacity of 14.73 mg/g is obtained using an initial tannic acid concentration of 175 mg/L and a pH value of 8.14.

Table 5. Optimal conditions of tannic acid adsorption onto calcite

Q (mg/g)	Ci (mg/L)	pH
14.73	175	8.14

The optimal obtained conditions of initial tannic acid concentration and solution pH are close to those obtained in our previous work by optimization conventional method (Tangarfa et al., 2019). While, the low significance of ionic strength is confirmed by some researchers indicating similarly that the presence of sodium chloride, as an electrolyte, in aqueous solution had a slight influence on tannic acid adsorption (Lin et al., 2011).

5. Model validation

In order to evaluate the model precision, experimental tests of studied adsorption process were performed under predicted optimal conditions in quintuplicate. The obtained experimental adsorption capacity of tannic acid is expressed as the mean of the quintuplicate. The experimental test results are summarized in Table 6.

Table 6. Model validation results

Optimal conditions		Q (mg/g)	
C (mg/L)	pH	Q experimental (mg/g)	Q predicted (mg/g)
175	8.14	14.67	14.73

From these results, we conclude that experimental adsorption capacity is very close to that obtained by Box-Cox model. Thus, this model can predict very well the studied adsorption under chosen experimental conditions.

6. Conclusions

Tannic acid adsorption onto calcite as a function of initial tannic concentration, solution pH and ionic strength was experimentally conducted out by Box-Behnken design. In order to predict experimental data obtained by an adequate statistical model, three analysis methods consisting of OLS, FSS and BSS with and without constant were exploited within Statgraphics Centurium 18. To select the satisfactory models, the six obtained statistical models were compared by Analysis of variance at 95 % based on P-Value, correlation factor and Mean Absolute Error. Two statistical models were obtained corresponding to FSS and BSS without constant with an accepted correlation factor and a Mean absolute error of approximately 90 % and 1.65, respectively. Furthermore, these results were confirmed by residual analysis. Therefore, a non-normal distribution of observed data predicted by FSS and BBS without constant was shown. To improve these two models significance, a Box-Cox transformation was performed and allowed to obtain a better statistical model with a high correlation factor (99.86 %) and a low Mean absolute Error (0.35). The transformed adsorption capacity was dependent on initial tannic acid concentration and solution pH as well as their interaction. These dependent variables were optimized using 3D response surface methodology. Optimization results indicated that about 14.67 mg/g of adsorption capacity is obtained using an initial tannic acid concentration of 175 mg/L and a solution pH of 8.14. The obtained results of this study have a potential application to better understand flotation behaviour of calcite using tannic acid as a reagent. Thus, further experimental investigation is required to exploit all these results in calcite flotation using tannins as depressants.

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