Behavior and Mechanism of Tannic Acid Adsorption on the Calcite Surface: Isothermal, Kinetic, and Thermodynamic Studies

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ABSTRACT: Tannic acid is a calcite flotation agent widely used in mineral processing. To better understand the physicochemical reactivity of tannic acid toward calcite, the present work focused on studying the mechanisms involved during the adsorption process. Hence, in order to determine the optimal physicochemical parameters, tannic acid adsorption onto calcite was investigated at various experimental conditions such as contact time, initial tannic acid concentration, solution pH, particle size, and temperature. The obtained results showed that the adsorption capacity of tannic acid increased significantly with initial tannic acid concentration. Furthermore, tannic acid adsorption onto calcite was highly dependent on solution pH, and the optimal adsorption amount was found to be at pH 8. Therefore, the behavior controlling the studied adsorption process could be attributed to ion exchange. Moreover, the adsorption mechanism has been determined by isothermal, kinetic, and thermodynamic studies. Thus, the Sips isotherm model was the one that best predicted equilibrium data. Adsorption kinetics followed a pseudo-second-order model, indicating that the adsorption process was controlled by the chemical reaction. The estimated thermodynamic parameters revealed that the adsorption reaction was exothermic in nature and the system entropy decreased nonsignificantly during this process. Based on these results, the study of the physicochemical interaction between tannins and carbonates has potential application in mineral processing as well as in other fields.

1. INTRODUCTION

Flotation is known to have an increasing emphasis in ores’ valorization through the adsorption of chemical reagents, including sodium oleate as a collector and acidized sodium silicate as a depressant, on mineral surfaces. Unfortunately, some of these chemicals are expensive and may affect the environment as well as human health. Thus, the use of environment-friendly reagents, such as tannins, is a sustainable alternative. Tannins can be defined as polyphenolic groups that can be derived from the breakdown of plant biomass, containing fruits, roots, seeds, and bark. Because of their high number of adjacent hydroxyl groups, tannins present a significant affinity to metal ions, including calcium ion. On the other hand, calcite is one of the most calcium-containing minerals and an important component of sedimentary rocks, which can be treated with tannins, such as quebracho, tannic acid, valonea, and so forth.

Indeed, quebracho tannin has been used as an effective depressant in the flotation process for the separation of scheelite, fluorite, and calcite. The experimental study of the effect of tannic acid as a depressant on the fluorite flotation behavior showed that the acidic conditions significantly enhanced the selective depression of calcite. Tannic acid adsorption onto calcite has also been studied by photoelectric spectroscopy, which revealed that the hydroxyl groups of tannins are preferentially adsorbed on calcite sites. Furthermore, tannic acid has been used in the reverse flotation of phosphates as an efficient method to separate phosphates from carbonates. In a recent study of valonea, tannin adsorption was seen on fluorite as well as barite and calcite, and it is noted that zeta potential measurements showed a stronger affinity of tannins toward calcite compared to those of barite and fluorite. On the other hand, many studies were carried out on tannin adsorption in water treatment, which revealed a strong interaction between various substrates and tannins, among which the substrates considered included activated carbon, clays, bentonites, collagen fibers, deacetylated Konjac glucomannan, carbon, and so forth. However, none of the previously cited work related to mineral processing shows clearly the mechanism of tannin adsorption.

The goal of the present work is to carry out a detailed experimental study of tannic acid adsorption onto calcite in order to better understand the surface physicochemical phenomena involved during tannin use in mineral processing. To this end, the effect of significant physicochemical parameters (solution pH, contact time, particle size, initial
tannic acid concentration, and temperature) on the adsorption behavior was studied to achieve the optimal conditions. The obtained results were then exploited to determine the adsorption mechanism by isothermal, kinetic, and thermodynamic investigations.

2. RESULTS AND DISCUSSION

2.1. Contact Time Effect. The contact time effect on the adsorption capacity of tannic acid studied at room temperature is represented in Figure 1.

This figure shows that tannic acid adsorption kinetic can be delimited into three steps. The first step of about few minutes was extremely rapid during which 75.5% of tannic acid was adsorbed onto calcite. Then, a slow step followed progressively until the adsorption process achieved the equilibrium. The initial rapid adsorption can be explained by the availability of active sites for tannic acid adsorption onto calcite. While the slow adsorption behavior observed in the second step can be attributed to the decrease in the number of active sites of the adsorbent. The equilibrium time of tannic acid adsorption on the calcite mineral was finally found to be equal to 30 min. This value was considered as an appropriate contact time used for further experiments.

2.2. Particle Size Effect. Figure 2 indicates the adsorption capacity variation of tannic acid obtained as a function of initial tannic acid concentration for two different calcite particle size ranges.

It can be seen from the obtained results that the adsorbed tannic acid increases as the calcite particle size decreases. This may be due to a large number of smaller particles which lead to more available exchange surface in the adsorption system.

2.3. Initial Tannic Acid Concentration Effect. At room temperature, the initial tannic acid concentration effect on adsorption is given in Figure 3.

These results show clearly that the adsorption capacity of tannic acid increases with initial concentration until equilibrium. This was reached at 200 mg/L of initial tannic acid concentration. The increase of adsorbed tannic acid was probably due to the increase of the adsorbate concentration gradient between the solution and adsorbent surface. On the other hand, the equilibrium was related to the saturation of active adsorption sites at adsorbate higher concentration.

2.4. Modeling of Adsorption Isotherms. In order to describe the tannic acid adsorption mechanism onto calcite, three adsorption isotherm models were tested in the present study: Langmuir, Freundlich, and Sips. The Langmuir isotherm model assumed that the adsorption occurs on a homogeneous surface by monolayer adsorption. Furthermore, the adsorption sites are well determined, identical, and energetically equivalent without interaction between adsorbed molecules. This model is written as

$$q = \frac{q_{\text{max}} K L C_e}{1 + K L C_e}$$

where $C_e$ (mg/L) is the equilibrium adsorbate concentration, $q$ (mg/g) is the equilibrium adsorbed amount per unit of adsorbent mass, $q_{\text{max}}$ (mg/g) is the maximum adsorption capacity, and $K_L$ (L/g) is the Langmuir constant.

On the other hand, the Freundlich isotherm model is based on a multilayer adsorption on a heterogeneous surface.
\[ q = K_f C_e^{1/n} \]  
\[ q = q_{\text{max}} \frac{K_s C_e^{1/n}}{1 + K_s C_e^{1/n}} \]  

where \( K_f \) [(mg/g)/(mg/L)\(^{1/n}\)] and \( n \) are the Freundlich constant indicators of adsorption capacity and intensity, respectively.

The Sips model is a combination between Freundlich and Langmuir. At low sorbate concentrations, it reduces to Freundlich isotherm, whereas at high sorbate concentrations, it is assimilated to Langmuir isotherm.\(^{36,37}\) The Sips model is represented by

The adsorption isotherms are obtained by the graphical representation of the equilibrium adsorbed tannic acid as a function of the equilibrium solution concentration at different values of initial solution pH (Figure 4).

\[ q = q_{\text{max}} \frac{K_s C_e^{1/n}}{1 + K_s C_e^{1/n}} \]  

where \( n \) and \( K_s \) (L/mg) are the heterogeneity index and the adsorption affinity constant, respectively.

To get through the interaction system between tannic acid and the calcite surface, the previously mentioned models (Langmuir, Freundlich, and Sips) have been tested on the basis of experimental equilibrium data using the nonlinear fitting method (Figure 5).

The obtained estimated parameters of the models are represented in Table 1.

The latter shows clearly that the Sips model is the best one, which describes tannic acid adsorption onto calcite (\( R^2 \) close to 1) for different tested solution pH values. The same result was obtained by tannic acid adsorption study on zeolite.\(^{38}\) Table 1 indicates that the adsorbed amount changes in terms of pH. At pH 6, a high adsorption amount of 29.08 mg/g is reached, whereas at pH 8 and 10, the adsorbed amounts are 13.55 and 4.10 mg/g, respectively. It can be concluded that tannic acid adsorption onto calcite is highly dependent on pH solution. This may be due to different positive and negative surface species of calcite (CaOH\(^{2+}\), CaHCO\(_3\), CaOH, and CaCO\(^3-\)) as a function of pH solution.\(^{39}\)

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**Figure 4.** Tannic acid adsorption isotherms onto calcite at different values of solution pH.

**Figure 5.** Nonlinear fitting of tannic acid adsorption isotherms onto calcite at different values of pH solution. (a) pH 6, (b) pH 8, (c) pH 10.
Because of the dissolution of calcite in acidic medium,²⁰ the high adsorbed amount at pH 6 can be attributed to the adsorption process as well as the precipitation reaction. Effectively, some researchers showed that at the pH value of 5, the precipitation of polyfunctional tannins with metal ions including the calcium ion Ca²⁺ may be involved.⁴¹,⁴² At pH 8, a weak tannic acid is completely ionized.⁵³ However, the calcite surface becomes less positive (zeta potential ≈ 4 mV) than at pH 6 (zeta potential ≈ 12 mV).⁶⁸ Thus, a lower affinity (2.89 × 10⁻⁵ L/mg) and a decrease of the adsorbed amount were observed. Under these conditions, the n low value was also observed. This resulted in a weak attraction between tannic acid and calcite.⁴⁵ Another possible reason for the decrease in adsorption at pH 8 is the competition between tannic acid functional groups and calcite negative species (CaCO₃⁻). Moreover, a competition between hydroxyl groups of both the acidic medium and tannic acid can occur. All these results show that the interaction between tannic acid functional groups and calcite surface species can be attributed to an ion exchange mechanism. Furthermore, the obtained appropriate pH value of tannic acid adsorption onto calcite is 8. The same pH value was obtained in the study of phenol adsorption on coal ash by Sharan et al.⁴⁷

### 2.5. Kinetic Study

Kinetics are an important characteristic in adsorption mechanism studies. To this end, the pseudo-first- and -second-order models are most commonly used.⁴⁶,⁴⁹

\[
\frac{dq}{dt} = k_1 \times (q_e - q) \tag{4}
\]

\[
\frac{dq}{dt} = k_2 \times (q_e - q)^2 \tag{5}
\]

where \(q_e\) and \(q\) (mg/g) are the adsorbed amounts at equilibrium and time, respectively, \(t\) (min) is the adsorption process time, and \(k_1\) and \(k_2\) (min⁻¹) are pseudo-first- and -second-order adsorption rate constants, respectively. These two equations can be given for the pseudo-nth-order model by⁴⁶

\[
\frac{dq}{dt} = k \times (q_e - q)^n \tag{6}
\]

The integration of eq 7 is written as

\[
q = q_e - [(n - 1)k t + q_e^{(1-n)}]^{1/(n-1)} \tag{7}
\]

In this work, the general nth-order model was used to predict the obtained experimental data of adsorbed tannic acid as a function of time at different initial tannic acid concentrations (Figure 6).

Kinetic parameters (\(q_e, n,\) and \(k\)) were estimated by minimizing the sum of squared error between calculated and experimental values using Microsoft Excel Solver and are represented in Table 2.

Table 1. Sips Model Parameters at Different Values of pH Solution

| pH | \(R^2\) | \(K_s\) (L/mg) | \(q_{eq}\) (mg/g) | \(R^2\) | \(K_s\) [(mg/g)/(mg/L)⁰.⁵] | \(n\) | \(R^2\) | \(K_s\) (L/mg) | \(n\) | \(q_{eq}\) (mg/g) |
|----|--------|---------------|----------------|--------|----------------------------|-----|--------|---------------|-----|----------------|
| 6  | 0.9861 | 0.02          | 10.81         | 0.9943 | 0.52                       | 1.78| 0.9947 | 0.02          | 1.52| 29.04          |
| 8  | 0.8833 | 0.01          | 43.47         | 0.8581 | 0.44                       | 1.16| 0.9939 | 2.92 × 10⁻³   | 0.29| 13.55          |
| 10 | 0.9924 | 0.01          | 4.76          | 0.973  | 0.14                       | 1.64| 0.9925 | 0.008         | 0.87| 4.10           |

Figure 6. Pseudo-nth-order model of tannic acid adsorption onto calcite at various initial tannic acid concentrations (\(C_{calcite} = 10\) g/L; particle size\(_{calcite} = 40-80\) μm; pH = 8; room temperature).

Table 2. Pseudo-nth-Order Model Parameters at Different Initial Tannic Acid Concentrations

| Concentration (mg/L) | \(q_{eq}\) (mg/g) |
|----------------------|-----------------|
| 50                   | 3.93            |
| 75                   | 6.46            |
| 100                  | 7.89            |
| 125                  | 9.92            |
| 175                  | 13.24           |

Figure 6 shows good agreement between experimental results and the pseudo-nth-order kinetic model. This is confirmed by the high determination coefficient \(R^2 > 0.9996\) (Table 2). Table 2 indicates that for all tested concentrations, experimental and calculated values of adsorbed tannic acid at equilibrium \(q_e\) are very close. In addition, the reaction order is very close to 2, which means that the pseudo-second-order model is the best one to predict the investigated adsorption kinetics. Therefore, the adsorption mechanism is a chemisorption process where tannic acid molecules are linked by covalent bonds with calcite surface atoms.⁵¹ This result is similar to that obtained by tannin adsorption onto treated coal fly ash.⁵²

### 2.6. Thermodynamic Study

In addition to the isothermal and kinetic studies, the adsorption thermodynamic aspect of tannic acid onto calcite was also investigated. The Gibbs free energies \(G\) (kJ/mol) were evaluated by the Gibbs–Helmholtz expression

\[
\Delta G = -RT \ln K \tag{8}
\]

where \(K\) (L/mg) is the equilibrium constant evaluated from Sips parameters \(K_s\) (Table 3), \(T\) (Kelvin) is the temperature, and \(R\) (8.314 J/mol K) is the universal gas constant.

Comparing the three tested models at different temperatures, it is clearly shown that the Sips model gave the best
description of the mechanism of tannic acid adsorption onto calcite ($R^2$ close to 1, see Table 3).

On the other hand, the adsorbed amount and the affinity constant ($K_s$) decrease with temperature. This can be explained by an exothermic adsorption process.45 Thus, the value of $n$ decreases as a function of temperature, and consequently, the affinity becomes low at high temperatures.45

The enthalpy $\Delta H$ (kJ/mol) and the entropy $\Delta S$ (kJ/mol·K) were determined from the slope and the intercept of Van’t Hoff representation (Figure 7) using the following equations

$$
\Delta G = \Delta H - T \Delta S
$$

$$
\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
$$

The calculated thermodynamic parameter values are summarized in Table 4.

### 3. CONCLUSIONS

The present study investigated the adsorption performance of tannic acid onto calcite. Experimental results indicated an adsorption capacity of 13.36 mg/g using optimal conditions of adsorption parameters. Adsorption isothermal data agreed well with the Sips model, with a high determination coefficient ($R^2$ close to 1), suggesting an adsorption capacity of 13.54 mg/g at room temperature and at pH 8 which is very close to that obtained experimentally. Furthermore, tannic acid adsorption onto calcite is strongly dependent on solution pH. Thus, the mechanism controlling tannic acid adsorption is an ion exchange. Moreover, adsorption kinetics of tannic acid can be well described by the pseudo-second-order model at different initial tannic acid concentrations. Therefore, tannic acid molecules are linked by covalent bonds with calcite surface atoms. On the other hand, thermodynamic study indicated an exothermic and a chemical adsorption process. All these results could be used to better understand the interaction between tannins and carbonates and thus to achieve good performance in terms of optimal conditions of adsorption in mineral processing.

### 4. EXPERIMENTAL SECTION

#### 4.1. Adsorbent Preparation.

Calcite sample was obtained from the El hammam mine located about 80 km of Meknes in Morocco. X-ray diffraction (XRD) analysis of the mineral was carried out (Figure 8).

The obtained $\Delta G$ positive values indicate a nonspontaneous low interaction between calcite and tannic acid. This indicates the presence of an energy barrier via the retention process.54 The negative value of $\Delta H$ ($-233.86$ kJ/mol) confirms the exothermic nature of tannic acid adsorption.55 The absolute value of $\Delta H$ also permits to distinguish between the physical and chemical adsorption nature.56 Hence, the values between 8 and 25 kJ/mol show a physical adsorption, whereas the values between 83 and 830 kJ/mol indicate a chemisorption process.

In our study, the high value of $\Delta H$ shows a chemical adsorption process. The negative sign of the $\Delta S$ value ($-0.84$ kJ/mol·K) suggests a nonsignificant decrease in the freedom degree at the solid–liquid interface during adsorption.45 Furthermore, the low value of $\Delta S$ reveals that no significant change occurred during tannic acid adsorption onto calcite.53 These results are similar to those obtained by tannin adsorption onto coal ash.52
The obtained result confirms the calcite purity. The sample was crushed using a jaw and cylindrical crusher, ground in a mechanical grounder and then sieved to several fractions in order to collect the +40–80 and +80–160 μm particle sizes for further investigations.

4.2. Adsorbate Preparation. Tannic acid (C₇₆H₅₂O₄₆) was used as a representative organic reagent supplied from Sigma-Aldrich. Its molecular weight is 1701.20 Da. Its physicochemical analysis was done using Fourier transform infrared (FT-IR) spectroscopy (Figure 9).

![Figure 9. FT-IR spectra of tannic acid.](image)

This shows the presence of five characteristic bands corresponding to carboxylic groups of tannic acid. The latter was dehydrated in an oven at 95 °C for 1 h. Tannic acid (1 g) was dissolved in 100 mL of distilled water to prepare a 1% (w/v) stock solution, which was then diluted in distilled water to obtain desired concentrations.

4.3. Adsorption Procedure. For each investigated experiment, 1 g of calcite was added to 100 mL of required initial tannic acid concentration in a pyrex beaker (250 mL) at room temperature and fixed solution pH. The adsorbent–adsorbate mixture was shaken at 250 rpm for 30 min to achieve adsorption equilibrium. The obtained solution was then decanted and analyzed by UV–vis spectrophotometry at 278 nm to determine the equilibrium tannic acid concentration. The adsorption capacity of tannic acid was calculated by

$$q = \frac{(C_i - C_e) \times V}{m}$$  \hspace{1cm} (11)

where $C_i$ and $C_e$ (mg/L) are the initial and equilibrium tannic acid concentrations, respectively, $V$ (L) is the solution volume, and $m$ (g) is the adsorbant mass.

The study of the parameters affecting the tannic acid adsorption onto calcite was considered at different experimental conditions. The kinetic monitoring was performed during different time intervals ranging from 0 to 60 min using an initial tannic acid concentration of 100 mg/L. The adsorbent particle size effect was studied for two fractions of +40–80 and +80–160 μm. The initial tannic acid concentration effect was investigated in the range from 5 to 200 mg/L at different values of solution pH (6, 8, and 10). Moreover, the kinetic study was conducted at different contact time intervals (0–20 min) and with various initial tannic acid concentrations from 50 to 175 mg/L. The temperature effect was studied within the temperature range between 30 and 60 °C.

4.4. Statistical Analysis. The study of the parameters affecting the tannic acid adsorption onto calcite was performed in triplicate. All graph data were expressed as the mean of the triplicate, and standard deviations were analyzed statistically using one-way analysis of variance (ANOVA), followed by the Tukey test at the 5% level. Any differences with $p > 0.05$ were not considered to be statistically significant.

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