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The behaviour of tannic acid adsorption on fluorite surface: Isotherm, kinetic and thermodynamic studies

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Abstract: Fluorite is an important mineral to produce hydrofluoric acid. As fluorite resources contain calcite as a gangue mineral, the separation between these two calcium containing minerals is difficult. Tannic acid is the most commonly used reagent as a depressant to separate fluorite from calcite by flotation. To enhance this separation, it is so primordial to understand tannic acid physicochemical reactivity via these minerals. Therefore, the aim of this work is to investigate the mechanism of tannic acid adsorption on the fluorite surface by experimental study using isotherm, kinetic and thermodynamic. Adsorption isotherm modelling results showed that the adsorption process is well described by Sips model. On the other hand, the kinetic and thermodynamic require firstly the adsorption study as a function of three main reactional parameters including initial tannic acid concentration, solution pH and temperature. This study showed that acidic pH as well as initial tannic acid concentration increase and temperature decrease promote the studied adsorption. These finding were then exploited to determine the adsorption mechanism by pseudo n order kinetic model adjustment to experimental kinetic data using nonlinear regression method. Obtained high correlation coefficient and low mean absolute error at 95 % confidence level showed good agreement of experimental kinetic data with the tested model. These results revealed that the mechanism of tannic acid adsorption onto fluorite was attributed to a chemical reaction. In addition, the thermodynamic study showed that the studied adsorption process was exothermic.

Keywords: fluorite, tannic acid, adsorption, reactional parameters, kinetic, modelling, isotherm, thermodynamic

1. Introduction

Tannic acid is a natural organic component derived from plant biomass decomposition (Lin et al., 2011; Wang et al., 2011; Deng et al., 2012). It has many industrial uses including mineral processing (Rutledge and Anderson 2015). As this organic reagent is characterized by phenolic and hydroxylic groups, it can strongly interact with metal ions including calcium ion (Nakano et al., 2001; Şengil et al., 2009; Şengil and Özacar, 2009). Thus, tannic acid use in mineral processing has drawn worldwide attention. It is particularly a highly useful reagent to separate fluorite from calcite.

These two calcium containing minerals have similar solubility and the same active calcium ion that interacts with anionic reagents (Z. Gao et al., 2015; Xu et al., 2016). Due to the similarity of fluorite and calcite surface properties, their separation is almost impossible. Flotation using tannic acid as a depressant is showed as the most commonly used method to separate between fluorite and calcite (Chen et al., 2011; Mohammadkhani et al., 2011; Rutledge and Anderson, 2015). However, this separation is often still a problematic (Chen et al., 2011; Mohammadkhani et al., 2011; Rai et al., 2011; Z. Gao et al., 2015; Rutledge and Anderson, 2015; Xu et al., 2016; Zheng et al., 2018).

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This flotation separation technique depends mainly on tannic acid adsorption phenomenon on fluorite and calcite surface. Therefore, a deep investigation of this phenomenon is required to better understand the physicochemical affinity of tannic acid phenolic and hydroxylic groups via fluorite and calcite minerals. This can certainly provide valuable information allowing improvement of the flotation separation process.

According to the literature, the tannic acid adsorption onto fluorite and calcite has been conducted out by adsorption and zeta potential tests as well as X ray photoelectron spectroscopy and ultra violet spectrophotometry analysis (Zhang et al., 2018). This study results showed that carboxyl and phenolic hydroxyl groups of tannic acid interact with calcium ions on both fluorite and calcite surfaces. The above mentioned techniques were also used in other study of adsorption of propyl gallate as tannic acid derivative onto fluorite (J. Gao et al., 2018). It has been demonstrated that phenolic hydroxyl group oxygen atoms can bond to calcium ions onto both fluorite and calcite. It is worthwhile to point out that these earlier studies were limited to brief investigations to reveal that there is a reaction adsorption between tannins and fluorite and calcite surfaces. However, they did not indicate the possible interaction mechanism if it is electrostatic, hydrophobic, physical or chemical. Therefore, there is a paucity of literature regarding methods to evaluate the adsorption mechanism. In our previous works (Tangarfa et al., 2019; Tangarfa et al., 2021), tannic acid adsorption behavior onto calcite has been deeply examined conducting out isotherm, kinetic and thermodynamic studies as well as optimization response surface methodology. Obtained results showed that ion exchange reaction occurs between tannic acid phenolic groups and calcium ions onto calcite. In addition, it has been demonstrated that initial tannic acid concentration and solution pH are the most significant parameters affecting the tannic acid adsorption onto calcite.

In this work, adsorption of aqueous tannic acid on fluorite surface was deeply investigated. The studied adsorption by isotherm modelling was well descriebed by Sips model. The performed study of reactional parameter effect showed that the chosen parameters, including initial tannic acid concentration, solution pH and temperature, affect significantly tannic acid adsorption onto fluorite. It was also indicated that this studied process is attributed to a chemical interaction according to the reaction order n estimated at approximately 2 as well as to exothermic nature.

2. Materials and methods

2.1. Adsorbent and adsorbate preparation

The preparation and characterization of commercial tannic acid used as an adsorbate has been deeply described in our previous studies (Tangarfa et al., 2019; Tangarfa et al., 2021). 10 g/L of tannic acid stock solution was prepared and diluated to desired concentrations for further experiments. Fluorite sample employed as an adsorbent was provided by El hammam mine of Meknes in Morocco. It was washed with distilled water to g/removre surface impurities and dried in the oven at 90 °C during 24 hours. Then, it was crushed by a jaw and cylindrical crusher, ground using a mechanical grounder and sieved into -80, +40 µm fraction for further experiments. X Ray diffraction (XRD) analysis (Fig. 1) was used to confirm fluorite purity (greater than 99 %).

2.2. Adsorption isotherm experiments

The experiments were performed using 1 g of fluorite added to 100 mL of tannic acid for various initial concentrations (10-110 mg/L) into pyrex beaker of 250 mL at solution pH and room temperature. The fluorite−tannic acid mixture was shaken at 250 tours/min for 20 min to attain adsorption equilibrium. Preliminary experiments showed that stirring rate has no significant effect upon studied adsorption and 20 minutes were enough to reach adsorption equilibrium. After this equilibrium, the mixture was decanted, filtered and analyzed by Ultra Violet-Visible (UV-Vis) spectrophotometer at maximum absorbance of tannic acid which is 278 nm wavelength (this value was experimentally obtained by UV-Vis spectrophotometer; it is attributed to tannic acid characteristic band) to determine equilibrium tannic acid concentration. This concentration was used to calculate the adsorbed tannic acid amount by the following expression:

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

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

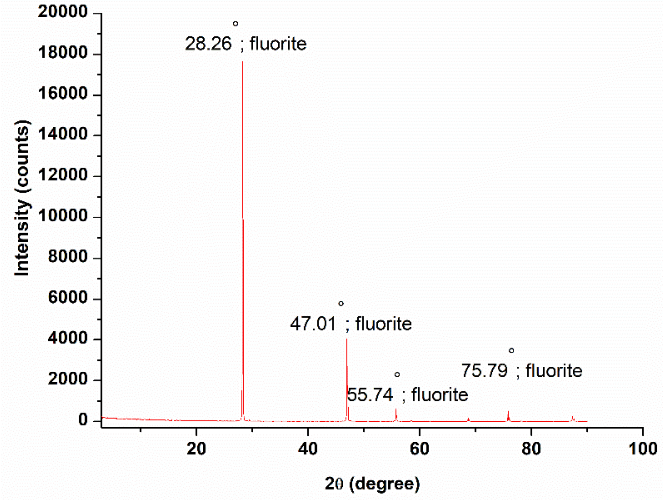

Fig. 1. XRD spectra of fluorite mineral

2.3. Adsorption kinetic experiments

Adsorption kinetic experiments were conducted out in pyrex beaker of 250 mL placed in a thermostatic water bath equipped with an electric shaker. 1 g of fluorite sample was added into 100 mL of tannic acid at desired concentrations (20; 60; 100 mg/L), pH values (5; 7.5; 10) and temperatures (30; 45; 60 °C). it is important to precise that these parameters were selected based on bibliographic studies. While, the variation range of each parameter was chosen according to preliminary tests. Continuous electric stirring of 250 tours/min for 20 min was used to shake the obtained adsorbate-adsorbent mixture. Supernatant aliquots were withdrawn at different time intervals (0; 3; 6; 9; 15; 20 min) and filtered through filter paper. Obtained filtrate was then analyzed by UV-Vis spectrophotometer to determine equilibrium tannic acid concentration and calculate the adsorbed tannic acid amount by the equation (1).

In order to ensure data reliability, repeatability and reproducibility, all adsorption experiments were performed in triplicate using mean values in kinetic data. Thus, analysis of variance at 5 % significance level was employed using one-way analysis of variance to consider significant differences between means. In addition, if the P_{value} is less than 0.05, the null hypothesis of equal means is rejected at the 5 % significance level.

2.4. Adsorption kinetic modeling

In literature, several kinetic models (particularly pseudo first and second order models) have been used and tested to predict adsorption mechanism and hence to determine adsorption kinetic, especially process rate constant (Ho and McKay 1999; Zhan and Zhao 2003). In this study, pseudo n order kinetic model was employed as an appropriate tool to estimate the adsorption reaction rate constant and order (OZER 2006). Its mathematical model is commonly given as (Ho and McKay, 1999; Zhan and Zhao, 2003):

$$\frac{dq}{dt} = k(q_e - q)^n \tag{2}$$

The corresponding nonlinear expression of this equation is expressed as:

$$q = q_e - \left[(n-1)kt + q_e^{(1-n)}\right]^{1/1-n} \tag{3}$$

where q_e and q (mg/g) are adsorbed amounts at equilibrium and time t, respectively, t (min) is the adsorption process time, n is the reaction order and k (min−1) is the pseudo n order adsorption rate constant. Kinetic parameters of this model (q_e, k and n) were estimated by nonlinear regression using Steepest-Descent method of Statgraphics centurium18 software.

3. Results and discussion

3.1. Adsorption isotherm modelling

The mechanism of tannic acid adsorption onto fluorite was determined using the three most commonly isotherm models: Langmuir, Freundlich and Sips models.

Langmuir isotherm model permits to describe monolayer adsorption and homogeneous formation with fixed number of defined sites energetically identical and with no lateral interaction between adsorbed molecules (Langmuir, 1917; Langmuir, 1918; Pérez Marín et al., 2007; Vijayaraghavan et al., 2006). Langmuir isotherm is expressed by:

$$q = \frac{q_e K_L C_e}{1+K_L C_e} \tag{4}$$

where C_e (mg/L) is the equilibrium adsorbate concentration, q (mg/g) is the equilibrium adsorbed amount per unit of adsorbent mass, q_e (mg/g) is the maximum adsorption capacity, and K_L (L/g) is the Langmuir constant.

Freundlich isotherm model is used for multilayer and heterogeneous adsorption with non-adsorption heat uniform distribution (Freundlich 1907). This isotherm equation is provided by:

$$q = K_F C_e^{\frac{1}{n}} \tag{5}$$

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

Sips isotherm model is a combination between Langmuir and Freundlich isotherm models and iused to describ the adsorption mechanism in heterogeneous systems (Günay et al., 2007). It reduces to Freundlich model at low sorbate concentrations. While, it reduces to Langmuir model at high sorbate concentrations (Pérez-Marín et al., 2007). It mathematical equation is given as follow:

$$q = q_{max} \frac{K_S C_e^{\frac{1}{n}}}{1+K_S C_e^{\frac{1}{n}}} \tag{6}$$

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

The above models were adjusted to experimental data using a non-linear method to determine adsorption isotherm model parameters. Fig 2. show non-linear fitting of tannic acid adsorption onto fluorite. While, calculated correlation coefficient (R^2) values of each model are presented in Table 1.

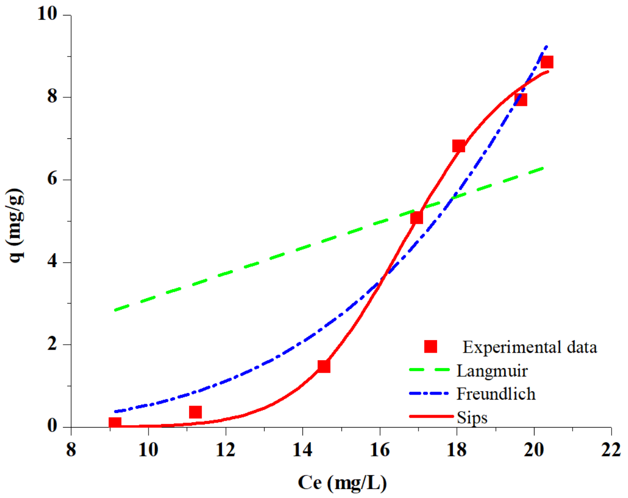

Fig. 2. Non-linear fitting of tannic acid adsorption onto fluorite

Table 1. R² of tested models

	Langmuir	Freundlich	Sips
R^2	0.5368	0.9639	0.9970

We can see from Fig.2 and based on the highest R^2 obtained in Table 2 that Sips model was statistically significant compared to Langmuir and Freundlich models. These results are similar to those related to tannic acid adsorption on zeolite and calcite surfaces (Lin et al., 2011; Tangarfa et al., 2019). Estimated parameters of Sips model are summarized in Table 2. The parameter 1/n is lower than 1 suggesting that the stuied adsorption is attriuted to heterogeneous system. However, this information can not be sufficient to know if this heterogeneity is related to the adsorbent surface or the adsorbate or a combination of both (Do, 1998).

Table 2. Sips Model parameters

q_e (mg/g)	K_s (L/mg)	1/n
9.55774	5.5982×10^{-15}	0.08596

3.2. Effect of reactional parameters

To better understand the reactivity of tannic acid via fluorite surface, effects of adsorption reactional parameters (initial tannic acid concentration, solution pH and temperature) were evaluated by exploiting adsorption kinetic experiment results of tannic acid onto fluorite.

3.2.1. Effect of initial tannic acid concentration

The adsorbate initial concentration as an adsorption reactional parameter plays an important role to improve molecule mass transfer of the adsorbate towards adsorbent preferential sites (Dönmez and Aksu, 2002). Initial tannic acid concentration effect on studied adsorption (adsorbed amount via time) using 10 g/L of fluorite, pH of 7.5 and temperature of 45 °C is shown in Fig. 3.

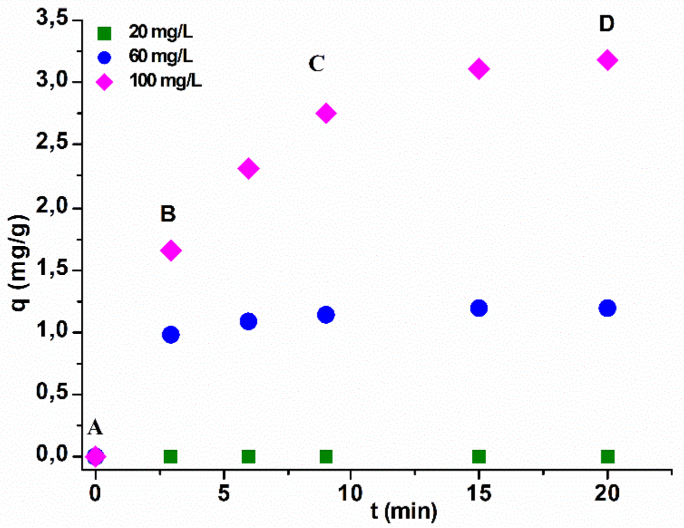

Fig. 3. Effect of initial tannic acid concentration and contact time on tannic acid adsorption onto fluorite

As shown in this figure, the adsorption amount increases with increasing initial tannic acid concentration. This process is so rapid for the first 3 min from A to B with an adsorption capacity varying from 0.004 to 1.7 mg/g as a function of concentration. Then it proceeds at a moderate rate from B to C to finally reach equilibrium at D within 20 min. The equilibrium adsorption capacity of tannic acid at 20, 60 and 100 mg/L are 0.01, 1.2 and 3.2 mg/g, respectively. The first rapid step can be explained by active site availability onto fluorite that promote their adsorption by tannic acid phenolic groups (Das et al. 2014). While, the second moderate step can be attributed to the decrease of adsorbent active site number (Shukla et al. 2002). In addition to these finding, it can be seen from Figure 2 that the adsorption capacity increases with tannic acid concentration. This is could be due to an increase of the concentration gradient, driving force and active site availability (Uddin, et al. 2018).

In other investigations (Lin et al., 2011; Wang et al., 2011), similar trends have been reported for tannic acid adsorption by an amino functionalized magnetic nano adsorbent and surfactant-modified zeolite. Furthermore, it has been demonstrated that the adsorption equilibrium is reached at 120 min.

3.2.2. Effect of pH solution

The solution pH is an important variable that influence significantly the adsorption process. Tannic acid adsorption onto fluorite as a function of contact time for different pH values, 10 g/L of fluorite, 60 mg/L of tannic acid concentration and 45 °C of temperature is shown in Fig. 4.

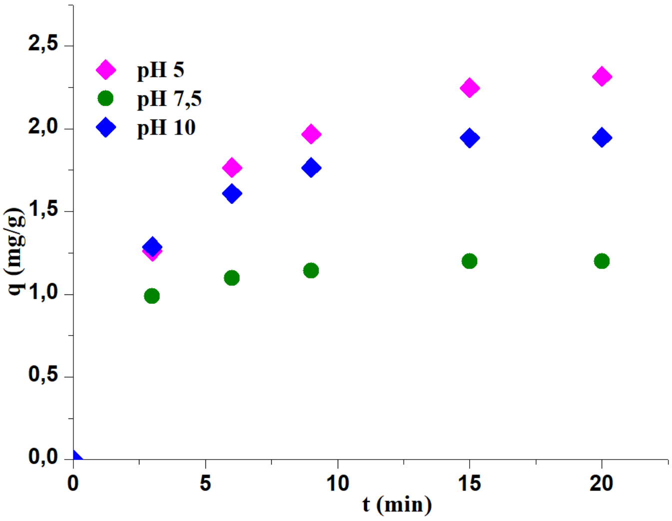

Fig. 4. Effect of solution pH and contact time on tannic acid adsorption onto fluorite

It is so clear from these results that the adsorbed tannic acid amount is high at pH 5 with a maximum adsorption capacity of 2.3 mg/g. While at pH 7.5 and 10, the maximum adsorption capacities are 1,2 and 1.9 mg/g, respectively. Therefore, tannic acid adsorption onto fluorite increases with decrease of pH solution. This is could be due to the presence of different positive and negative fluorite species in the solution as a function of solution pH. It is previously demonstrated by Zhang et al from zeta potential measurements that fluorite has an isoelectric point at approximately pH 7.5 (Zhang et al. 2018). In this case, fluorite surface has positive zeta potential below 7.5 and negative one above 7.5. In addition, tannic acid molecules dissociate and become ions at pH above 4.5 (JAn and Dultz, 2007). Based on above finding, we can deduce that the high adsorption capacity obtained at pH 5 could be attributed to the strong electrostatic interaction between the positive fluorite surface and tannic acid phenolic groups. While, the low tannic acid adsorption observed at pH 7.5 could be explained by the weak hydrogen bonding interaction between tannic aid molecules and fluorite neutral surface. At pH 10, tannic acid molecules become more reactive (An and Dultz, 2007) and fluorite surface is negative. Thus, a repulsion at the interface fluorite/tannic acid could be occurred.

We can effectively conclude from the above results that tannin adsorption behavior on mineral surfaces containing metal ions depends strongly on solution pH (An and Huang, 2012; Bagheban Shahri and Niazi, 2015). Indeed, it can influence the adsorbent surface charge as well as the adsorbate molecule nature.

3.2.3. Effect of temperature

The temperature effect evaluation gives valuable information about the adsorption nature (Alkan et al., 2007). Fig. 5 exhibits adsorbed amount versus contact time graph at different temperature values using 10 g/L of fluorite, 60 mg/L of tannic acid and 7.5 of pH.

This figure demonstrates that the equilibrium tannic acid adsorption capacity decreases as the temperature increases indicating that tannic acid adsorption on the adsorbent was disfavored at higher temperatures. This is may be due to a decrease in tannic acid ion mobility in the solution with an increase of the temperature. This can be confirmed by Alkan et al and Tsay et al works concerning anionic dye adsorption onto sepiolite and herbicide paraquat adsorption onto activated bleaching earth, respectively (Tsai et al., 2004; Alkan et al., 2007). In addition, Similar results were observed by Huiqin et al. as well as Anirudhan and Ramachandran using treated coal fly ash and cationic surfactant modified bentonite clay as adsorbents, respectively (Anirudhan and Ramachandran 2006; Li et al. 2013).

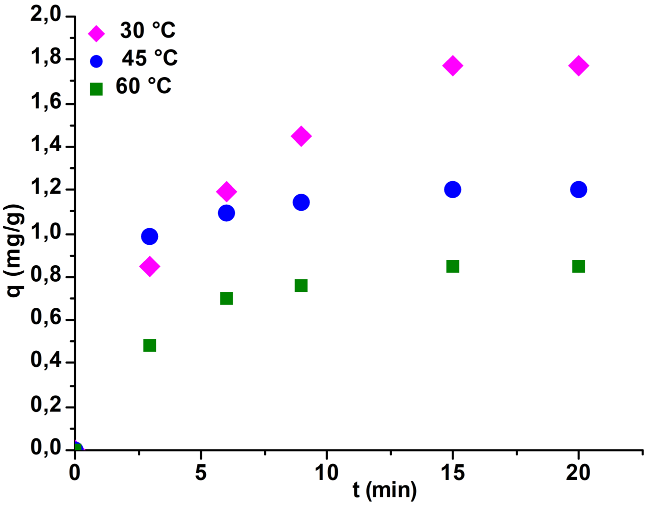

Fig. 5. Effect of temperature and contact time on tannic acid adsorption onto fluorite

3.3. Kinetic modelling results

Obtained experimental kinetic data as well as nonlinear kinetic model as a function of time are given in Fig. 6 under different operating conditions (10 g/L of fluorite, 20, 60 and 100 mg/L of initial tannic acid concentration, 5, 7 and 10 of pH and 30, 45 and 60 °C of temperature). Kinetic parameters of the tested model were estimated by nonlinear regression using Steepest-Descent method of Statgraphics centurium18 software. Obtained results are summarized in Table 3.

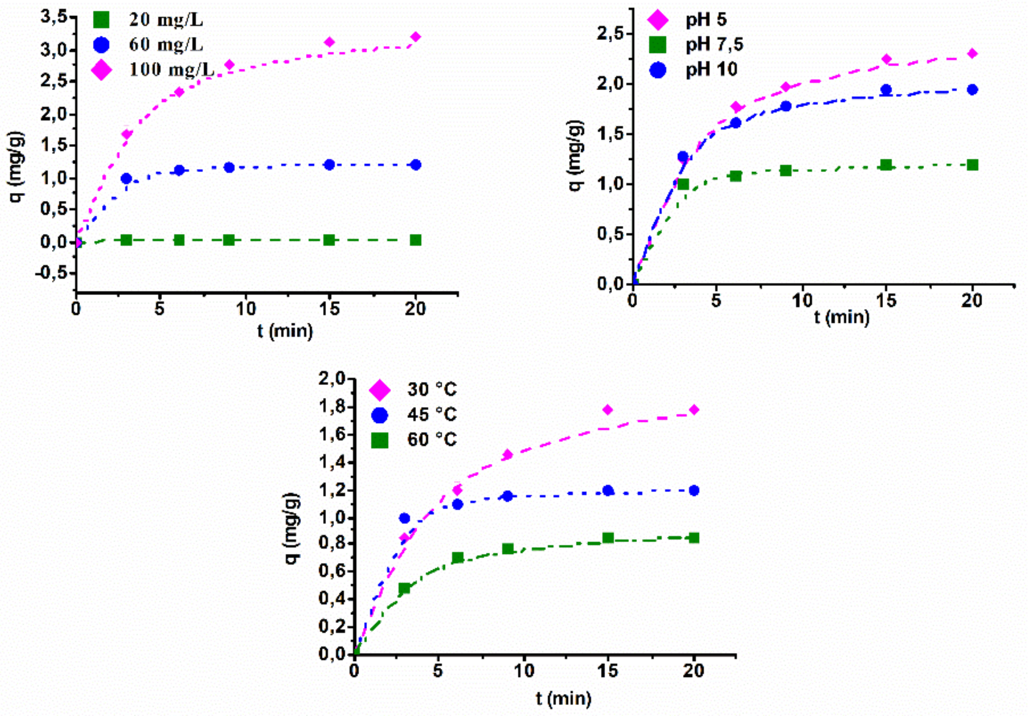

Fig. 6. Pseudo n order kinetic model of tannic acid adsorption onto fluorite at various initial tannic acid concentrations, solution pH and temperature

Table 3. Pseudo n order kinetic model parameters of tannic acid adsorption onto fluorite at various reactional parametrs

Kinetic parameters	C_i (mg/L)			pH			T (°K)		
	20	60	100	5	7.5	10	303	318	333
$q_{e.exp}$ (mg/g)	0.010	1.20	3.18	2.32	1.20	1.95	1.77	1.20	0.85
$q_{e.est}$ (mg/g)	0.013	1.23	3.49	2.59	1.23	2.09	2.09	1.23	0.94
n	1.96	1.94	1.94	1.93	1.94	1.95	1.93	1.94	1.91
k (min^{-1})	9.77	1.08	0.11	0.14	1.08	0.28	0.12	0.21	1.08
R^2 (%)	99.43	99.94	99.09	99.79	99.94	99.77	99.25	99.94	99.35
MAE	0.0002	0.0069	0.0914	0.0271	0.0069	0.0238	0.0359	0.0069	0.0170

The shape of these plots depicted in this figure indicates that experimental kinetic data are in good agreement with pseudo n order kinetic model. This is noted by the high correlation coefficient R^2 (99.09-99.94 %) and the low mean absolute error MAE (0.0002 – 0.09) at different studied conditions of initial tannic acid concentration, pH and temperature (see Table 1). Furthermore, experimental adsorption capacity values q_e^{exp} are very close to the estimated ones q_e^{est} confirming that experimental data are very well predicted by the suggested kinetic model. The adsorption reaction order n is very close to 2 for all experimental conditions suggesting that experimental data follows pseudo second order kinetic model. Thus, we can conclude that the mechanism of tannic acid adsorption onto fluorite is a chemisorption reaction where tannic acid molecules are linked by covalent bonds with fluorite surface atoms (Mohan et al., 2006). These results are similar to those obtained in other investigations of tannin adsorption onto treated coal fly ash and tannic acid adsorption onto calcite (Li et al., 2013; Tangarfa et al., 2019).

3.4. Thermodynamic study

To better understand interactions between tannic acid phenolic groups and fluorite surface, it is important to determine thermodynamic parameters. For this purpose, the results related to the variation of the pseudo n order adsorption rate constant (k) in terms of temperature obtained in Table 1 were exploited to estimate thermodynamic parameter values of the enthalpy ΔH°, the entropyΔS°, and the Gibbs free energie ΔG° by the Eyring equation (Doğan and Alkan, 2003):

$$\mathrm{Ln}\frac{k}{T} = \mathrm{Ln}\frac{k_B}{h} + \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{7}$$

here, k_B and h are Boltzmann and Planck constants, respectively. ΔH° and ΔS° can be calculated from the slope (-ΔH/R) and the intercept ($Lnk_B/h+\Delta S/R$) of the line equation (4), respectively (see Fig. 6). Obtained results are presented in Table 2. The parameter ΔG° can be written as a function of ΔH° and ΔS° and calculated according to the following equation (see Table 2):

$$\Delta G° = \Delta H° - T\Delta S° \tag{8}$$

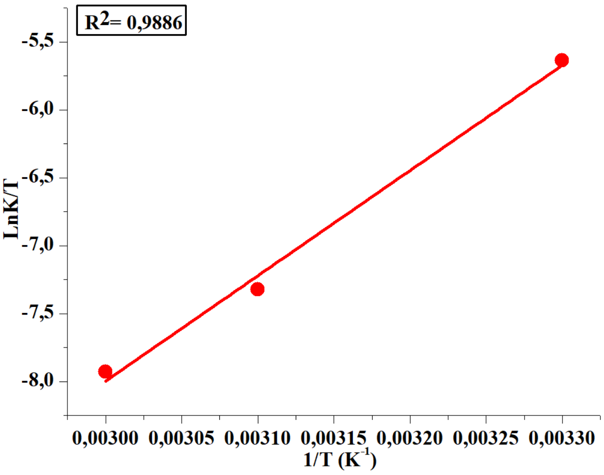

Fig. 6. Graphical representation of the variation of lnK/T versus 1/T for tannic acid adsorption onto fluorite

Table 1. Thermodynamic parameters of tannic acid adsorption onto fluorite

T (°K)	ΔH° (kJ.mol-1)	ΔS° (kJ/mol.°K)	ΔG° (kJ.mol-1)
303	-61.91	-0.402	59.89
318	-	-	65.93
333	-	-	71.96

From the results obtained in Table 2, we found that the studied adsorption process provides positive values of ΔG° suggesting that the adsorption reactions require an external energy to convert the reagents into products (Saha and Chowdhury 2011). The negative value of ΔH° implies that the adsorption process is exothermic. While, the negative value of ΔS° suggests that the adsorption process reflects that no significant change occured in adsorbent internal structures during the adsorption process. All these results are similar to those obtained by the adsorption study of tannins on coal ash(Li et al., 2013).

4. Conclusions

The objective of the present paper was to determine tannic acid adsorption mechanism onto fluorite. Adsorption isotherm study showed that experimental data were well described by Sips Model. In addition, to better understand the physicochemical reactivity of tannic acid towards fluorite surface, it is so necessary to firstly evaluate the adsorption main reactional parameters effect (initial tannic acid concentration, solution pH and temperature) on the studied adsorption process. It has been clearly shown that tannic acid adsorption increases with an increase of initial tannic acid concentration as well as a decrease of temperature with a maximum adsorption capacity at pH 5. These results were then exploited to estimate kinetic parameters of pseudo n order model using experimental kinetic data by a nonlinear regression method (Steepest-Descent of Statgraphics centurium18 software). Based on analysis of variance at 95 %, the tested kinetic model revealed a high correlation coefficient of approximately 99 % and a low mean absolute error less than 0,09 under various conditions of initial tannic acid concentration, pH and temperature. Under the same conditions, experimental and estimated adsorption capacities were very close. In addition to these results, the reaction order of the tested model was estimated at approximately 2. based on all above finding, we can conclude that the adsorption kinetic is well described by pseudo second order kinetic model. Therefore, tannic acid phenolic groups are adsorbed on fluorite surface via chemical interactions. In other words, tannic acid molecules are linked by covalent bonds with fluorite surface atoms. Furthermore, thermodynamic study showed that the studied adsorption is attributed to exothermic nature. These results are necessary and useful in order to better understand the physicochemical reactivity of tannins via calcium mineral surface including fluorite. Thus, they required to be exploited and used to enhance the fluorite valorisation by flotation in mineral processing.

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