STABILITY OF A NATURAL PALYGORSKITE AFTER A CYCLE OF ADSORPTION-DESORPTION OF AN EMERGING POLLUTANT
ESTABILIDAD DE UNA PALYGORSKITA NATURAL DESPUÉS DE UN CICLO DE ADSORCIÓN-DESORCIÓN DE UN CONTAMINANTE EMERGENTE

D. Hernández[a], L. Quiñones[a], C. Charnay[b], M. Velázquez[c], A. Rivera[a†]

a) Institute of Materials Science and Technology (IMRE), University of Havana, Havana, Cuba; aramis@imre.uh.cu[†]
b) Institut Charles Gerhardt Montpellier (ICGM), Université Montpellier, France
c) Research Center for Mining Metallurgy Industries (CIPIMM), La Havana, Cuba
† corresponding author

The use of different types of supports for organic species adsorption [1, 2] in environmental applications is vital for decontamination. Special attention is given to naturals materials with adsorptive properties [3–6]. However, even when many authors work on the adsorption of organic pollutants by natural matrices, it is not common to investigate the physical and chemical properties of the matrices after being submitted to an adsorption-desorption cycle. The main motivation of this paper is to evaluate the structural stability of the natural clay palygorskite–an adsorbent of organic contaminants–after an adsorption–desorption process.

Natural Cuban clay type Palygorskite (*Pal*) is an excellent adsorbent of organic molecules [7]. It is a fibrous clay with structure 2 : 1 formed by tetrahedral silica sheets (SiO_4^{4-}) periodically inverted with respect to the tetrahedral bases leading to an interruption in the octahedral sheets ($AlO_3(OH)_3^{6-}$), and the formation of an open-channel structure [5, 8, 9]. Three water types are present in the structure (zeolitic, coordinated and structural water [10,11]), as well as exchangeable cations in the tunnels. From previous work [12] it is known that Pal acts like an effective adsorbent of sulfamethoxazole (SMX) at acid pH, room temperature and an initial concentration of 3 mg/mL. This drugs is classified as emerging contaminant, i.e., chemical species of common used present in water resources which have the potential to cause adverse ecological and (or) human health effects [13].

In order to demonstrate the possibility to reuse the Pal support in adsorption-desorption cycles, the material resulting of the desorption process (labeled as Pal DE) was characterized by X-ray diffraction (XRD), attenuated total reflection (ATR) infrared spectroscopy and zeta potential (ZP). The X-ray diffraction (XRD) experiments for the samples Pal and Pal DE were conducted on a Philips Xpert diffractometer, using Cu−Kα radiation (λ = 1.54 å) at room temperature for a range from 4 to 70°. ATR spectra were collected using a Perkin Elmer UATR Two FTIR Spectrometer in the range of 400 – 4000 cm^{-1}. The surface charge of clay particles was evaluated using a zeta potential analyzer (Malvern Zetasizer Nano NS Instrument). For the analysis, 1 mg of the samples (Pal or Pal DE) was dispersed fully in 2 mL of a deionized water suspension at different pH under ultrasonic stirring for 15 min. The measurements were made in triplicate and the averages were calculated.

As can be observed in figure 1, the main mineralogical phase present in the raw sample (*Pal*) and that resulting from desorption study (*Pal DE*) was palygorskite (*P*). Other mineral phases, montmorillonite (*Mt*) and quartz (*Q*), were also identified [14], which could be considered like spurious phases.
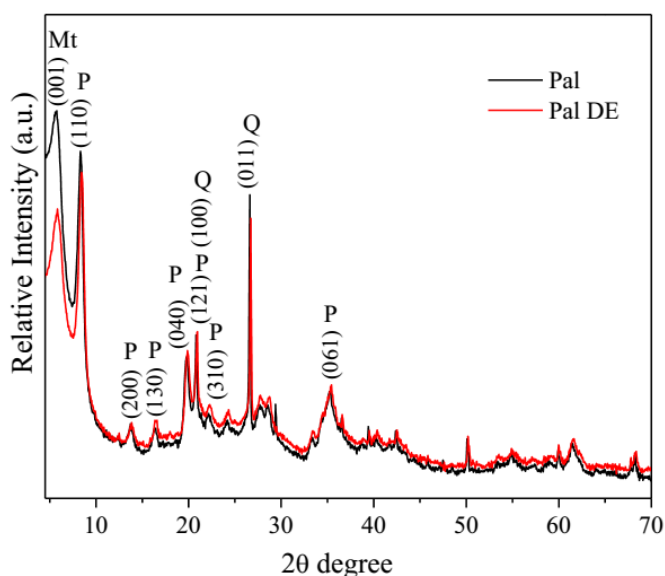

Figure 1. Diffraction patterns for Pal and Pal DE samples.

In the literature, the comparison between experimental and theoretical powder XRD patterns has allowed to note that most palygorskite samples are mixtures of

both monoclinic and orthorhombic polymorphs [15, 16]. Reflections corresponding to d-spacings between 4.0 and 4.5 å, called "Chisholm zone" [17], allow to determine if the palygorskite under study is mainly orthorhombic, monoclinic or either a mixture of both phases. However, in natural materials–as the *Pal* sample presented here–the presence in this zone of reflections associated to spurious phases (like quartz phase, *Q*) can difficult this analysis.

In addition, a decrease in the intensity of the 001 basal reflection of the montmorillonite spurious phase was detected in the sample *Pal DE*. This might be due to possible dissolution of the *Mt* spurious phase by the pH action during the SMX adsorption process, which takes place at acid pH (pH$\approx$ 3) [18]. It can produce local changes in the material, which do not imply structural variation in the main phase, the paligorskite [19].

No significant variations were observed in the interplanar distances values of the characteristic diffraction maximums of palygorskite phase between the *Pal* and *Pal DE* samples. It suggests no structural changes in the material after an adsorption-desorption cycle, confirming its long range order stability.

ATR spectra of drug SMX (emerging contaminant from wastewater), the Pal-SMX composite, and the samples *Pal* and *Pal DE* are shown in figure 2. In the $Pal-SMX$ spectrum, compared to the raw material (*Pal*), the appearance of signals associated with the presence of the organic molecule can be noted. However, for sample *Pal DE* these signals disappear as result of desorption process. As can be seen in the figure, very similar ATR spectra were obtained for the samples *Pal* and *Pal DE* (see figure 2): no variation in the characteristic bands of the clay were observed indicating the reversibility of the process as well as the possible reuse of the support material.
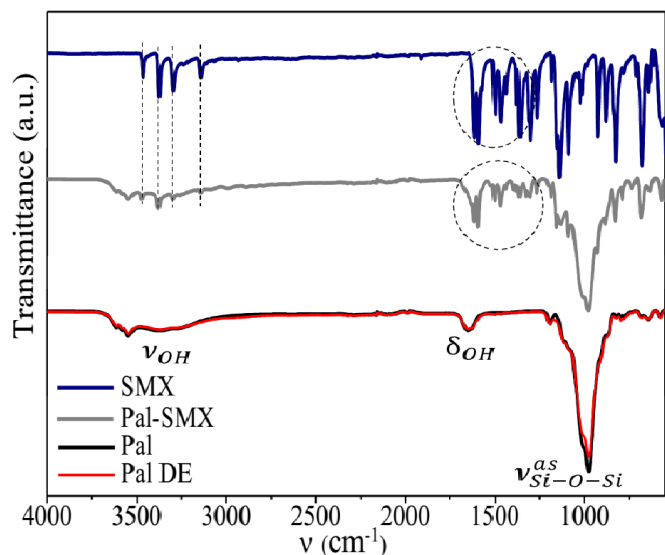

Figure 2. ATR spectra for samples of sulfamethoxazole (SMX), raw material (*Pal*), resulting composite of adsorption process ($Pal-SMX$) and material after the desorption process (*Pal DE*). In dotted lines the signals associated to the emerging pollutant.

Zeta potential results indicated that the surface charge of the samples Pal and Pal DE, before and after of the adsorption-desorption processes, was negative ($\approx$ −25 mV at pH values from 4 to 10). Within the pH range studied, no isoelectric point was observed for both materials. These negative values are associated with dominance of permanent basal charge due to imbalanced isomorphous substitution in tetrahedral and octahedral sheets (for example, Al^{3+} substituting Si^{4+} in the crystal lattice). A similar result has been reported in the literature for 2:1 clays [20, 21]. In the present study, the quantitative and qualitative behavior obtained for both samples was basically the same. It could indicate the material capacity to recover its electrokinetic stability and thus the adsorptive properties, pointing to its potential reuse.

In summary, the different analysis support the hypothesis that the Pal raw material can be reused as an efficient adsorbent of the emerging contaminant SMX, based on the total material integrity and stability after the adsorption-desorption process.

REFERENCES

[1] L. Valdés, S. A. Martín, D. Hernández, L. Lazo, L. C. de Ménorval, and A. Rivera, Rev. Cubana. Fís. **34**, 35 (2017).

[2] D. Hernández, L. Lazo, L. Valdes, L. C. de Ménorval, Z. Rozynek, and A. Rivera, Appl. Clay Sci. **161**, 395 (2018).

[3] J. Akhtar, N. A. S. Amin, and K. Shahzad, Desalin. Water Treat. **57**, 12842 (2016).

[4] K.-L. Chen, L.-C. Liu, and W.-R. Chen, Environ. Pollut. **231**, 1163 (2017).

[5] S. Ismadji, F. Edi, and A. Ayucitra, in Clay materials for environmental remediation, edited by S. K. Sharma (Springer, London, 2015), pp. 5.

[6] M. Leal, V. Martínez-Hernández, R. Meffe, J. Lillo, and I. de Bustamante, Chemosphere 175, 534 (2017).

[7] S. A. Martín, L. Valdés, F. Mérida, L. C. de Ménorval, M. Velázquez, and A. Rivera, Clay Miner. **53**, 193 (2018).

[8] E. Galan, Clay Miner. **31**, 443 (1996).

[9] H. H. Murray, Clay Miner. **34**, 39 (1999).

[10] M. Suárez and E. García-Romero, Appl. Clay Sci. **31**, 154 (2006).

[11] D. A. McKeown, J. E. Post, and E. S. Etz, Clay Miner. **50**, 667 (2002).

[12] L. Quiñones, Tesis de Licenciatura, Universidad de La Habana, 2018.

[13] N. Bolong, A. F. Ismail, M. R. Salim, and T. Matsuura, Desalination **239**, 229 (2009).

[14] Mineralogy Database, http://webmineral.com/ (2019).

[15] J. E. Chisholm, Can. Mineral. **30**, 61 (1992).

[16] J. E. Post and P. J. Heaney, Am. Mineral. **93**, 667 (2008).

[17] J. García-Rivas, M. Sánchez del Río, E. García-Romero, and M. Suárez, Applied Clay Science **148**, 39 (2017).

[18] M. Rozalén, F. J. Huertas, and P. V. Brady, Geochimica et Cosmochimica Acta **73**, 3752 (2009).

[19] V. Gionis, G. H. Kacandes, J. D. Kastritis, and G. D. Chryssikos, American Mineralogist **91**, 1125 (2006).

[20] M. Duc, F. Gaboriaud, and F. Thomas, J. Colloid Interf. Sci. **289**, 139 (2005).

[21] R. Rusmin, B. Sarkar, B. Biswas, J. Churchman, Y. Liu, and R. Naidu, Appl. Clay Sci. **134**, 95 (2016).