

REACTIVE DYE ADSORPTION DESORPTION AND STAMPING BY HALLOYSITE

Daniel López-Rodríguez^{a1*}, Bàrbara Micó-Vicent^{b1}, Eva Bou-Belda^{a2}, Pablo Díaz-García^{a3}

^a Departamento de Ingeniería Textil y Papelera, Universitat Politècnica de València Plaza Ferrándiz y Carbonell s/n, Alcoi, (Alicante), Spain.
^{a1} dalorod@upv.es, ^{a2} evbobel@upvnet.upv.es

^b Departamento de Ingeniería Gráfica, Universitat Politècnica de València Plaza Ferrándiz y Carbonell s/n, Alcoi, (Alicante), Spain.
^{b1} barmivi@upv.es

Abstract:

The scientific community is continuously developing new methods for the recovery and purification of water, since the precious resources of our planet are increasingly scarce and must work to save and clean our waters. One of the methods used is the use of adsorbent and absorbent materials that remove from the water those substances that are harmful to the environment are nanoclays. In this work, the effect of a nanoclay, specifically halloysite, to adsorb reactive dyes has been used as an example of a technique. As an example of this type of coloring substances, Reactive Yellow 2 has been used, which has been subjected to the adsorbent action of the mineral, having an adsorption of 78% in the proposed experiment. Subsequently, it has undergone a desorption process by applying temperature to the dye-clay hybrid, so that later, thanks to the effect of solvents (HCL and / or NaOH), the desorption process in aqueous solution can be completed, obtaining a recovery from the dye up to 17.67% adsorbed, which is interpreted as a very good result. At the same time, the ability to stamp the HNT has been tested once the dye has been adsorbed and used on a Polyester (PES) / Cotton (CO) textile, demonstrating the viability of this process and evaluating its results by rubbing and washing fastness tests.

Keywords: halloysite; nanoclay; textile; pigment; stamping.

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1. Introduction

Discharges into natural effluents is an environmental problem that is constantly growing and that causes important problems for people's health, so many scientists focus on research work that tries to alleviate this problem. Many are the techniques that are used such as ultrafiltration, ion exchange, reverse osmosis etc. However, the cost of many of these processes and their complexity greatly limits the power to make use of when reducing or eliminating any type of impurity in the water and more economical solutions have to be found that can perform this same task. In the same way, it will also try to find a method that does not require sophisticated technology for its use or is highly complex.

The part of the textile chemical industry is the one that most affects wastewater and is the industry with the highest chemical activity on earth (Wakkal et al., 2019). The concentration of the colorants in the effluents is around 50-1000 ppm, although cases of lower 10-50 ppm can be found (Mathew et al., 2019). The nature of the composition depends on the type of dye that can be classified, also taking into account the fixation and estimated losses in the effluent. Thus, it is very important to improve the ability of industries to remove dyes from effluents. The development of low-cost absorbents through the integration of advanced technology can advance this area significantly (Sanz Carbonell, 2016).

To achieve these objectives, nanoclays can be used, which we can find them in nature or they can be synthesized in the laboratory and in any case they have a great adsorbent capacity due to their affinity for water. Those obtained artificially in the laboratory have been manipulated with the aim of modifying and increasing their usability. (Micó-Vicent, 2016). The objective of this work is to reproduce the adsorption results that have been carried out in previous studies which explain the capacity of nanoclays, as has been shown in previous works (Carretero et al., 2007; Guillermin et al., 2019; López Arbeloa et al., 2002; Moujahid et al., 2019; Ogawa et al., 2017) and also to demonstrate experimentally its reuse, either by achieving desorption of the dye or also how the product obtained from the adsorption of the dye by clay can be used in another textile process such as printing on a polyester / cotton fabrics with acceptable fastness results. The features of halloysite give it very high adsorptive properties and at the same time it establishes very strong ion exchanges that allow the colorant to fix in the clay. What's more, Previous works show that these bonding forces between the dye and the clay protect the dye from the action of sunlight, friction, water, etc., providing the resulting hybrid with better solidity values than when a conventional pigment is used.

*Corresponding author: Daniel López-Rodríguez, dalorod@upv.es

2. Materials

For this research, the reactive dye Reactive Yellow 2 C.I. 18972 (Figure 1) from the manufacturer Clariant. Halloysite (Figure 2) from the manufacturer Aldrich has been chosen as the adsorbent substance for the dyes. In the stamping process, a recipe was used consisting of Color Center brand resin and referenced as Center Resin STK / 100, a fixer from the Archroma brand referenced as Lupintrol SE liq. and in order to achieve the appropriate thickness, a thickener of the synthetic type from the manufacturer Archroma referenced as Lutexal CSN liq is added. The stamping was carried out on a 50% Cotton and 50% Polyester PES / CO fabric.

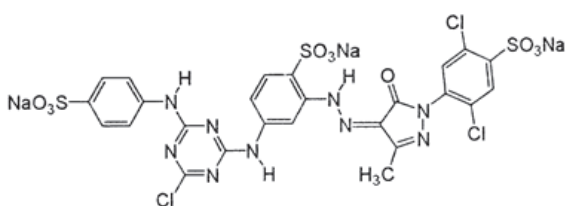


Figure 1: Reactive Yellow 2.

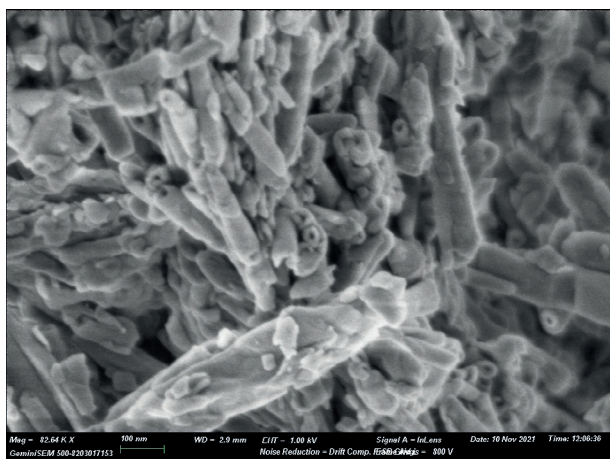


Figure 2: Halloysite SEM.

A great deal of work has been devoted to the research of adsorption elements such as iron minerals, nanoclays, biological adsorbents, etc. For this research work has been oriented on the use of a nanoclay called Halloysite so that it can adsorb substances that are solubilized in water such as dyes from the textile industry and thus recover water for later use in other purposes. Thus, clay minerals have acquired remarkable importance due to their natural origin, the possibility of chemically synthesizing them and the unique characteristics they possess (Lvov et al., 2016). Thus, it is the example of Halloysite, which is an example of a 1:1 clay mineral that can be found in great abundance in nature and that has also been classified within biocompatible materials. Halloysite nanotubes have an approximate diameter of 40-70 nm while their length can be 200-2000 nm. Its external surface is negatively charged and is composed of SiO_2 while in contrast the internal area has a positive charge and is composed of Al_2O_3 (Zhao et al., 2016). The use of halloysite nanotubes (HNT) has increased greatly

thanks to their nature cylindrical that gives it properties such as a large area regarding its size, drug release, economics and its thermal stability (Lazzara et al., 2018; Liu et al., 2014; Yendluri et al., 2017; Yuan et al., 2015).

To explain its aforementioned characteristics, it can be seen that HNT belongs to the family of aluminosilicates, in which a layer of octahedral alumina alternates with another of tetrahedral silica. Due to the effect of this discordance in the alignment of the two types of layers described, a hollow tubular shape characteristic of this nanoclay is generated, which gives it its specific characteristics generated by its nanoarchitecture (Pاسبakhsh et al., 2013). It should be taken into account that the properties of the HNT derive to a large extent from its specific geological deposit, as is collected in a large part of the consulted bibliography (Agafonov et al., 2020; Blagojević et al., 2020; Cavallaro et al., 2018; Makaremi et al., 2017; Pاسبakhsh et al., 2013; Zhang et al., 2020). Their biocompatibility makes them very suitable for recover certain solutions such as the one contained Methylene blue (MB) (Zhao and Liu 2008), Azo dyes (Farrokhi-Rad et al., 2018), Triaryl and diaryl methane dyes (Mudhoo et al., 2019) and Xanthine dyes (Zhao et al., 2013).

3. Experimental process

To carry out the experiments and obtain the results that will be shown below, a V-670 double-beam spectrophotometer utilizes a unique, single monochromator design covering a wavelength range from 190 to 2700 nm (3200 nm option). was used to assess the color of the clay-dye hybrid, a Zuzi absorption spectrometer UV-visible 4251/50 to be able to calculate the concentration of non-adsorbed dye and a Spectrophotometer CM-3600d reflection Full wavelength range from 360-740 nm with 10 nm pitch to evaluate the color intensity from the stamping.

To obtain the hybrids, the Lambert-Beer lines of each colorant have been previously made. A dye concentration of $1 \text{ g}\cdot\text{L}^{-1}$ and a clay concentration of $3 \text{ g}\cdot\text{L}^{-1}$ were used. The dye was then introduced into the clay, stirring for 24 hours in 100 mL of dye solution, to later filter it and let it dry. The adsorption of the colorant by the nanoclay is practically absolute, leaving the initial solution very clean. After drying and collecting the clay, a printing paste has been made with the hybrid obtained.

3.1. Adsorption-Desorption

The experimental process can be divided into two parts. The first focuses on the process of adsorption of the dye by the nanoclay, optimizing the process to achieve the highest possible adsorption with the highest fixation to demonstrate the effectiveness of this clay in the elimination of reactive dye in aqueous solutions. The second part focuses on the inverse process in which the desorption of the colorant in the clay is sought to allow its reuse in a new dyeing bath.

3.1.1. Adsorption

1 L of an aqueous solution of Reactive Yellow 2 is prepared at a concentration of $16 \text{ g}\cdot\text{L}^{-1}$ to which $8 \text{ g}\cdot\text{L}^{-1}$

of Halloysite in powder form is added. The mixture was subjected to magnetic stirring for 2 hours at maximum revolutions and then lowered to minimum stirring until 24 hours of interaction. After this period, the solution is filtered with filter paper for 48 hours to drain the clay as much as possible and obtain the dry clay.

3.1.2. Desorption

The desorption process follows the experimental model published by the authors Momina, Shahadat Mohammad and Suzylawatilsamil (Momina et al., 2020) show how to proceed with the desorption of MB (methylene blue) by subjecting the clay-dye hybrid to temperature and then using various solvents such as HCl and NaOH. For this work, a factorial design of experiments has been used as shown in Table 1, which allows obtaining the maximum relevant information with the least possible number of experiments.

Table 1: Design of experiments for desorption of reactive dye in Halloysite.

sample n°	DOE desorption		
	pH (basic-acid) HCl or NaOH	Temperature 150 or 200 °C	Agitation 0 or 1200 r.p.m.
1	acid	150	1200
2	acid	150	0
3	acid	200	1200
4	acid	200	0
5	basic	150	1200
6	basic	150	0
7	basic	200	1200
8	basic	200	0

The process is started by heating the sample of the dry and solid hybrid collected from the experimental part of adsorption at about 150-200 °C for 45 minutes. With this, the bonds between adsorbent and colorant are weakened. In the next step, the HCl or NaOH is introduced according to the experiment sample and is subjected to stirring for 30 minutes. Finally the mixture is filtered to separate the clay solids.

3.2. Stamping

The proposal is to get the Halloysite to have the maximum intensity possible of color for the next production of the paste to be used in the stamping, Thus, the adsorption with the nanoclay is carried out in the following way. 1000 mL of dye solution were taken at a concentration of 1 g·L⁻¹. A concentration of 3 g·L⁻¹ the nanoclay was introduced and all of this was subjected to mechanical agitation (Silva et al., 2012) during the first two hours at maximum revolutions and then lower it to 600 r.p.m. until the 24 h totals from this stirring process. The next step is to filter the mixture of dissolution and HT for a minimum of 72 hours to obtain the most drained hybrid possible. With the rest of the aqueous solution that the filtering process gives off, was analyzed it using a UV-visible 4251/50 absorption spectrophotometer in order to calculate the amount of dye that has not been retained by the nanoclay using the Lambert-Beer curves. The solid residue that

has remained in the filter is measured in a V-670 double-beam spectrophotometer to quantify the intensity of color.

In the stamping procedure, a recipe was used consisting of Color Center brand resin and referenced as Center Resin STK/100, a fixer from the Archroma brand referenced as Lupintrol SE liq. and in order to achieve the appropriate thickness, a thickener of the synthetic type from the manufacturer Archroma referenced as Lutexal CSN liq is added. The stamping It was carried out in an openwork textile with a composition 50% polyester 50% cotton, applying 4 scraping passes to subsequently dry it for 15 minutes at 60 °C and then heat set it at 180 °C for 3 s. on a pressure plate. In order to quantify the color obtained, were used Spectrophotometer CM-3600d Minolta CM-3600d reflection spectrophotometer Full wavelength range from 360-740 nm with 10 nm pitch.

4. Results

4.1. Adsorption-Desorption

The results of each stage of the experimental phase, adsorption and desorption, are differentiated. It is especially important for this work to achieve the highest adsorption and desorption in both phases.

4.1.1. Adsorption

After 24 hours of action of the mineral to adsorb the colorant, the residual concentration of Reactive Yellow 2 that has remained is checked, this being 0.22 g·L⁻¹ so it can be deduced that the adsorption of the clay has been of the 78% calculated with Equation 1. It should be noted that it is in this specific case and these conditions are used since it was intended that the halloysite be as saturated as possible with dye to promote good conditions in the desorption step. By varying the clay / dye concentration ratio, it is possible to achieve adsorption close to 100%, as has been demonstrated in previous works (López et al., 2020).

Equation 1: Calculation of adsorbed dye.

$$\% = 100 \frac{C_i - C_f}{C_i} \quad (1)$$

4.1.2. Desorption

Regarding the results of the desorption obtained after the process and calculated with Equations 1 and 2 described by the authors Momina, Shahadat Mohammad and Suzylawatilsamil, they can be observed in Table 2.

Equation 2: Lambert-Beer equation for calculate the concentration Reactive Yellow dye.

$$y = 14.943x - 0.0021 \quad (2)$$

The aforementioned authors achieved higher desorption levels, but working with another clay and another dye so the result can be comparable. In their work they reached 70% desorption using similar procedures (Momina et al., 2020).

Table 2: Amounts desorbed by the hybrid.

Sample nº	g/L recovered	% desorption
1	0.56	7.218
2	0.55	7.109
3	0.60	7.654
4	0.58	7.425
5	1.37	17.657
6	1.27	16.264
7	1.22	15.742
8	1.07	13.760

4.2. Stamping

As can be seen in Table 3, the results collected confirm the adsorption capacity of Halloysite since it has achieved that the concentration of dye has gone from $3 \text{ g}\cdot\text{L}^{-1}$ that was initially to a concentration of between $3.08\cdot 10^{-4} \text{ g}\cdot\text{L}^{-1}$ and $3.21\cdot 10^{-4} \text{ g}\cdot\text{L}^{-1}$. These are very good results as it was thickened and as a consequence a hybrid with a high concentration of colorant and a good intensity of color.

Table 3: Difference in concentration after adsorption.

Sample	Final conc. $\text{g}\cdot\text{L}^{-1}$	% adsorption
1	$3.08\cdot 10^{-4}$	99.85
2	$3.21\cdot 10^{-4}$	99.36

It is important to obtain a reference of the amount of color that is achieved with the printing process, for which a reflectance measurement has been used and the Kubelka-Munk theory (K/S) is taken as a reference, thanks to which you can define the values that quantify the light interaction circumstances that are none other than the light diffusion coefficient (S) and the light adsorption coefficient (K) (Nyankson et al., 2019). The result of this analysis was carried out with the samples exposed to the normalized illuminant D65 in the visible wavelength range between 400 and 700 nm, which resulted in a maximum reflectance at 400 nm. The results of the reflection and the average intensity of the color calculated are expressed in Table 2. To assess the durability of the printing carried out, the samples were subjected to two tests of fastness to washing in accordance with the ISO 105-C06: 1994 standard and dry rubbing according to the UNE-EN ISO 105-X12 standard. For both cases, an assessment of the discharges has been carried out using the gray scale, obtaining the results that shows in Table 4.

Table 4: K/S color strength at 400 nm and fastnesses.

	Sample 1	Sample 2
K/S (400 nm)	0.1926 ± 0.061	0.4552 ± 0.0712
Fastness washing	4	4
Fastness rubbing	4	4

5. Conclusions

In view of the results obtained, the adsorbent capacity of Halloysite against pollutants in the textile industry of the reactive dyes type is demonstrated. For the conditions described, 78% adsorption has been reached, although

it is true that increasing the concentration of nanoclay or lowering that of dyes it is assumed that it is possible to achieve much higher adsorption, as occurs with the use of other nanoclays reaching around the 90%.

On the other hand, the works of Momina, Shahadat Mohammad and Suzylawatilsamil are confirmed since following their experimental design good desorption levels are achieved, up to 17.67%. The importance of the variables used in the experiment can be seen that these deviation values can be reduced to 7.22%, which demonstrates the importance of the variables used. Although the levels described by the authors are not reached, although they carried out the experiments with bentonite and methylene blue, not with the clay and dye used in this work. Thus, this work can be continued using other clays and dye to see which clays are more efficient for each type of dye and thus optimize the selection of nanoclay.

Regarding stamping, it can be concluded that both the trials and previous results of the authors of this work as well as those of other authors have been reproduced in this work. Halloysite shows that it has a characteristic ability to adsorb dye and fix it. It has also been shown that the clay-dye hydride that is formed can be used in a pigment printing phase, notably improving conventional methods, since they improve the solidity results of other stampings. It can be seen how the staging of the colored clay has been a success.. You can see how a stamping with the hybrid and the stamping paste has been made, leaving the colored fabric in the area of application. The samples obtained show good coatings, use and intensity of color, fulfilling the intended objective. In future studies, printing recipes with a higher concentration of hybrid can be sought to increase the intensity of the printed color, as well as to increase the amount of colorant adsorbed on the clay in order to also seek an increase in the intensity of color which from a subjective appreciation is thought to be increased.

Regarding the fastnesses, they can be considered as acceptable, without neglecting that it is a pigmentary type printing in which the colorants do not show affinity for the fiber, and that being protected by the structure of the clay that previously has been adsorbed, improve its resistance to external agents. Also note that although the color intensities of the samples are acceptable, they are not too high, so that in future tests the fastness tests may be affected. This is due to the fact that, the higher the concentration of color, it may be more susceptible to detach it and produce a color, or on the contrary, find that the intensity is maintained even after the test thanks to the effect of the nanoclay.

References

- Agafonov, A. V., Kudryakova, N. O., Ramenskaya, L. M., & Grishina, E. P. (2020). The Confinement and Anion Type Effect on the Physicochemical Properties of Ionic Liquid/Halloysite Nanoclay Ionogels. *Arabian Journal of Chemistry*, 13(12), 9090–9104. <https://doi.org/10.1016/j.arabjc.2020.10.033>
- Blagojevic, B., Cetojevic-Simin, D., Parisi, F., Lazzara, G., & Popovic, B. M. (2020). Halloysite Nanotubes as a Carrier of Cornelian Cherry (*Cornus Mas L.*) Bioactives. *Lwt*, 134(June). <https://doi.org/10.1016/j.lwt.2020.110247>
- Carretero, M. I., Pozo, M., Sánchez, C., García, F. J., Medina, J. A., & Bernabé, J. M. (2007). Comparison of Saponite and Montmorillonite Behaviour during Static and Stirring Maturation with Seawater for Pelotherapy. *Applied Clay Science*, 36(1–3), 161–73.
- Cavallaro, G., Chiappisi, L., Pasbakhsh, P., Gradzielski, M., & Lazzara, G. (2018). A Structural Comparison of Halloysite Nanotubes of Different Origin by Small-Angle Neutron Scattering (SANS) and Electric Birefringence. *Applied Clay Science*, 160, 71–80. <https://doi.org/10.1016/j.clay.2017.12.044>
- Farrokhi-Rad, M., Mohammadalipour, M., & Shahrabi, T. (2018). Electrophoretically Deposited Halloysite Nanotubes Coating as the Adsorbent for the Removal of Methylene Blue from Aqueous Solution. *Journal of the European Ceramic Society*, 38(10), 3650–59. <https://doi.org/10.1016/j.jeurceramsoc.2018.03.048>
- Guillermin, D., Debroyse, T., Trigueiro, P., de Viguierie, L., Rigaud, B., Morlet-Savary, F., Balme, S., Janot, J.M., Tielens, F., Michot, L., Lalevee, J., Walter, P., & Jaber, M. (2019). New Pigments Based on Carminic Acid and Smectites: A Molecular Investigation. *Dyes and Pigments*, 160, 971–82. <https://doi.org/10.1016/j.dyepig.2018.07.021>
- Lazzara, G., Cavallaro, G., Panchal, A., Fakhruilln, R., Stavitskaya, A., Vinokurov, V., & Lvov, Y. (2018). An Assembly of Organic-Inorganic Composites Using Halloysite Clay Nanotubes. *Current Opinion in Colloid & Interface Science*, 35, 42–50. <https://doi.org/10.1016/j.cocis.2018.01.002>
- Liu, M., Jia, Z., Jia, D., & Zhou, C. (2014). Recent Advance in Research on Halloysite Nanotubes-Polymer Nanocomposite. *Progress in Polymer Science*, 39(8), 1498–1525. <https://doi.org/10.1016/j.progpolymsci.2014.04.004>
- López Arbeloa, F., Martínez, V. M., Prieto, J. B., & López Arbeloa, I. (2002). Adsorption of Rhodamine 3B Dye on Saponite Colloidal Particles in Aqueous Suspensions. *Langmuir*, 18(7), 2658–64. <https://doi.org/10.1021/la0113163>
- López, D., Micó-Vicent, B., Bonet-Aracil, M., & Bou-Belda, E. (2020). Study of the effect of the concentration of hydrotalcite in the recovery of colorants in textile wastewater. *Annals of the University of Oradea: Fascicle of Textiles, Leatherwork* (Online) 21(1), 61–64. <http://hdl.handle.net/10251/167210>
- Lvov, Y. M., DeVilliers, M. M., & Fakhruilln, R. F. (2016). The Application of Halloysite Tubule Nanoclay in Drug Delivery. *Expert Opinion on Drug Delivery*, 13(7), 977–86. <https://doi.org/10.1517/17425247.2016.1169271>
- Makaremi, M., Pasbakhsh, P., Cavallaro, G., Lazzara, G., Aw, Y. K., Lee, S. M., & Milioto, S. (2017). Effect of Morphology and Size of Halloysite Nanotubes on Functional Pectin Bionanocomposites for Food Packaging Applications. *ACS Applied Materials & Interfaces*, 9(20), 17476–88. <https://doi.org/10.1021/acsami.7b04297>
- Mathew, M. L., Gopalakrishnan, A., Aravindakumar, C. T., & Aravind, U. K. (2019). Low – Cost Multilayered Green Fiber for the Treatment of Textile Industry Waste Water. *Journal of Hazardous Materials*, 365, 297–305. <https://doi.org/10.1016/j.jhazmat.2018.11.014>
- Micó-Vicent, B. (2016). *Optimizació de la síntesis de nanopigmentos de origen natural para biopolímeros mediante el uso de diseño de experimentos*. Doctoral dissertation, Universitat Politècnica de València.
- Momina, S., & Suzylawati, I. (2020). Study of the Adsorption/Desorption of MB Dye Solution Using Bentonite Adsorbent Coating. *Journal of Water Process Engineering*, 34(July 2019). <https://doi.org/10.1016/j.jwpe.2020.101155>
- Moujahid, E. M., Lahkale, R., Ouassif, H., Bouragba, F. Z., & Elhatimi, W. (2019). New Organic Dye/Anionic Clay Hybrid Pigments: Preparation, Optical Properties and Structural Stability. *Dyes and Pigments*, 162, 998–1004. <https://doi.org/10.1016/j.dyepig.2018.11.021>
- Mudhoo, A., Gautam, R. K., Ncibi, M. C., Zhao, F., Garg, V. K., & Sillanpää, M. (2019). Green Synthesis, Activation and Functionalization of Adsorbents for Dye Sequestration. *Environmental Chemistry Letters*, 17(1), 157–93. <https://doi.org/10.1007/s10311-018-0784-x>
- Nyankson, E., Agyei-Tuffour, B., Annan, E., Yaya, A., Mensah, B., Onwona-Agyeman, B., ... & Efavi, J. K. (2019). Ag₂CO₃-Halloysite Nanotubes Composite with Enhanced Removal Efficiency for Water Soluble Dyes. *Heliyon*, 5(6), e01969. <https://doi.org/10.1016/j.heliyon.2019.e01969>

- Ogawa, M., Takee, R., Okabe, Y., & Seki, Y. (2017). Bio-Geo Hybrid Pigment; Clay-Anthocyanin Complex Which Changes Color Depending on the Atmosphere. *Dyes and Pigments*, 139, 561–65. <https://doi.org/10.1016/j.dyepig.2016.12.054>
- Pasbakhsh, P., Churchman, G. J., & Keeling, J. L. (2013). Characterisation of Properties of Various Halloysites Relevant to Their Use as Nanotubes and Microfibre Fillers. *Applied Clay Science*, 74, 47–57. <https://doi.org/10.1016/j.clay.2012.06.014>
- Sanz Carbonell, J. F. (2016). *Tratamiento de aguas textiles industriales mediante fotocatalisis solar y reutilización en nuevas tinturas*. Doctoral Thesis, Universitat Politècnica de València. <https://doi.org/10.4995/Thesis/10251/59384>
- Silva, M. M., Oliveira, M. M., Avelino, M. C., Fonseca, M. G., Almeida, R. K., & Silva Filho, E. C. (2012). Adsorption of an Industrial Anionic Dye by Modified-KSF-Montmorillonite: Evaluation of the Kinetic, Thermodynamic and Equilibrium Data. *Chemical Engineering Journal*, 203, 259–68. <https://doi.org/10.1016/j.cej.2012.07.009>
- Wakkal, M., Khiari, B., & Zagrouba, F. (2019). Textile Wastewater Treatment by Agro-Industrial Waste: Equilibrium Modelling, Thermodynamics and Mass Transfer Mechanisms of Cationic Dyes Adsorption onto Low-Cost Lignocellulosic Adsorbent. *Journal of the Taiwan Institute of Chemical Engineers*, 96, 439–52. <https://doi.org/10.1016/j.jtice.2018.12.014>
- Yendluri, R., Otto, D. P., De Villiers, M. M., Vinokurov, V., & Lvov, Y. M. (2017). Application of Halloysite Clay Nanotubes as a Pharmaceutical Excipient. *International Journal of Pharmaceutics*, 521(1–2), 267–73. <https://doi.org/10.1016/j.ijpharm.2017.02.055>
- Yuan, P., Tan, D., & Annabi-Bergaya, F. (2015). Properties and Applications of Halloysite Nanotubes: Recent Research Advances and Future Prospects. *Applied Clay Science*, 112, 75–93. <https://doi.org/10.1016/j.clay.2015.05.001>
- Zhang, B., Yuan, P., Guo, H., Deng, L., Li, Y., Li, L., Wang, Q., & Liu, D. (2020). Effect of Curing Conditions on the Microstructure and Mechanical Performance of Geopolymers Derived from Nanosized Tubular Halloysite. *Construction and Building Materials*, 268, 121186. <https://doi.org/10.1016/j.conbuildmat.2020.121186>
- Zhao, M., & Liu, P. (2008). Adsorption Behavior of Methylene Blue on Halloysite Nanotubes. *Microporous and Mesoporous Materials*, 112(1–3), 419–24. <https://doi.org/10.1016/j.micromeso.2007.10.018>
- Zhao, N., Liu, Y., Zhao, X., & Song, H. (2016). Liquid Crystal Self-Assembly of Halloysite Nanotubes in Ionic Liquids: A Novel Soft Nanocomposite Ionogel Electrolyte with High Anisotropic Ionic Conductivity and Thermal Stability. *Nanoscale*, 8(3), 1545–54. <https://doi.org/10.1039/C5NR06888F>
- Zhao, Y., Abdullayev, E., Vasiliev, A., & Lvov, Y. (2013). Halloysite Nanotubule Clay for Efficient Water Purification. *Journal of Colloid and Interface Science*, 406, 121–29. <https://doi.org/10.1016/j.jcis.2013.05.072>