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Adsorption of tannic acid on fluorite surface: experimental and modelling studies

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Abstract: Fluorite is an important industry mineral that can coexist with gangue minerals including calcite. However, fluorite and calcite have similar surface properties that can avoid their separation. Flotation by tannic acid adsorption onto calcite and fluorite is the method commonly applied to separate between these two calcium minerals. In this work, the mechanism of tannic acid adsorption onto fluorite is determined by experimental adsorption isotherm modelling using Langmuir, Freundlich and Sips models. Modelling results indicate that the adsorption process is well described by Sips model. On the other hand, the effect of particle size on studied adsorption was evaluated. The obtained results show that this parameter has a significant effect on tannic acid adsorption.

1 INTRODUCTION

Fluorite is an important non-renewable mineral and an indispensable chemical material which has been the subject of several scientific researches in various fields, such as renewable energies, new materials synthesis, optoelectronics and metallurgy (Garand and Mucci, 2004; Zhang and Song, 2003; Zheng et al., 2018). Calcium fluoride is primarily used for hydrofluoric acid production, the manufacture of steel, glasses and ceramics. It is also used in laser field, optics and thus electronics (Engelhardt et al., 2000; Zheng et al., 2018).

However, this valuable mineral can be found with gangue minerals such as calcite (Antti and Forssberg, 1989; Hiçyılmaz et al., 1993; Shi et al., 2014). In this case, a separation between calcite and fluorite is necessary. Flotation using tannic acid as a depressant is the most effective technique to separate fluorite and calcite minerals (Lin et al., 2011a; Song et al., 2006; Zawala et al., 2008). This technique is achieved by tannic acid adsorption onto calcite and fluorite. Due to the similar physico-chemical properties of these two calcium minerals, this separation is difficult to achieve. So, it is so important to determine and

understand tannic acid reactivity via calcite and fluorite minerals. In our previous work (Tangarfa et al., 2019), the mechanism of tannic acid adsorption onto calcite was evaluated and it has been shown that tannic acid molecules are linked with calcite surface atoms by covalent bonds. To our knowledge, tannic acid reactivity via fluorite surface has not been reported.

Based on these considerations, the objective of this work is to evaluate the particle size effect on tannic acid adsorption onto calcite and to determine the adsorption process mechanism using isotherm studies.

2 MATERIALS AND METHODS

2.1 Material preparation

Pure fluorite sample as an adsorbent was obtained from El hammam mine located about 80 km of Meknes city in Morocco. X-ray diffraction (XRD) analysis (Figure 1) of the mineral confirmed that this sample has a purity greater than 99 %. The fluorite mineral was crushed, ground and sieved to various

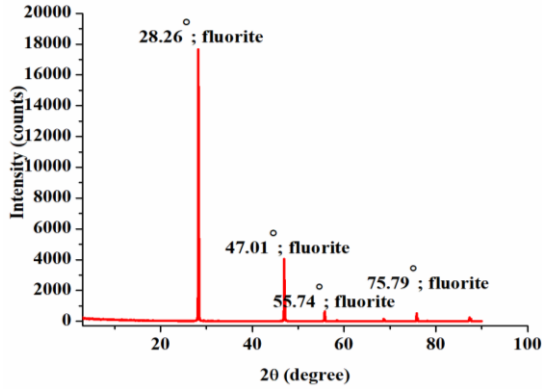


Figure 1: XRD of fluorite sample.

fractions to collect -80+40 μm ; -160+80 μm and -315+160 μm for further investigations.

The pure chemical reagent (greater than 95%) supplied from Sigma Aldrich and used an adsorbate is tannic acid ($\text{C}_{76}\text{H}_{52}\text{O}_{46}$). A stock solution of 10 g/L was prepared by dissolving 1 g of tannic acid into 100 mL of distilled water. It was then diluted to obtain desired concentrations for further investigations.

2.2 Adsorption experimental methodology

To evaluate tannic acid adsorption onto fluorite at different particle size, 1 g of this mineral (-80+40 μm ; -160+80 μm and -315+160 μm) was dispersed in 100 mL of various concentrations of tannic acid (10-110 mg/L) at solution pH. The fluorite-tannic acid mixture was then shaken at 250 tours/minutes and room temperature for 20 minutes. Preliminary tests showed that 20 minutes were enough to reach equilibrium for tannic acid adsorption onto fluorite. After this equilibrium, the mixture was decanted, filtered and analysed by Ultra Visible spectrophotometer at 278 nm to determine the equilibrium tannic acid concentration. The adsorption capacity was then calculated using the following expression:

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

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 adsorbent mass.

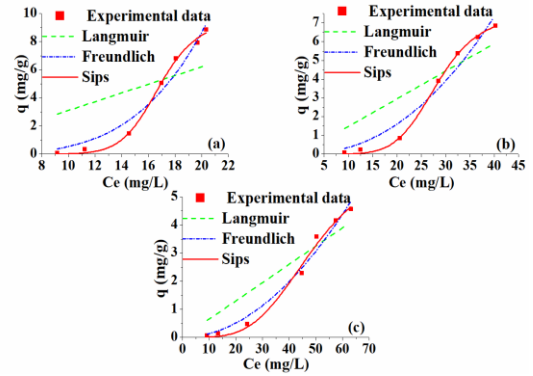


Figure 2: Non-linear fitting of tannic acid adsorption onto fluorite at different values of particle size. (a) -80+40 μm ; (b) -160+80 μm ; (c) -315+160 μm .

3 ADSORPTION ISOTHERM MODELLING: RESULTS AND DISCUSSION

Several adsorption isotherm models have been extensively used for adsorption system modelling, such as Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Sips, etc. (Dubinin, 1969; Khan et al., 1996; Langmuir, 1918, 1917, 1916). To determine tannic acid adsorption mechanism onto fluorite at constant temperature, three most commonly isotherm models were tested: Langmuir, Freundlich and Sips models (Langmuir, 1918, 1917, 1916). Langmuir isotherm model allows to describe the formation of a homogeneous and a monolayer adsorption with a fixed number of defined sites that are energetically identical as well as with no lateral interaction between adsorbed molecules (Kundu and Gupta, 2006; Pérez-Marín et al., 2007; Vijayaraghavan et al., 2006). The mathematical expression of Langmuir isotherm is written by follow:

$$Q = \frac{Q_e K_L C_e}{1 + K_L C_e} \quad (2)$$

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.

While, Freundlich isotherm model can be applied to heterogeneous and multilayer adsorption with a non-uniform distribution of adsorption heat (Freundlich, 1907). Its equation is given by:

Table 1: R² of tested models at different values of particle size.

	Langmuir	Freundlich	Sips
-80+40 μm	0,5368	0,9639	0,9970
-160+80 μm	0,7864	0,9620	0,9990
-160+80 μm	0,5815	0,9805	0,9914

Table 2: Sips Model parameters at different values of particle size.

	Q _e	K _s	1/n
-80+40 μm	9,55774	5,5982E ⁻¹⁵	0,08596
-160+80 μm	7,53363	5,6459E ⁻¹⁰	0,15691
-315+160 μm	6,44958	2,13494E ⁻⁷	0,25419

$$Q = C_e^{\frac{1}{n}} K_F \quad (3)$$

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

Furthermore, Sips isotherm model is a combined form of Langmuir and Freundlich isotherm models used to predict the adsorption in heterogeneous systems (Günay et al., 2007). At low sorbate concentrations, it reduces to Freundlich model. While, at high sorbate concentrations, it predicts a monolayer adsorption characteristics to Langmuir model (Pérez-Marín et al., 2007).

The mathematical expression of Sips model is written as follow:

$$Q = Q_e \frac{K_s C_e^{\frac{1}{n}}}{1 + K_s C_e^{\frac{1}{n}}} \quad (4)$$

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

To determine adsorption isotherm model parameters, experimental data were fitted to Langmuir, Freundlich and Sips models using a non-linear method. **Figure 2** show experimental data and their non-linear plots of studied models at different values of particle size. While, the statistical analysis shows calculated correlation coefficient R² values of each model at different values of particle size as presented in **Table 1**.

Based on the highest R² value, it's so clear from obtained plots that Sips model (0,991 to 0,999) was statistically significant compared to Langmuir

(0,536-0,786) and Freundlich (0,962 – 0,980) models at all studied particle size. Similar results have been reported for tannic acid adsorption on zeolite and calcite surfaces (Lin et al., 2011b; Tangarfa et al., 2019). **Table 2** summarize the estimated parameters of Sips model.

As seen in **Table 2**, the adsorption capacity decreases with particle size. This could be due to high surface area of the adsorbent in this particle size as indicated by Barka et al and Police et al (Barka et al., 2013; Police et al., 2020).

The parameter (1/n) is lower than 1 at all studied cases suggesting that tannic acid adsorption onto fluorite is a heterogeneous system. However, this information cannot determine if the heterogeneity correspond to the adsorbent surface or the adsorbate or a combination of both (Do, 1998).

4 CONCLUSIONS

The present study investigated the adsorption performance of tannic acid onto fluorite under different concentration (10-110 mg/L) and various particle size range (-80+40 μm; -160+80 μm and -315+160 μm) in order to evaluate particle size effect on studied adsorption process as well as its mechanism. The adsorption experiments conducted out indicated that a maximum adsorption capacity of tannic acid is obtained using -80,+40 μm particle size fraction. While adsorption isotherm modelling results showed that experimental data were better fitted to Sips than to Langmuir and Freundlich models suggesting that tannic acid adsorption onto fluorite is a heterogeneous system. All these results are

promising and could be employed to better understand the tannic acid reactivity via fluorite surface in mineral processing.

REFERENCES

- Antti, B.M., Forssberg, E., 1989. Pulp chemistry in industrial mineral flotation. Studies of surface complex on calcite and apatite surfaces using FTIR spectroscopy. *Minerals Engineering* 2, 217–227. [https://doi.org/10.1016/0892-6875\(89\)90042-3](https://doi.org/10.1016/0892-6875(89)90042-3)
- Barka, N., Ouzaouit, K., Abdennouri, M., Makhfouk, M. El, 2013. Dried prickly pear cactus (*Opuntia ficus indica*) cladodes as a low-cost and eco-friendly biosorbent for dyes removal from aqueous solutions. *Journal of the Taiwan Institute of Chemical Engineers* 44, 52–60. <https://doi.org/10.1016/j.jtice.2012.09.007>
- Do, D.D., 1998. Adsorption Analysis: Equilibria and Kinetics, *Chemical Engineering*. <https://doi.org/10.1142/9781860943829>
- Dubinin, M.M., 1969. The potential theory of adsorption of gas. *THEORY OF ADSORPTION OF GASES AND VAP.* *Chemical Reviews* 60, 235–241.
- Engelhardt, J.B., Dabringhaus, H., Wandelt, K., 2000. Atomic force microscopy study of the CaF₂(111) surface: From cleavage via island to evaporation topographies. *Surface Science* 448, 187–200. [https://doi.org/10.1016/S0039-6028\(99\)01194-2](https://doi.org/10.1016/S0039-6028(99)01194-2)
- Freundlich, H., 1907. Über die Adsorption in Lösungen. *Zeitschrift für Physikalische Chemie* 57U, 385–470. <https://doi.org/10.1515/zpch-1907-5723>
- Garand, A., Mucci, A., 2004. The solubility of fluorite as a function of ionic strength and solution composition at 25°C and 1 atm total pressure. *Marine Chemistry* 91, 27–35. <https://doi.org/10.1016/j.marchem.2004.04.002>
- Günay, A., Arslankaya, E., Tosun, I., 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials* 146, 362–371. <https://doi.org/10.1016/j.jhazmat.2006.12.034>
- Hiçyılmaz, C., Atalay, Ü., Özbayoglu, G., 1993. Selective flotation of scheelite using amines. *Minerals Engineering* 6, 313–320. [https://doi.org/10.1016/0892-6875\(93\)90039-P](https://doi.org/10.1016/0892-6875(93)90039-P)
- Khan, A.R., Al-Waheab, I.R., Al-Haddad, A., 1996. A generalized equation for adsorption isotherms for multi-component organic pollutants in dilute aqueous solution. *Environmental Technology (United Kingdom)* 17, 13–23. <https://doi.org/10.1080/09593331708616356>
- Kundu, S., Gupta, A.K., 2006. Arsenic adsorption onto iron oxide-coated cement (IOCC): Regression analysis of equilibrium data with several isotherm models and their optimization. *Chemical Engineering Journal* 122, 93–106. <https://doi.org/10.1016/j.cej.2006.06.002>
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society* 40, 1361–1403. <https://doi.org/10.1021/ja02242a004>
- Langmuir, I., 1917. The constitution and fundamental properties of solids and liquids. II. Liquids. *Journal of the American Chemical Society* 39, 1848–1906. <https://doi.org/10.1021/ja02254a006>
- Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American Chemical Society* 38, 2221–2295. <https://doi.org/10.1021/ja02268a002>
- Lin, J., Zhan, Y., Zhu, Z., Xing, Y., 2011a. Adsorption of tannic acid from aqueous solution onto surfactant-modified zeolite. *Journal of Hazardous Materials* 193, 102–111. <https://doi.org/10.1016/j.jhazmat.2011.07.035>
- Lin, J., Zhan, Y., Zhu, Z., Xing, Y., 2011b. Adsorption of tannic acid from aqueous solution onto surfactant-modified zeolite. *Journal of Hazardous Materials* 193, 102–111. <https://doi.org/10.1016/j.jhazmat.2011.07.035>
- Pérez-Marín, A.B., Zapata, V.M., Ortuño, J.F., Aguilar, M., Sáez, J., Lloréns, M., 2007. Removal of cadmium from aqueous solutions by adsorption onto orange waste. *Journal of Hazardous Materials* 139, 122–131. <https://doi.org/10.1016/j.jhazmat.2006.06.008>
- Police, S., Maity, S., Kumar, D., Kumar, C., 2020. Environmental Chemistry and Ecotoxicology Effect of coal fly ash 's particle size on U adsorption in water samples and thermodynamic study on adsorption. *Environmental Chemistry and Ecotoxicology* 2, 32–38. <https://doi.org/10.1016/j.eneco.2020.01.005>
- Shi, Q., Feng, Q., Zhang, G., Deng, H., 2014. A novel method to improve depressants actions on calcite flotation. *Minerals Engineering* 55, 186–189.

<https://doi.org/10.1016/J.MINENG.2013.10.010>

- Song, S., Lopez-Valdivieso, A., Martinez-Martinez, C., Torres-Armenta, R., 2006. Improving fluorite flotation from ores by dispersion processing. *Minerals Engineering* 19, 912–917. <https://doi.org/10.1016/j.mineng.2005.10.005>
- Tangarfa, M., Semlali Aouragh Hassani, N., Alaoui, A., 2019. Behavior and Mechanism of Tannic Acid Adsorption on the Calcite Surface: Isothermal, Kinetic, and Thermodynamic Studies. *ACS Omega* acsomega.9b02259. <https://doi.org/10.1021/acsomega.9b02259>
- Vijayaraghavan, K., Padmesh, T.V.N., Palanivelu, K., Velan, M., 2006. Biosorption of nickel(II) ions onto *Sargassum wightii*: Application of two-parameter and three-parameter isotherm models. *Journal of Hazardous Materials* 133, 304–308. <https://doi.org/10.1016/j.jhazmat.2005.10.016>
- Zawala, J., Drzymala, J., Malysa, K., 2008. An investigation into the mechanism of the three-phase contact formation at fluorite surface by colliding bubble. *International Journal of Mineral Processing* 88, 72–79. <https://doi.org/10.1016/j.minpro.2008.06.006>
- Zhang, Y., Song, S., 2003. Beneficiation of fluorite by flotation in a new chemical scheme. *Minerals Engineering* 16, 597–600. [https://doi.org/10.1016/S0892-6875\(03\)00136-5](https://doi.org/10.1016/S0892-6875(03)00136-5)
- Zheng, R., Ren, Z., Gao, H., Chen, Z., Qian, Y., Li, Y., 2018. Effects of crystal chemistry on sodium oleate adsorption on fluorite surface investigated by molecular dynamics simulation. *Minerals Engineering* 124, 77–85. <https://doi.org/10.1016/j.mineng.2018.05.017>