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STUDY OF THE EFFECT OF THE CONCENTRATION OF HYDROTALCITE IN THE RECOVERY OF COLORANTS IN TEXTILE WASTEWATER

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Abstract: *The absorption capacity of calcined hydrotalcite at different concentrations in a solution of 0.05 g • L-1 of 4 different dyes has been compared; Direct Blue 199, Direct Red 23, Direct Blue 71 and Reactive Yellow. For this, the Lambert-Beer lines of each dye have been previously made. Two different concentrations of clay, 5 and 10 g • L-1, have been worked. Then the dye has been introduced into the clay by stirring for 24 hours in 100 ml of solution of each dye, to later filter it and allow to dry. In all cases, the absorption of the dye by the nanoclay has been almost absolute, leaving the initial solution very clean, which are excellent results from the point of view of cleaning wastewater. However, when obtaining very similar results when scaling it to an industrial production, it would be more optimal to use the lowest concentration in order to reduce costs. Finally, a color measurement was made using a Jasco V-670 spectrophotometer, double beam spectrophotometer between 190- 2700 nm and color differences are calculated and represented in a color chart. Again, no large differences are observed and reinforce the idea of using a low concentration.*

Key words: *nanoclay, dye recovery, clay pigment, direct dye recovery, reactive dye recovery.*

1. INTRODUCTION

In the last decades, environmental alerts have grown, which increases the concern for caring for the environment. The textile industry discharges organic and inorganic residues that produce bioaccumulations and can cause high degrees of toxicity. The part of the textile chemical industry is the one that most affects wastewater and is the industry with the greatest chemical activity on earth [1]. The recycling of industrial wastewater has been a need that is becoming increasingly noticeable. The concentration of dyes in the effluents is around 50-1000 ppm, although cases of lower 10-50 ppm can be found [2]. Currently there is a wide variety of nanoclays and many of them have a very efficient capacity to help recover dyes from wastewater. Nanoclay is the general term used to refer to mineral clays with a phosilicate or lamellar structure with dimensions of the order of nm and surfaces of 50-150 nm or more. The mineral base can be synthetic or natural, and is hydrophilic. The clay surface can be modified with specific compounds to improve its affinity and be able to make them compatible, for example, with polymers. The surface area of the nanoclays is very large, around 750 m2 / g. When small amounts of these materials are incorporated into polymeric matrices, the result is called a nanocomposite [3]. This work aims to study the absorption capacity of dyes in the textile industry through the use of nanoclays. Previous work has demonstrated the efficacy of this type of element and the success of the corresponding trials [4-9]. The characteristics of clays give them a great capacity to absorb the dye and, above all, the ability to fix these dye molecules within their structure. Once the colorant has been introduced into the clay, we will see how the new hybrid compound acquires a characteristic color, which makes it susceptible of being used later, for example, as a pigment.

2. MATERIALS AND METHODS

Different dyes were used in this study. Direct dyes were: Direct Blue 199 CI 74.180, Direct Red 23 CI 29160, Direct Blue 71 CI 34140 as Reactive dye: Reactive Drimaren Yellow HF-3GL was studied. As clay we used calcinated hydrotalcite (HC) which was prepared according to Dos Santos R.M.M. [10] In figure 1 a SEM image of HC nanoclay is shown.

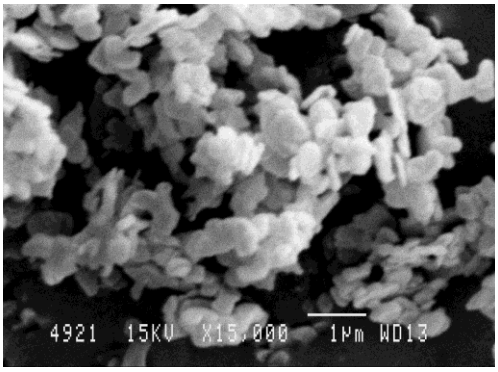

Fig 1. *SEM image of HC*

Dilutions of each of the dye were prepared to obtain the Lambert-Beer line [11] . With these lines we can know the concentration of dye that remains in the wastewater once the clay is applied. Table 1 shows the equations of the lines and the regression (R).

Table 1. *Lambert-Beer line equations and* R^2

Colorant	Equation	R^2
Direct Blue 199	y = 21.784 x - 0.015	0.9982
Reactive Yellow	y= 14.943 x – 0.0021	0.9993
Direct Red 23	y= 34.357 x – 0.0148	0.9991
Direct Blue 71	y= 17,09 x – 0.0233	0.9987

100 mL of concentration solution 0.05 $g\cdot L^{-1}$ were taken by each dye. We introduce 10 $g\cdot L^{-1}$ and 5 $g\cdot L^{-1}$ of the clay were introduced and mixture was put under stirring [12], during the first two hours at maximum stirring and then it went to 600 r.p.m. The solution is then filtered with the clay for 48 hours and measure with the spectrophotometer to calculate the concentration of dye that has not been absorbed by the clay [13, 14]. The nanoclays with the dye were measured in a Jasco V-670, double beam spectrophotometer between 190-2700 nm and the color differences were calculated.

3. RESULTS AND DISCUSSSION

The results in Table 2 show how after the clay action the dye concretions have gone from $5 \cdot 10^{-2}$ $g \cdot L^{-1}$ to values between $3.41 \cdot 10^{-4}$ and $1.6 \cdot 10^{-3}$ $g \cdot L^{-1}$. A bigger approach can be seen in the reactive dye with respect to direct dyes. No significant differences are observed between the use of different concentrations of nanoclay

Table 2. *Difference in concentration after HC absorption*

	Sample ref.	HC conc. $g \cdot L^{-1}$	Initial conc $g \cdot L^{-1}$	Final conc $g \cdot L^{-1}$	% absorption
Direct Blue 199	B199-5	5	0.05	$7.80 \cdot 10^{-4}$	98.44
	B199-10	10	0.05	$7.80 \cdot 10^{-4}$	98.44
Direct Red 23	DR-5	5	0.05	$5.47 \cdot 10^{-4}$	98.91
	DR-10	10	0.05	$5.76 \cdot 10^{-4}$	98,85
Direct Blue 71	B71-5	5	0.05	$1.54 \cdot 10^{-3}$	96.92
	B71-10	10	0.05	$1.60 \cdot 10^{-3}$	96,80
Reactive Yellow	RY-5	5	0.05	$4.08 \cdot 10^{-4}$	99.18
	RY-10	10	0.05	$3.41 \cdot 10^{-4}$	99.32

The color measurements of the dye-clay hybrids represented in chromatic diagrams are shown Figure 2. As in the absortion results, no significant differences were observed between the compounds obtained at 5 or 10 $g \cdot L^{-1}$

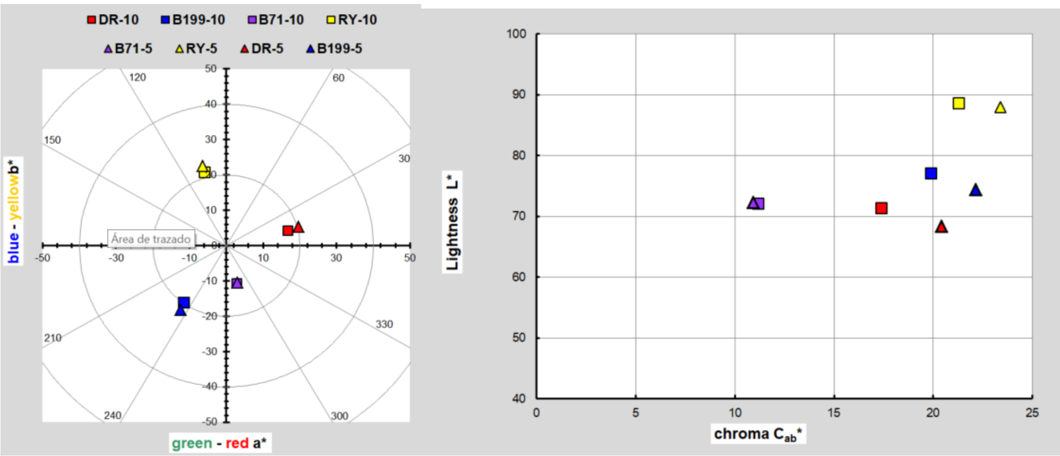

Fig. 2: *Color measurements of HC nanoclays using different concentration of dye*

4. CONCLUSIONS

In view of the results, we can conclude that the results and interpretations provided in other studies are reproduced in our trials. The HC shows a great capacity for absorption and fixation of the dye within its structure. Furthermore, the increased use of this nanoclay has not shown very different results both in the absorption of dye and the color obtained in the hybrid, despite using twice the concentration. So in case of industrializing this method it would be interesting to work at the best possible concentration of clay that provides the most optimal results, allowing to reduce costs and avoid the unnecessary use of material.

REFERENCES

[1] M. Wakkel, B. Khiari, and F. Zagrouba, "Textile wastewater treatment by agro-industrial waste: Equilibrium modelling, thermodynamics and mass transfer mechanisms of cationic dyes adsorption onto low-cost lignocellulosic adsorbent," *J. Taiwan Inst. Chem. Eng.*, vol. 96, pp. 439–452, Mar. 2019.

[2] M. L. Mathew, A. Gopalakrishnan, C. T. Aravindakumar, and U. K. Aravind, "Low – cost multilayered green fiber for the treatment of textile industry waste water," *J. Hazard. Mater.*, vol. 365, pp. 297–305, Mar. 2019.

[3] F. M. Micó Vicent, Barbara; Martinez Verdu and J. E. Gilabert Perez, "Optimización de la síntesis de nanopigmentos de origen natural para biopolímeros mediante el uso del diseño de experimentos."

[4] M. Ogawa, R. Takee, Y. Okabe, and Y. Seki, "Bio-geo hybrid pigment; clay-anthocyanin complex which changes color depending on the atmosphere," *Dye. Pigment.*, vol. 139, pp. 561–565, Apr. 2017, doi: 10.1016/J.DYEPIG.2016.12.054.

[5] F. López Arbeloa, V. Martínez Martínez, J. Bañuelos Prieto, and I. López Arbeloa, "Adsorption of Rhodamine 3B dye on Saponite colloidal particles in aqueous suspensions," *Langmuir*, vol. 18, no. 7, pp. 2658–2664, 2002, doi: 10.1021/la0113163.

[6] M. I. Carretero, M. Pozo, C. Sánchez, F. J. García, J. A. Medina, and J. M. Bernabé, "Comparison of saponite and montmorillonite behaviour during static and stirring maturation with seawater for pelotherapy," *Appl. Clay Sci.*, vol. 36, no. 1–3, pp. 161–173, Apr. 2007, doi: 10.1016/J.CLAY.2006.05.010.

[7] D. Guillermin *et al.*, "New pigments based on carminic acid and smectites: A molecular investigation," *Dye. Pigment.*, vol. 160, pp. 971–982, Jan. 2019, doi: 10.1016/J.DYEPIG.2018.07.021.

[8] E. M. Moujahid, R. Lahkale, H. Ouassif, F. Z. Bouragba, and W. Elhatimi, "New organic dye/anionic clay hybrid pigments: Preparation, optical properties and structural stability," *Dye. Pigment.*, vol. 162, pp. 998–1004, Mar. 2019, doi: 10.1016/J.DYEPIG.2018.11.021.

[9] J.-Z. Yi and L.-M. Zhang, "Removal of methylene blue dye from aqueous solution by adsorption onto sodium humate/polyacrylamide/clay hybrid hydrogels," *Bioresour. Technol.*, vol. 99, no. 7, pp. 2182–2186, May 2008, doi: 10.1016/J.BIORTECH.2007.05.028.

[10] dos Santos, R. M. M., Gonçalves, R. G. L., Constantino, V. R. L., da Costa, L. M., da Silva, L. H. M., Tronto, J., & Pinto, F. G. (2013). Removal of Acid Green 68: 1 from aqueous solutions by calcined and uncalcined layered double hydroxides. Applied Clay Science, 80, 89-195.

[11] J. L. Bigman, "Monitoring of Chemicals and Water," *Handb. Silicon Wafer Clean. Technol.*, pp. 619–657, Jan. 2018, doi: 10.1016/B978-0-323-51084-4.00011-3.

[12] 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, 259-268.

[13] B. Micó-Vicent, FM Martínez-Verdú (2017) Method for optimising the synthesis of hybrid nanopigments,WO2017072382A1.

[14] H. Fischer, L.F. Batenburg, (2001) Coloring Pigment, patent WO0104216.