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Studies of Adsorption-Desorption of Methylene Blue in a Fixed-Bed Reactor Filled with Cotton and Tanine Industry Waste

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Abstract– ***In this paper, a laboratory scale fixed-bed reactor filled with cotton husk and quebracho chips was used to test the capabilities of these materials to be employed as dyes adsorbent materials in effluent treatment of textile industries. The adsorption-desorption processes of methylene blue on both adsorbents were studied and the number of effective cycles was determined in each case. Desorbent efficiency of three substances was evaluated: NaCl 0.1 M, ethanol 50% (V/V) and tap water. As much as three adsorption-desorption cycles were obtained in all cases.***

Keywords-- ***Methylene blue, fixed-bed reactor, cotton husk, quebracho chip.***

I. Introduction

Dyes, chemicals and water are used in the manufacturing process of textile industries. Dyes resistance to degradation in any of its forms has been so perfected, that in current clothes, life color is already comparable to fabric or garment life itself [1]. High production capacity made prices lower and novel products with great availability. Chemistry and technology development allowed dyes production by petroleum derivatives synthesis. Synthetic artificial dyes characteristics are superior to natural dyes, both for their physicochemical properties and for the functional advantages they show [2]. This is also seen during the dyeing process, especially with regard to the overall velocity. Textile industry produces large quantities of colored effluents with high persistence [3]. Various methods are available to treat colored effluents [4, 5, 6]. However, the most efficient for color removing in industrial effluents is considered the adsorption method. The adsorbent usually used is activated carbon, although its high cost makes it necessary to research alternative adsorbents [7].

In the north of Argentine, in Chaco, the ginner and the tannin industries are the most commonly found and they produce large amount of solid wastes [8, 9, 10]. All the solid waste generated by both industries is not treated properly. This paper studies the possibilities to be used as adsorbent to treat the other important industry of this zone, textile industry, so a step closer to circular economy is intended.

The use of a fixed-bed reactor for water treatment is a practical and economical option, the operation is continuous, and the process could be well controlled [11]. Industrial application involves fixed-bed adsorption reactors in which the sorbate is continuously in contact with a certain amount of fresh sorbent [12]. Sorbent regeneration can be important to keep costs down and allowing the possibility of dye extracted recovering from the liquid phase [1, 2]. The previous studies are about equilibrium or batch-contact systems. Only limited studies are available on fixed-bed adsorption using column design models. Furthermore, it is often difficult to apply batch experimental data to fixed-bed adsorbents because isotherms cannot provide accurate scale-up data in fixed-bed systems. The problem in designing columns is that it is difficult to predict how much time they will last before regeneration or replacement becomes necessary [13]. Adsorption-desorption design processes in fixed-bed columns requires a deep understanding of the breakthrough curve dynamics, which entails a study and design of process modeling [14].

II. MATERIALS AND METHODS

A basic dye was selected for the test, Methylene Blue (MB). The stock solution (400 mg/L) was prepared by dissolving the required amount of MB, Cicarelli™ 95% purity, in distilled water. The quantification of MB was obtained by spectrophotometry using a UV/Visible Spectrometer model Lambda 25 from PerkinElmer™, at different wavelengths: 430 nm, 500 nm and 663 nm [15].

For adsorption-desorption test three desorbent solutions were tested: a 0.1 M of sodium chloride (p.a, Biopack™) solution; a 50% (V/V) solution of ethanol; and tap water.

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A. Adsorbent Characterization

Cotton husk (CH) and quebracho chips (QC), conditioning and characterization methods were described in previous work [16, 17].

In this work, its shapes and characteristic dimensions were determined by image analysis. This knowledge can help to interpret the variations in the breakthrough curves. To obtain an image of a sample, a desktop scanner HP Scanjet G3110 with transparency adapter was used. The use of a transparency adapter has the advantage of obtaining images of projected areas without using complex algorithms, typical of images taken directly. The sample is placed inside a Petri dish, taking care that the particles are not in contact with each other. Images processing for dimensions measurement were done with free distribution program ImageJ ® version 1.52ª [18]. In this program, the digitalized color image is converted to gray levels and then binarized. In such images, the projected area of each particle is assimilated to an ellipse which axes, major and minor, match with their length and width [19]. For each of the objects in the sample, the ellipse that best fits with one of the predefined ImageJ functions is obtained. For these ellipses, the program also allows to obtain the value of the length of their major and minor axes, which correspond to the length and width of each of the objects present in the image.

B Fixed-bed reactor tests

Experiments were carried out in a 16 mm diameter and 200 mm high acrylic cylinder as the upward-flow fixed-bed reactor. The solutions were impulse by a peristaltic pump at 80 mL/h for CH and 40mL/h for QC. For the hydraulic test, 1 g of adsorbent was placed inside it.

For adsorption test, MB solution was pumped and samples were taken every 30 minutes for 24 hours, until the bed was saturated. Then, a desorbent solutions was pumped until the output concentration was constant. Sampling was carried out in the same way as in the adsorption step. Furthermore, the number of adsorption-desorption cycles was determined. The breakthrough curves were plotted using the adsorption test results: C/C_0 vs. time (h) were plotted; C is the concentration of MB at the reactor outlet and C_0, constant and equal to 400 mg/L, at the inlet.

The adsorption amount (q_{ads}, mg_{MB}/g_{ads}) and desorption amount (q_{des}, mg_{MB}/g_{ads}) were determinate using the equation 1 and equation 2, respectly.

$$q_{ads} = \frac{Q.C_{0a}}{m}\int_0^{t_R}\left(1-\frac{C}{C_{oa}}\right)dt \quad (1)$$

$$q_{des} = \frac{Q.C_{0d}}{m}\int_0^{t_R}\left(1-\frac{C}{C_{od}}\right)dt \quad (2)$$

Where Q is the fixed-bed reactor solution flow rate (mL/h); m is the adsorbent mass (g); C_{0a} is the inlet reactor MB concentration in the adsorption; C_{0d} is the first outlet reactor sample MB concentration in the desorption; t_R is the running time; and C is the MB concentration as a function of time, at the exit from the reactor [20].

C Breakthrough curves study

Three commonly used models to describe these breakthrough curves were tested in this work: the Adams.Bohart [21], the Yoon-Nelson [22] and the Thomas [23] models.

The Adams–Bohart model assumes that the adsorption rate is proportional to both the residual capacity of the adsorbent and the concentration of the adsorbing species. The Adams–Bohart model is used for the description of the initial part of the breakthrough curve. The expression is the following:

$$\frac{C}{C_0} = e^{\left[\frac{k_{AB}\,C_0\,V_{ef}}{F} - \frac{k_{AB}N_0Z}{U_0}\right]} \quad (3)$$

where C_0 is the dyes initial concentration (mg L^{-1}), k_{AB} is the kinetic constant (L mg^{-1} min^{-1}), F is the flow rate (cm^3 min^{-1}), Z is the bed depth of column (cm), N_0 is the saturation concentration (mg L^{-1}) and V_{ef} is the volume of effluent solution (ml). Values describing the characteristic operational parameters (k_{AB} and N_0) of the column can be calculated using nonlinear regression analysis according to Eq. (3). From this equation, values describing the characteristic operational parameters of the column can be determined from a plot of C/C_0 against V_{ef} at a given bed height and flow rate using the nonlinear regressive method.

The Thomas model, has often been used to describe the breakthrough of a fixed-bed column and the influencing adsorption parameters of the column system. This model was expressed through the second-order law of kinetic reaction without the presence of axial dispersion even when the bed depth was at the minimum and the breakthrough occurred immediately after the flow started [11]. The Thomas model is expressed in a nonlinearized form, as shown in Eq. (4)

$$\frac{C}{C_0} = \frac{1}{1+\left[e^{\left(\frac{K_{TH}}{F}(q_0\,W - C_0V_{ef})\right)}\right]} \quad (4)$$

where C_0 is the dyes initial concentration (mg L^{-1}), K_{TH} is the kinetic constant of Thomas (L mg^{-1} min^{-1}), F is the flow rate (cm^3 min^{-1}), W is the amoung og adsorbent inside the reactor (g), q_0 is the saturation concentration on solid fase (mg L^{-1}) and V_{ef} is the volume of effluent solution (ml). Values describing the characteristic operational parameters (K_{TH} and q_0) of the column can be calculated using nonlinear regression analysis according to Eq. (4).

The Yoon–Nelson model was developed based on the theory of adsorption and breakthrough of adsorbate probability. This model is straightforward and involves less column parameters and data, and is applicable for a single

component system. The Yoon–Nelson model [22] is described in Eq. (5).

$$\frac{C}{C_0} = \frac{e^{\left[K_{YN}\left(\frac{V_{ef}}{F} - t_{50}\right)\right]}}{1 + e^{\left[K_{YN}\left(\frac{V_{ef}}{F} - t_{50}\right)\right]}} \quad (5)$$

The K_{YN} and t_{50} in this equation represent the Yoon–Nelson rate of constant (min^{-1}) and t_{50} is time required for 50% of adsorbate breakthrough (min). Other physical column parameters are not required for this model equation. From this equation, values of K_{YN} and t_{50} can be obtained using a nonlinear regressive method.

Statistical data processing and analysis was made using a free software RStudio version 1.3.1073.

III. RESULTS AND DISCUSSION

A CH and QC characteristics

Fig. 1 shows the digitalized color image an enlarged portion of the analyzed CH and QC. It can be seen the overlapping between the binarized images and the ellipses that best fit each particle.

CH data analysis showed that the sample had a heterogeneous size distribution. Regarding the largest diameter of the ellipse, 77.3% of all particles have a length between 0.096 mm and 1 mm, total particle average is 0.56 mm. The smaller diameter, represented by 91.0% of the total between 0.096 mm and 0.5 mm, total sample average was 0.29 mm.

QC data analysis showed that the sample had a heterogeneous size distribution. Regarding the largest diameter of the ellipse, 79.7% of all particles have a length between 0.1 mm and 0,6 mm, total particle average is 0.35 mm. The smaller diameter, represented by 83.5% of the total between 0.04 mm and 0.24 mm, total sample average was 0.14 mm.

B Fixed bed reactor tests

Figure 2 shows the MB breakthrough curves experimentally obtained for CH and QC. The final saturation time, for a $C/C_0 > 0.8$, is higher than 25 h for both adsorbents, due to the resistance to mass transfer in the particles (McCabe et al., 2007). Breakthrough point are located at $C/C_0 = 0.05$ and t = 2,16 h for CH and t = 2,4 h for QC, observed in the insets of Figure 2. After the breakthrough point, both curves present a steep slope indicating the increase in resistance to mass transfer, so the adsorbent will be practically saturated when this point is reached [20].

An increase in the diameter or area per unit mass of the particle causes a delay in the breaking point and a relaxation or stretching of the rupture curve. The time to reach the saturation point can be quadratically increased, resulting in a much more elongated sigmoid curve [24]. This was observed in the case of CH considering the shape and characteristic length of its particles.

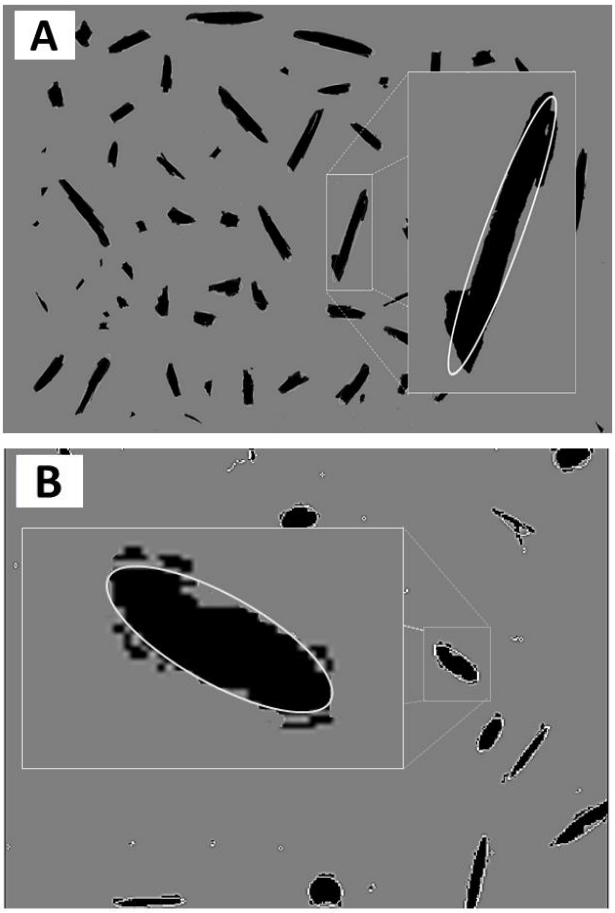

Fig. 1 Digitalized color image with an enlarged portion of the analyzed and ellipses that best fit to area for A) CH and, B) QC.

In order to evaluate the relationship of the column parameters, three adsorption models (Adams–Bohart, Yoon Nelson and Thomas) were applied to the data obtained from the experimental studies.

The Adams-Bohart model permit to estimate the maximum volumetric adsorption capacity (N_0) and the kinetic constant (K_{AB}). The calculated values of N_0, K_{AB}, correlation coefficients (R^2) for the breakthrough curves were presented in Table 2. The Yoon–Nelson model is applied in the current work to predict the breakthrough activities. This model is known to be a simple theoretical model because less column data is needed for the construction of the model values, and it is suitable for the single component system [25]. The values of k_{YN} and t_{50} were presented in Table 2. The Yoon–Nelson predicted that the 50% breakthrough for MB onto CH and onto QC were at 4.7 and 4.3 h, respectively. This values are similar with the obtained from the experimental data, 5.7 and 3.8 h for CH and QC, respectively.

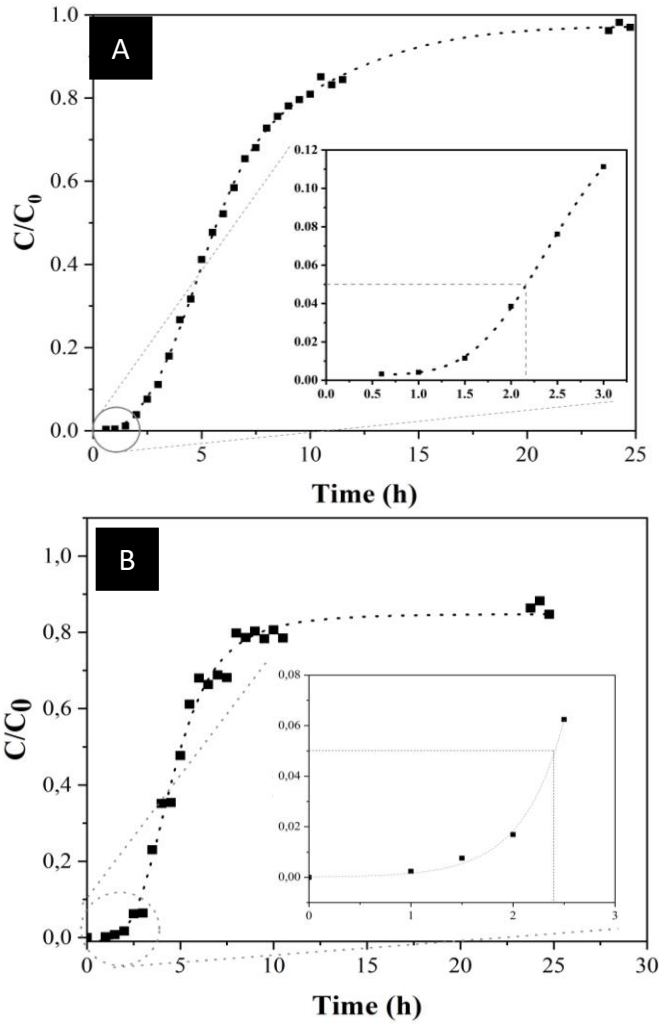

Fig. 2 Breakthrough curve of MB (C0MB = 400mg/L) on: A) CH; B) QC. In the inset rectangle the first fraction of the curve is zoomed.

The Thomas model also evaluate the kinetic coefficient (K_{TH}) and MB adsorption capacity (q_0) from the respective breakthrough curves, the obtained values are presented in Table 2. The q_0 from the model are similar to those obtained experimentally from the equilibrium isotherm by other authors (170 mg MB/g_{CH} and 70 mg MB/g_{QC}) [16, 17].

C Adsorption-desorption cycles study

The values of q_{ads} and q_{des} for the different adsorbent-desorbent systems are summarized in Table 2. Total capacities to adsorb MB are similar from the different systems. After 5 cycles the total amount of MB adsorbed onto CH using NaCl and water as desorbents were similar, while ethanol is used as desorbent a posterior adsorption of 27% lower was found. NaCl had the highest desorption performance in all cycles followed by tap water and ethanol. In the case of QH, the total amount adsorbed were better when using tap water, and de lower one was found using NaCl. On the other hand, NaCl had the highest desorption capacity in all cycles followed by tap water and ethanol. The results suggests that with the increase of cycling times, the adsorption capacities decreased. The same result was presented by Li et al., [26].

TABLE I
THOMAS, ADAMS BOHART AND YOON–NELSON PARAMETERS OBTAINED FROM EXPERIMENTAL BREAKTHROUGH CURVES

	Essay parameters		Model	K_{TH} (mL.mg^{-1}.h^{-1})	K_{AB} (mL.mg^{-1}.h^{-1})	K_{YN} (h^{-1})	$q_{0calc.}$ (mg.g^{-1})	$t_{50calc.}$ (h^{-1})	R^2
CH	C_0 (mg.mL^{-1})	0,43	Thomas	3,2	--	--	161	--	0,96
	F (mL.h^{-1})	80							
	V_{total} (ml)	1980	Adams Bhoart	--	2,9	--	--	--	0,95
	q_e exp. (mg.g^{-1})	244							
	T_{50} (h)	3,8	Yoon Nelson	--	--	1,4	--	4,7	0,96
	W (g)	1							
QC	C_0 (mg.mL^{-1})	0,38	Thomas	4,7	--	--	65,2	--	0,98
	F (mL.h^{-1})	40							
	V_{total} (mL)	990	Adams Bhoart	--	4,3	--	--	--	0,97
	q_e exp. (mg.g^{-1})	123							
	T_{50} (h)	4,5	Yoon Nelson	--	--	1,8	--	4,3	0,98
	W (g)	1							

In the case of NaCl, the first adsorption cycle has the longest breakthrough time. In the following cycles the amount of MB adsorbed decreases progressively, it could be caused by the adsorbate molecules occupying the active sites and making it difficult for new molecules to approach to them [27]. The q_{des} values are lower than those of q_{ads}, in both materials, indicating a strong adsorbate-adsorbent interaction [20]. NaCl solutions are efficient for removing MB in fixed-bed reactor with lignocellulosic materials [28]. The presence of Na^+ cations compete with the MB molecules for the active sites of the materials, producing the removal of MB. Same conclusion was obtained with MB in kaolin [29, 15].

Analyzing ethanol performance, on both CH and QC, in the first three adsorption cycles, a progressive decrease in q_{ads} is observed, the first cycle having the greatest dye uptake, while desorption varies throughout the process. The fluctuations of q_{ads} and q_{des} from the 4th cycle onwards can be explained by the release and formation of MB multilayers on the adsorbent surface [30]. This process would involve the combination of strong interactions between MB molecules and active sites and weak interactions between MB molecules, corresponding to a multilayer adsorption phenomenon. A similar performance was observed with blue BF-5G reagent on carbonized bone [31].

TABLE II
EXPERIMENTAL VALUES OBTAINED FOR Q_{ADS} AND Q_{DES} USING DIFFERENT DESORBENTS IN MG_{MB}/G_{ADS}.

	Cycle	NaCl		Ethanol		Tap Water	
		q_{Ads}	q_{Des}	q_{Ads}	q_{Des}	q_{Ads}	q_{Des}
CH	1	244	122	266	26	296	38
	2	238	117	151	16	147	40
	3	158	96	60	36	238	48
	4	108	78	66	22	80	80
	5	110	58	87	27	97	52
	∑	858	471	630	127	858	257
QC	1	97	22	124	12	123	6
	2	66	25	87	11	67	17
	3	62	18	39	13	111	16
	4	42	16	41	13	29	11
	5	40	18	48	15	44	29
	∑	307	99	339	63	373	79

The results presented in Table 2, for tap water as desorbent, shows irregular q_{abs} and q_{des} values rising and falling in each cycle. This may be because there was no control over the composition of the tap water used as a desorbent, and the concentration of dissolved ions may vary periodically.

IV CONCLUSIONS

The MB adsorption-desorption process in a fixed-bed reactor filled with CH or QC were studied using NaCl, ethanol and tap water as desorbent solutions. NaCl and tap water showed a similar performance in the total amount of MB held by CH. Of the three systems, NaCl is considered to be the best desorbent, since it has greater capacity for removal and recovery of MB onto CH and has a regular performance that makes it predictable. The performance of the adsorption-desorption onto QC was better and predictable using ethanol as regenerated agent.

The Thomas and Yoon-Nelson models described well the breakthrough behaviors, the model parameters obtanined and the experimental data are similar. The kinetic of the process is greater for QC than CH. However, the adsorption capacity of CH was much higher than that of QC for both batch and column systems, implying its great potential for dye wastewater treatment.

In the present work it was also possible to determine the shapes and the characteristic lengths of the CH and QC, by means of images analysis. This knowledge helped to interpret the variations in the experimental breakthrough curves. This work will be useful for the subsequent design and scaling of larger fixed-bed reactors.

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REFERENCES

[1] A. L. Alemán Romero, *Evaluation Of Esterification On Rice Husk As A Strategy To Increase The Removal Capacity Of The Basic Red Dye 46*. Univerdad Nacional de Colombia Sede-Medellín. 2012

[2] A. Moreno, D. Figueroa, A Hormaza, "adsorption of methylene blue on rice hulls" *Prod. + Limpia*, vol. 7, pp. 9–18. 2012

[3] H. D Mansilla, C Lizama, A Gutarra, J Rodríguez, "Treatment of Liquid Waste from the Cellulose and Textile Industry". Evaluation, pp. 285-294. 2008.

[4] Z Aksu, A. I. Tatlı, O Tunç. "A Comparative Adsorption/Biosorption Study Of Acid Blue 161: Effect Of Temperature On Equilibrium And Kinetic Parameters." *Chem. Eng. J.* vol. 142, pp. 23–39. 2008.

[5] A Alemán, A Hormaza, M Álvarez. "Basic Red Removal From A Simulated Textile Effluent: A Case Application Of Rice Husks". *Prod. + Limpia* vol. 6, pp. 66–75. 2011.

[6] V K Garg, R Gupta, A Bala Yadav, R Kumar. "Dye Removal From Aqueous Solution By Adsorption On Treated Sawdust". *Bioresour. Technol*, vol. 89, pp. 121–124. 2003

[7] M Arthy, M P Saravanakumar. "Isotherm Modeling, Kinetic Study And Optimization Of Batch Parameters For Effective Removal Of Acid Blue 45 Using Tannery Waste." *Journal of Molecular Liquids*, vol. 187, pp. 189–200. 2013.

[8] C Cattáneo, *Statistical Report Year 2013*. Dir. bosques Subsecr. Recur. Nat. Minist. la Prod. Prov. del Chaco. 2013.

[9] A S Firpo. "Current Cotton Campaign and Some Considerations about the Future". *Camara Algodon Argentina*, vol. Diciembre, pp. 4–9. 2014

[10] C Valenzuela, O Mari, A Scavo. "Persistences and Transformations of the Traditional Cotton Sector in the Province of Chaco in Argentina." *Revista Universitaria de Geografía*, vol. 20, pp. 117–150. 2011.

[11] A P Lim, A Z Aris, "Continuous Fixed-Bed Column Study And Adsorption Modeling: Removal Of Cadmium (II) And Lead (II) Ions In Aqueous Solution By Dead Calcareous Skeletons". *Biochemical Engineering Journal*, vol. 87, pp. 50–61. 2014.

[12] M Shirzad-Siboni, S J Jafari, O Giahi, I Kim, I., S M Lee, J K Yang,. "Removal Of Acid Blue 113 And Reactive Black 5 Dye From Aqueous Solutions By Activated Red Mud." *Journal of Industrial and Engineering Chemistry*, vol. 20, pp. 1432-1437. 2014

[13] M R Samarghandi, M Hadi, G McKay. "Breakthrough Curve Analysis for Fixed-Bed Adsorption of Azo Dyes Using Novel Pine Cone—Derived Active Carbon." *Adsorption Science & Technology* vol. 32, pp. 791–806. 2015.

[14] G Mckay, J F Porter, G R Prasad. "The Removal of Dye Colours from Aqueous Solutions by Adsorption on Low-cost Materials." *Water, Air, and Soil Pollution* vol. 114, pp. 423–438. 1999.

[15] M T Yagub, T K Sen, S Afroze, H M Ang,. "Dye And Its Removal From Aqueous Solution By Adsorption: A Review." *Advances in Colloid and Interface Science* vol. 209 pp. 172–18. 2014

[16] M D Tenev, A Farías, C Torre, G Fontana, N Caracciolo, S Boeykens, "Cotton Industry Waste as Adsorbent for Methylene Blue. J. Sustain. Dev. Energy", *Journal of Sustainable Development of Energy, Water and Environment Systems*, vol. 7, pp. 667–677. 2019.

[17] M D Tenev, C Torre, G Fontana, V Gauto, M S Cleva, D Sanches Riveros, C Salamone, S Boeykens, "Adsorption-Desorption of Methylene Blue in a Fixed-Bed Reactor Filled with Cotton Industry Waste", *2 Latin American Conference on Sustainable Development of Energy, Water and Environment Systems – LA SDEWES* FIUBA. Buenos Aires. February 2020.

[18] C A Schneider, W S Rasband, K W Eliceiri, “NIH Image to ImageJ: 25 years of image analysis.” *Nature Methods* vol. 9, pp. 671–675. 2012.
[19] M S Cleva, G M Sampallo, A O Gonzales Thomas, C A Acosta, “Método para la determinación del volumen de una muestra de granos de arroz mediante el procesamiento digital de imágenes.” *RIA: Revista Investigaciones Agropecuarias* vol. 39, pp. 185–190. 2013
[20] W McCabe, J Smith, P Harriott, *Operaciones unitarias en ingeniería química*, 7ma ed. McGraw Hill/Interamericana Editores, México DF. 2007.
[21] G S Bohart, E Q Adam, “Some aspects of the behaviour of charcoal with respect to chlorine.” *Journal of the American Chemical Society* vol. 42, pp. 523–544. 1920.
[22] Y H E E Yoon, J H Nelson, “Application of Gas Adsorption Kinetics I . A Theoretical Model for Respirator Cartridge Service Life.” *American Industrial Hygiene Association Journal* vol. 45, pp. 509–516. 1984.
[23] H C Thomas, “Heterogeneous Ion Exchange in a Flowing System.” *Journal of the American Chemical Society*, vol. 66, pp. 1664–1666. 1944
[24] R. E. Treybal, *Operaciones De Transferencia De Masa*. 2a. ed. Mexico: McGraw-Hill Interamericana, 2000.
[25] L Das, P Das, A Bhowal, C Bhattachariee, “Treatment of malachite green dye containing solution using bio-degradable Sodium alginate/NaOH treated activated sugarcane baggsse charcoal beads: Batch, optimization using response surface methodology and continuous fixed bed column study.” *Journal of Environmental Management* vol. 276. Pp. 111272. 2020.
[26] W Li, Q Yue, P Tu, Z Ma, B Gao, J Li, X Xu, “Adsorption characteristics of dyes in columns of activated carbon prepared from paper mill sewage sludge.” *Chemical Engineering Journal*, vol. 178, pp. 197–203. 2011.
[27] C H Giles, T H MacEwan, S N Nakhwa, D Smith, “Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids.” *Journal of the Chemical Society* vol. 846, pp. 3973-3993. 1960.
[28] A A Azzaz, S Jellali, H Akrout, A A Assadi, L Bousselmi, “Dynamic investigations on cationic dye desorption from chemically modified lignocellulosic material using a low-cost eluent: Dye recovery and anodic oxidation efficiencies of the desorbed solutions.” *Journal of Cleaner Production* vol. 201, pp. 28–38. 2018.
[29] B K Nandi, A Goswami, M K Purkait, “Adsorption characteristics of brilliant green dye on kaolin.” *Journal of Hazardous Materials* vol. 161, pp. 387–395. 2009.
[30] F B Scheufele, A N Módenes, C E Borba, C Ribeiro, F R Espinoza-Quiñones, R Bergamasco, N C Pereira, “Monolayer-multilayer adsorption phenomenological model: Kinetics, equilibrium and thermodynamics.” *Chemical Engineering Journal* vol. 284, pp. 1328–1341. 2016.
[31] C H Maeda, C A Araki, A L Moretti, M A S D De Barros, P A Arroyo, Adsorption and desorption cycles of reactive blue BF-5G dye in a bone char fixed-bed column. *Environmental Science and Pollution Research* https://doi.org/10.1007/s11356-018-3644-0. Publish on line 2018