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

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ABSTRACT

The agricultural economy of Chaco province, in Argentina, is based in the cotton production. The environmental impact generated by their solid waste is significant. Textile industry use greater dye, chemical and water in the manufacturing process. Adsorption is considered the most efficient treatment for color removal. The commonly used adsorbent is activated carbon although low-cost alternatives are sought. In this paper, a laboratory scale fix-bed reactor filled with cotton husk as adsorbent material was used to carry out breakthrough curves and testing the adsorption-desorption process of methylene blue. The tests were made at 25°C with an 80 ml/hr flow rate. Desorption capacity of three substances was evaluated: NaCl 0.1 M, ethyl alcohol 50% V/V and tap water. As much as three adsorption-desorption cycles were obtained in all cases. The cotton husk is deeming possible as a low-cost material for dye adsorption. A fix-bed column is an effective type of reactor for the adsorption-desorption process study.

KEYWORDS

Methylene blue, fix-bed reactor, cotton

INTRODUCTION

In Chaco, cotton production is one of the most developed agricultural activities. This province generates 40 to 60% of all cotton harvested in Argentina, therefore its economy is based on this crop [1]. Although the ginning process efficiency has reduced the amount of generated waste, the volume is still significant [2]. Most ginners incinerate waste in open-air furnaces, without any kind of use, causing air pollution. Others dispose the waste on land where, in some cases, it is collected to feed cattle, brickworks, etc. [3].

The industry that most uses dyes, chemicals and water in its manufacturing processes is textile industry. The 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 [4]. High production capacity made prices lower, with novel products and easy 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 [5]. 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 and high biological oxygen demand (BOD_5) [6]. From an environmental point of view, dyes are toxic, carcinogenic and have mutagenic effects. Their use has many harmful effects on humans and affects the eyes, skin and causes respiratory problems and digestive tract irritation [7]. Various methods are available to treat colored effluents, such as coagulation, flocculation, reverse osmosis [8], precipitation, oxidation [9], reduction, membrane filtration, ultrasonic treatments, anaerobic and aerobic treatments, biochemical degradation, adsorption, microbiological decomposition and ozonisation [10]. However, the adsorption method is considered the most efficient for color removing in industrial effluents. The adsorbent usually used to treat them is activated carbon, although its high cost makes it necessary to research alternative adsorbents [11].

For this application, using a fixed bed reactor is practical and economical, operation is continuous, and the process is under control. Industrial application involves fixed-bed adsorption columns in which the sorbate is continuously in contact with a certain amount of fresh sorbent. Fixed-bed column is an effective tool for the sorption - desorption processes [12]. Sorption - 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. Sorbent regeneration can be important to keep costs down and allowing the possibility of dye extracted recovering from the liquid phase [4, 5]. This paper studies the dynamics of this process in a fixed-bed reactor on a laboratory scale, using an agro-industrial residue, cotton husk as an adsorbent material, and methylene blue (MB), a basic dye, as an adsorbate.

MATERIALS AND METHODS

The following describes materials preparation and characterization in the present work, the used reactor description and method data analysis that was carried out.

Adsorbate preparation

MB, 95% purity, Cicarelli brand, without prior treatment, was used to prepare a 400 mg/L solution with deionized water. Concentration was measured by spectrophotometry using a UV/Visible Spectrometer Lambda 25 PerkinElmer at different wavelengths, 430 nm, 500 nm and 663 nm.

Desorbent preparation

MB desorption was tested using three desorbing solutions. Sodium chloride, pro-analysis, Biopack brand, 0.1 M; 50% V/V solution of ethyl alcohol, 96% purity; and tap water.

Adsorbent preparation and characterization

Cotton husk, from now just named "cotton", conditioning and characterization method was described in previous work [15]. Its characteristic dimensions were determined, as described below.

Characteristic cotton dimensions determination. Length and width of cotton particles determination is complex to perform directly. Its dimensions (below than a millimeter) and its softness makes it difficult to obtain by conventional methods. Images of the particles were

used to determinate it. In such images, the projected area of each husk is assimilated to an ellipse which axes, major and minor, match with their length and width [16].

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 cotton particles are not in contact with each other.

Images processing for dimensions measurement were done with free distribution program ImageJ ® version 1.52ª [17]. In this program, the digitalized color image is converted to gray levels and then binarized. 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.

Fixed-bed reactor

Experiments were carried out in an upward-flow fixed-bed reactor. A 16 mm diameter, 200 mm high acrylic cylinder. The solutions were impulse by a peristaltic pump at 80 ml/h. For the tests, 1g of cotton was put inside then the hydraulic test was performed. MB solution was then pumped, taking samples every 30 minutes for 24 hours, until the fixed bed was saturated. Subsequently, the corresponding desorbent solution was changed until the output concentration was low enough. Sampling was carried out in the same way as in the adsorption process. Furthermore, the number of adsorption-desorption cycles for the analysis of the system performance was set at 5.

Breakthrough curve

C/C_0 vs. time (h) was plotted; C is the concentration of MB at the reactor outlet and C_0 at reactor entry, constant and equal to 400 mg/L. Breakthrough curve performance was evaluated by adsorption (q_{ads}, mg_{col}/g_{ads}, Eq. 1) and desorption capacity (q_{des}, mg_{col}/g_{ads}, Eq. 2).

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

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

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

RESULTS AND DISCUSSION

Results obtained from the characterization and adsorption-desorption cycles analysis are presented.

Cotton characteristic dimensions measurement

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

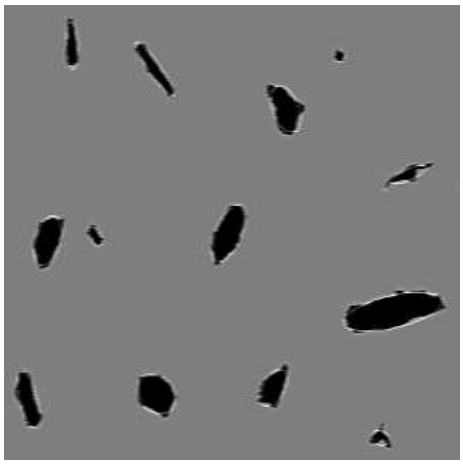


Figure 1. Amplified zone of the particles and ellipses that best fit.

Data analysis showed that the sample had a heterogeneous size distribution. Regarding the largest diameter of the ellipse, 77.31% 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 91.03% of the total between 0.096 mm and 0.5 mm, total sample average is 0.29 mm.

Breakthrough curve

Figure 2 shows the MB breakthrough curve. The final saturation time, for a $C/C_0 > 0.98$, is higher than 25 h, due to the resistance to mass transfer in the cotton particles [18]. Breakthrough point is located at $C/C_0 = 0.05$ and t = 2,16 h as observed in the inset in said Figure. After the breakthrough point, the curve presents a steep slope indicating the increase in resistance to mass transfer, so the cotton will be practically saturated when this point is reached [18].

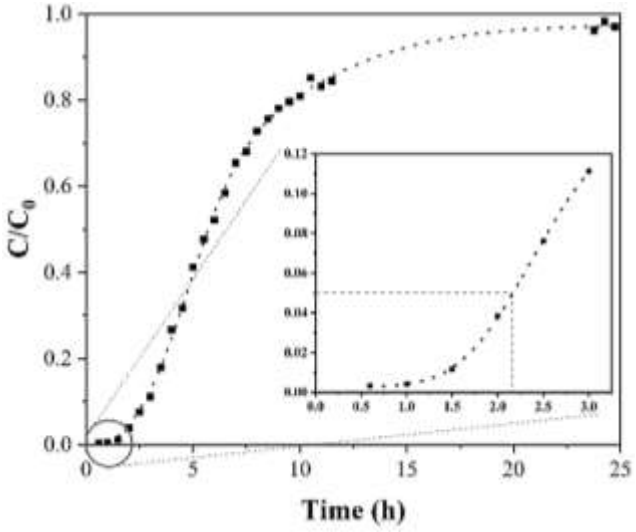
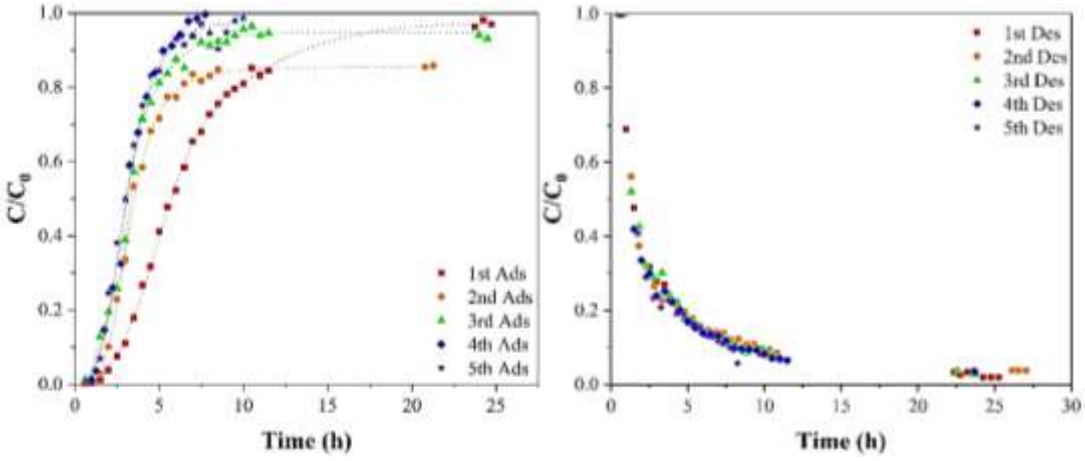


Figure 2. Rupture curve of MB in cotton

Regenerating effect of NaCl. NaCl solutions are efficient for removing MB in fixed-bed columns with lignocellulosic materials [19]. Removal capacity of MB retained in cotton was studied. Figure 3.a and 3.b shows different adsorption and desorption cycles, respectively, which the adsorbent material was subjected.



(a) (b)

Figure 3. Adsorption curves (a) and desorption curves (b) of MB with NaCl solution as desorbent.

The first adsorption curve, Figure 3.a, has the longest breakthrough time. In the following cycles the amount of MB adsorbed decreases progressively, could be that the adsorbate molecules occupy the active cotton sites making it difficult for new molecules to approach the vacant sites [20]. Superposition of the desorption curves, Figure 3.b, indicates that MB desorption process in cotton is similar in the different cycles.

Figure 4 summarizes the adsorbed (q_{ads}) and desorbed (q_{des}) amounts of MB in each cycle with NaCl solution as desorbent. The q_{des} values are lower than those of q_{ads} indicating a strong adsorbate-adsorbent interaction. This performance can be justified by a chemisorption phenomenon [18].

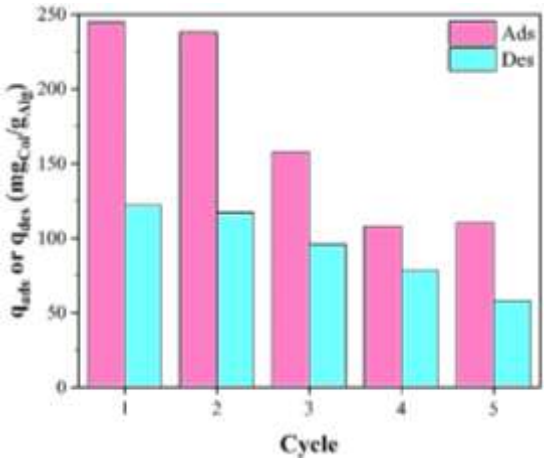
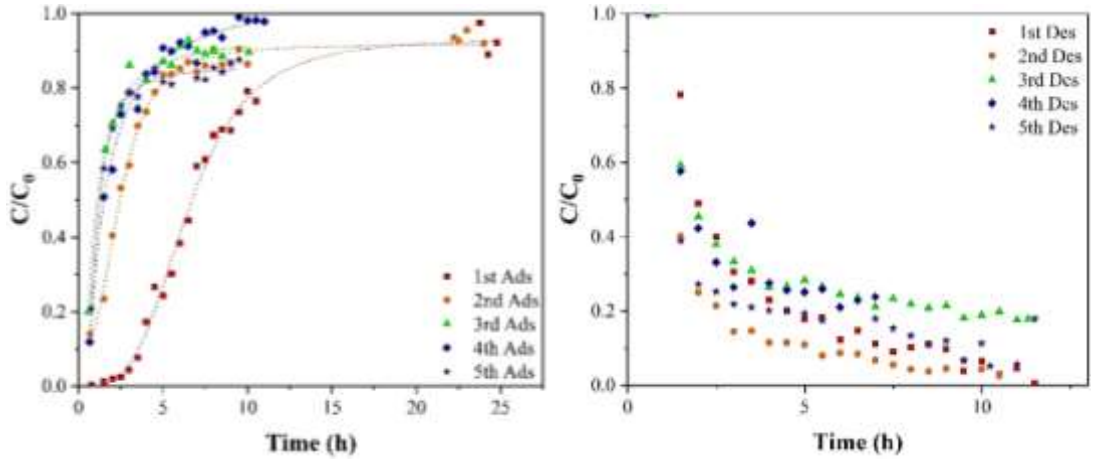


Figure 4. q_{ads} and q_{des} for cycles using NaCl.

As the cycles take place the amount of MB kept by the cotton drops, similarly in desorption. The presence of Na^+ cations compete with the MB molecules for the active sites of the cotton, producing the removal of MB [21]. The same result was obtained with MB in kaolin [22].

Regenerating effect of ethanol. In Figure 5.a, adsorption curves, it is observed that the initial section of the first cycle presents a large mass transfer, while in the later ones, the slopes of the curves are much higher than the first one, which means a high resistance to mass transfer [18]. In the desorption process, Figure 5.b, curves do not perform uniformly as NaCl does.



(a) (b)

Figure 5. Adsorption (a) and desorption (b) curves of MB with ethanol solution as desorbent.

The adsorbed (q_{ads}) and desorbed (q_{des}) amounts of MB in each cycle with ethanol solution as desorbent are summarizes in Figure 6.

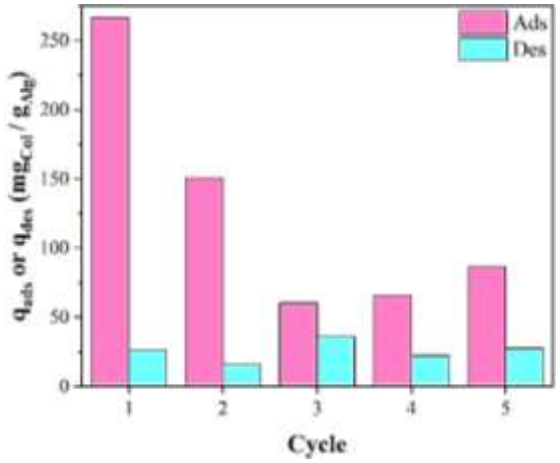
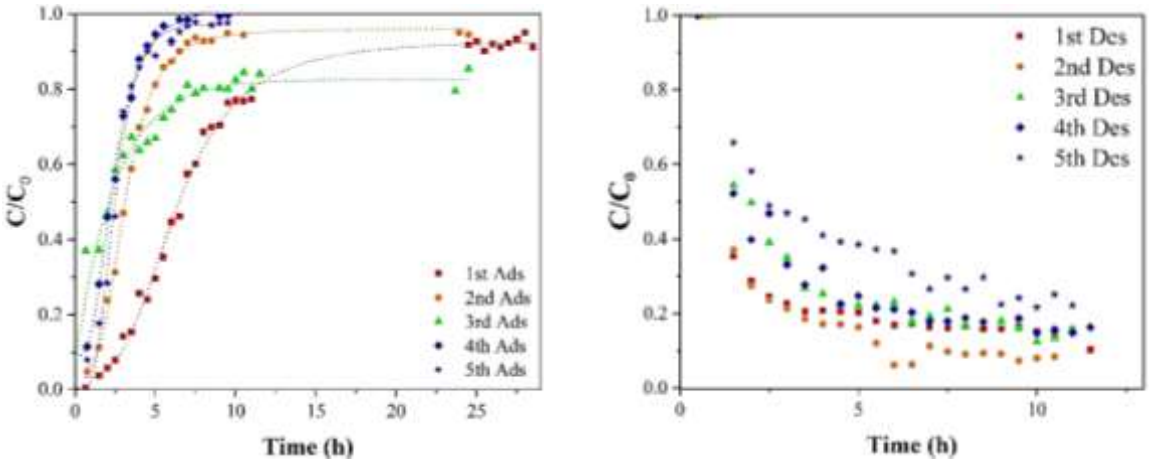


Figure 6. q_{ads} and q_{des} for cycles using ethanol.

In the first three adsorption cycles a progressive decrease in qads is observed, the first cycle having the greatest dye uptake; while desorption varies throughout the process. The fluctuations of qads and qdes, from the 4th cycle onwards, can be explained by the release and formation of MB multilayers on the cotton surface [23]. This process would involve the combination of strong interactions between MB molecules and active cotton sites associated with chemical adsorption; and weak interactions between MB molecules corresponding to a

multi-layer adsorption phenomenon. A similar performance is observed with blue BF-5G reagent on carbonized bone [24].

Water regenerating effect. Figure 7.a shows the adsorption process, being the first stage the one with the longest breakthrough time and q_{ads}. The desorption, Figure 7.b, shows irregular curves with q_{abs} and q_{des} values rising and falling in each cycle. This may be due to the fact that there was no control over the composition of the tap water used as a desorbent, and the concentration of dissolved ions may vary periodically.



(a) (b)

Figure 7. Adsorption curves (a) and desorption (b) of MB with tap water as desorbent.

The amounts of adsorbed and desorbed dyes in each cycle are summarized in Figure 8. Like NaCl (Figure 4) and ethanol (Figure 6), in the first cycle occurs the greatest removal of MB.

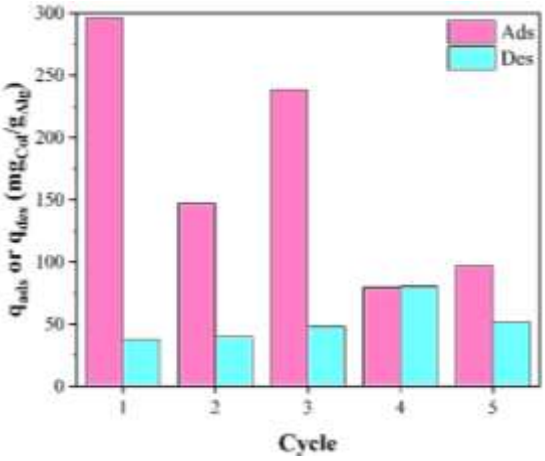


Figure 8. q_{ads} and q_{des} for cycles using tap water.

Comparison between NaCl, ethanol and tap water. Table 1 summarizes all the values of qads and q_{des} for the different adsorbent - desorbent systems. Total capacity to adsorb MB in the different systems presents similar results for Cotton - NaCl (Σq_{ads} = 858.86 mg_{col}/g_{ads}) and Cotton – tap water (Σq_{ads} = 857.97 mg_{col}/g_{ads}), while the MB-Ethanol process (Σq_{ads} = 629.69 mg_{col}/g_{ads}) had presented an adsorption 27% lower than the others. From the desorbents studied, NaCl had the highest desorption capacity in all cycles (Σq_{des} = 471.33 mg_{col}/g_{ads}) followed by tap water (Σq_{des} = 257.36 mg_{col}/g_{ads}) and ethanol (Σq_{des} = 127.1 mg_{col}/g_{ads}).

Table 1. Values of q_{ads} and q_{des} for all desorbents, in mg_{col}/g_{ads}.

	NaCl		Ethanol		Tap water	
Cycle	q_{ads}	q_{des}	q_{ads}	q_{des}	q_{ads}	q_{des}
1	244.53	122.13	266.35	26.20	296.17	37.59
2	238.07	117.09	150.71	15.55	147.00	39.70
3	157.94	95.92	60.37	35.66	238.23	48.05
4	107.92	78.42	65.52	22.37	79.49	80.18
5	110.41	57.77	86.73	27.32	97.08	51.84
Σ	858.86	471.33	629.69	127.11	857.97	257.36

CONCLUSIONS

In the present work it was possible to determine the characteristic lengths of the cotton, by means of images obtained with a scanner and the use of a method developed for such purpose.

The MB adsorption-desorption process in a cotton fixed-bed column was studied using NaCl, ethanol and tap water regenerating solutions. In the global adsorption process, NaCl and tap water show a similar performance in the total amount of MB held by cotton. Of the three systems, NaCl is considered to be the best desorbent, since it has greater capacity for removal and recovery of MB and has a regular performance that makes it predictable.

This work will be useful for the subsequent design and scaling of larger fixed-bed reactors.

NOMENCLATURE

Symbol	Meaning
C_f	Adsorbate final concentration (mg/L)
C	MB concentration in the reactor output (mg/L) at t time
C_{0a}; C_0	MB concentration in the reactor inlet, adsorption process (mg/L)
C_{0d}	First outlet reactor sample MB concentration, desorption process (mg/L)
C_i	Initial adsorbate concentration (mg/L)
m	Adsorbent mass (g)
MB	Methylene blue
Q	Flow of circulating MB solution (mL/h)
t	Time in which the sample is extracted (min)
t_R	Running time

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