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Cotton Industry Waste as Adsorbent for Methylene Blue

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ABSTRACT

Removing dyes used in the textile industry from the water bodies is a relevant task because of the importance of their high toxicity. The cotton industry waste is a big problem in the final disposal. Waste cotton fibrils were studied as adsorbent material to treat the coloured effluents of the textile industry. Washing with boiling water was determined as the most efficient method for cleaning. The material was physical characterized. After that, methylene blue adsorption tests were carried out to review the dry removal process at different pH. The Langmuir isotherm and the pseudo-second kinetic order models best described this adsorption process. The results would indicate that the process involve a chemisorptions.

KEYWORDS

Textile effluent, Dye, Methylene blue, Adsorption, Cotton waste.

INTRODUCTION

Cotton cultivation is one of the most developed agricultural activities in Chaco, Argentina. The economy of this State is mostly based on cotton crop. Chaco produces 40 to 60% of all the harvested cotton in Argentina. Big companies have settled down in this

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region because of the cotton manufacture and its value chain development [1]. Even though the efficiency of the ginning process has reduced the amount of generated waste, the volume is still significant. Most of the ginners incinerate their waste in open hearth furnaces causing air pollution. In other cases, ginners make the disposal on ground where the waste is used to feed cattle or make bricks. Nowadays, there are many hosiery manufacturers producing and selling their own brands in Chaco. However, there is still a huge potential for development the industry. Because of that, the State's role is important for the incentive for its development [2].

Textile industries use dyes, chemicals and water in their manufacturing processes. The degradation resistance of dyes has reached a high level. Currently the life time of the color is comparable with that of the colored clothes [3]. This is due to the development of synthetic dyes from petroleum derivatives. Their characteristics are superior to the natural ones [4].

The presence of dyes in water bodies is aesthetically undesirable and reduces the penetration of solar radiation [5] because of which the photosynthesis and photolysis are drastically affected [6]. The textile industry produces large quantities of colored effluents [7] of great persistence and high biological oxygen demand [8]. From a health point of view, dyes are toxic [9], carcinogenic and have mutagenic effects [10]. Also, they have detrimental effects on humans like afflictions in eyes, skin [11], respiratory system and irritation of the digestive tract [12]. To treat colored effluents there are several methods such as: coagulation, flocculation, reverse osmosis [13], precipitation, oxidation, reduction [14], membrane filtration, ultrasonic treatments, anaerobic and aerobic treatments, biochemical degradation, adsorption, microbiological decomposition and ozonation [15]. However, the adsorption method is considered the most efficient to remove color in industrial effluents [16]. The adsorbent usually used to treat them is activated carbon [17], but its cost is relatively high [18]. For this reason, the research on alternative materials [19], with natural origin and similar properties, easy to acquire and with minimal economic value has been greatly strengthened in recent years [20].

Adsorption with agroindustrial waste has become an adequate method for separation of contaminants in solution [21], allowing efficient retention, as well as the possible recovery and recycling of adsorbent materials, which also indicate environmental benefits [22]. Low cost adsorbents for elimination of dyes such as Methylene Blue (MB) in waste waters from textile, paper, printing and others industries [23], have been studied by several authors [24].

In this research, waste cotton fibrils, a mixture of short fibers, shells and dust, generated by the cotton industry, were tested as adsorbent material to treat the colored effluents of the textile industry. The most efficient method for cleaning the material was determined. Then this material was characterized and MB adsorption tests were carried out to evaluate the process of dye removal at different pH.

Valorizing these solid wastes with difficulty of disposal, and using them in the treatment of effluents of the same industry will contribute to the process of circular economy [25].

MATERIALS AND METHODS

Bags of waste from cotton fibrils were collected. Due its nature as waste material, cotton fibrils are too dirty to be used directly in MB adsorption tests.

Preparation and characterization of the adsorbent

A pretreatment was performed to obtain a homogeneous, clean and dry material suitable for use as an adsorbent, and that in turn, allows reproducible analysis, discarding factors that could alter development of the experiments.

Particle size classification. The material was sorted by size with 2 sieves, the first one with a mesh of 3.35 mm and the second one of 0.85 mm.

Washing technique determination. Different solutions and washing times were evaluated:

- 2N nitric acid (HNO_3). 2g of adsorbent material was placed in contact with 50 mL of 2N HNO_3 for 24 h with continuous agitation at 180 rpm. After that time, the material was filtered with filtering paper, then it was washed with 500 mL of running water at room temperature and finally with 500 mL of distilled water at boiling temperature;
- Water at room temperature. 5g of material was washed with portions of running water until a constant coloration was visually perceived in the water. 7 L of water were used;
- Boiling water. 10 g of material is placed into contact with 1 L of boiling water. This is repeated until no change in color is perceived. This process was repeated dividing this volume in different parts and during different times.

To define the most convenient method, color tests were performed by colorimetric measurements before and after each treatment. For the colorimetric test, 1 g of material was taken and put in contact with 50 mL of distilled water at 60 °C for 10 minutes and then filtered. The color of the filtered liquid was measured in Platinum-Cobalt units with a HACH device [26].

After each experiment the sample was dried in an oven at 60 °C for 24 hours, that is termed in this work as the Cleaned Adsorbent (CA).

Image analysis. Surface analysis of the adsorbent material (CA) was performed with a Field Emission Gun Scanning Electron Microscope (FEG-SEM) (Zeiss NTS-Supra 4). The accelerating voltage for the electronic beam was 3 kV. The samples were placed in a silicon plate.

Zero charge point study. The capacity of the surface and the type of active centers are indicated by a "significant factor" which is the "zero charge point" (zcp), it is defined as the pH at which the surface charge is zero. It is a value that is typically used to quantify the electro-kinetic properties of a surface.

The method used in this work was the addition of salts. Eight flasks with 50 mL of 0.1N potassium nitrate (KNO_3) solution were given to an initial pH between 4 to 11 with 0.1N sodium hydroxide (NaOH) or 0.1N hydrochloric acid (HCl) and 0.1 g of adsorbent material was added. They were placed in an orbital shaker for 20 h. After stabilization, the final pH's were measured (at 25 °C). These tests were carried out in duplicate. The results were plotted as $\Delta pH = pH_f - pH_i$ vs. pH_i. The pH_i corresponding to the zero ordinate is the zero charge point [27].

Total Reflection X-Ray Fluorescence (TXRF) studies. The impurities that could be released by the adsorbent were determined by contacting 100 mL of ultrapure water and 1 g of the adsorbent for 24 hours. After this contact time, a sample of 10 µL of the liquid phase was placed in a reflector sample holder and analyzed with a quantum S2 PICOFOX (BRUKER) spectrophotometer, with excitation by $Mo_{K\alpha}$ radiation, 600 µA current, 50 kV voltage, a frequency of counting of 3,217 counting per second (cps) and a count time of 200 s.

Preparation of the adsorbate

A stock solution of 500 mg/L of MB, a cationic dye, was prepared using distilled water and MB of 95% purity, Cicarrelli©, without previous treatment. From this stock

solution, dilutions were prepared. The different MB concentrations were measured by spectrophotometry, using a UV-Vis Spectrometer Lambda 25 PerkinElmer at different wavelengths (430 nm, 500 nm, and 663 nm) [27].

Adsorption studies

The dosage curves were made as preliminary studies. These experiments were carried out to establish the ratio between the mass of adsorbent and the initial concentration of dye that allows measuring confident variations of % removal (it is no more than an 80% of color removal).

For each test, 100 mg of CA were put in contact with 50 mL of MB solution at different initial concentrations (500, 400, 300, 250, 200, 150 and 50 mg/L) by triplicate. The samples were shaken at 200 rpm, for 24 hours to reach adsorption equilibrium in a Biological Oxygen Demand (BOD) incubator at 25 °C ±0.5 °C. Then, they were decanted and MB final concentration was determined by Vis-spectrophotometry in the supernatant [28]. The percentage of removal is calculated according to eq. (1):

$$\% \text{ removal} = \frac{C_\text{i} - C_\text{f}}{C_\text{i}} \times 100 \quad (1)$$

where C_i is the initial concentration, and C_f the final concentration.

For the equilibrium isotherm studies, batch tests were performed in triplicate, 50 mL of solution at different MB initial concentrations (500, 400, 300, 250, 200, 150 and 50 mg/L) in contact with 100 mg of CA. Samples were shaken for 24 h, at 200 rpm, filtered and a sample of 10 mL of the solution was taken to determine the final MB concentration by Vis-spectrophotometry.

For the kinetic experiments, a 400 mg/L solution was prepared from the MB stock solution. 100 mg of CA was contacted with 50 mL of this solution. It was shaken with an orbital shaker at 200 rpm, and periodically samples were removed (original, duplicate and triplicate), filtered and a sample of 10 mL of the solution was taken to determine the MB final concentration by spectrophotometry.

In order to study pH effects on the adsorption process, the equilibrium and kinetic tests were carried out at pH 4, 7 and 10.

DISCUSSION AND RESULTS

The design of a pre-treatment was required for the preparation, followed by the characterization. Later, the absorption and kinetics parameters were properly studied.

Preparation and characterization of the adsorbent

A study of a suitable and reproducible pre-treatment of the waste of cotton fibril was performed in order to discard factors that could alter its valuable properties as adsorbent. Then, the material obtained was characterized.

Particle size classification. Figure 1 shows the adsorbent material at different sizes.

Figure 1. Original and two different particle size samples of waste cotton fibrils

Only the finest fraction (particle size smaller than 0.85 mm) was selected, since this would allow a greater contact surface and better removal efficiency. In this way, a more homogenous and material free of larger foreign particles was obtained.

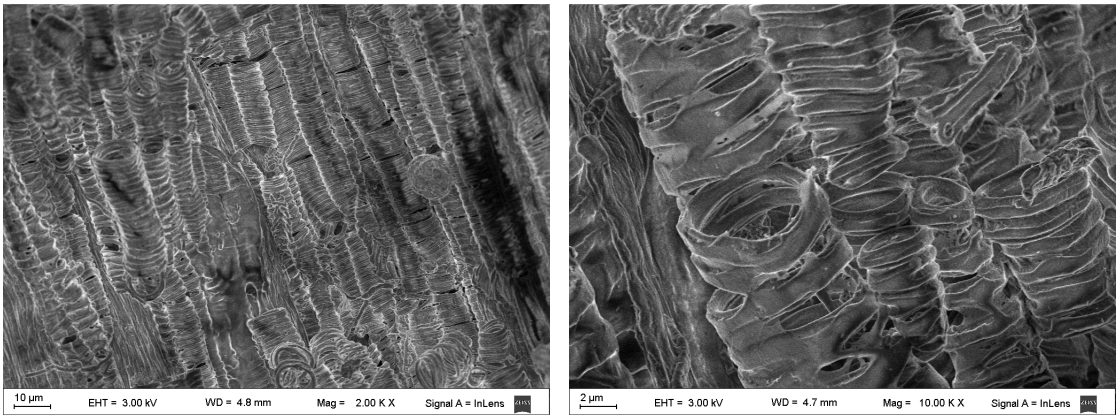
Determination of the washing technique. Table 1 shows the results of the colorimetric analysis of the adsorbent in order to determine the best washing method. In addition, it exhibits the percentage of color removal of each type of washing.

Table 1. Colorimetric analysis of adsorbent

Washing method	Initial color	Final color	% removal
HNO_3 2M	2630	354	86
Ambient temperature water	2630	2000	24
Boiling temperature water	2630	477	82

Although that the highest percentage of removal was obtained with the nitric acid solution (86%), it was decided to work with boiling water (82%) because the difference in removal is not significant. In addition, the use of water instead of a strong acid minimizes the contamination of the effluents. The consumption of water is 0.1 L per g of CA.

Image analysis. Figure 2 shows Scanning Electron Microscopy (SEM) images of CA. The fibrous and rough surface in CA that could be observed may be appropriate for use as an adsorbent material.



(a) (b)

Figure 2. SEM images of CA: magnification 2.00 KX (a) and magnification 10.00 KX (b)

Zero charge point determination. The pH value is used to describe the zcp only for systems where H^+/OH^- are the pH determining ions [22]. With the presence of basic functional groups, the adsorption of cationic dyes is favored at pH higher than the zcp. In terms of pH lower than the zcp, adsorption of anionic dyes is favored because the surface of the adsorbent is positively charged [29].

From the two experimental lines obtained (Figure 3) the zero charge point calculated results equal to 7. For the MB adsorption onto CA, it is expected that basic pH is favorable. These results are coincident with those obtained by Baghdadi *et al.* [30] on modified cotton.

TXRF studies. It was found that CA in contact with pure water released only traces of calcium and potassium chlorides. This is quite appropriate for its use in water treatment since it does not contaminate them with toxic species.

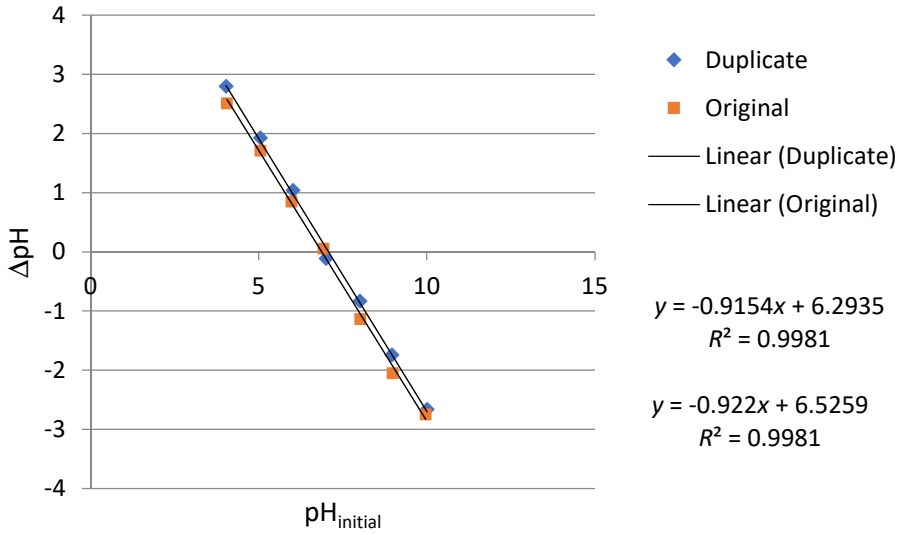


Figure 3. ΔpH vs. pH initial

Adsorption studies

Figure 4 shows the dosage curves obtained. The % removal decreases as the concentration of the MB solution does. It is observed in the figures that the initial MB concentration that reaches 80% removal is 400 mg/L at pH = 4 and 7, and at pH = 10 is 700 mg/L. As predicted by the zcp study, a higher removal of MB at basic pH was observed.

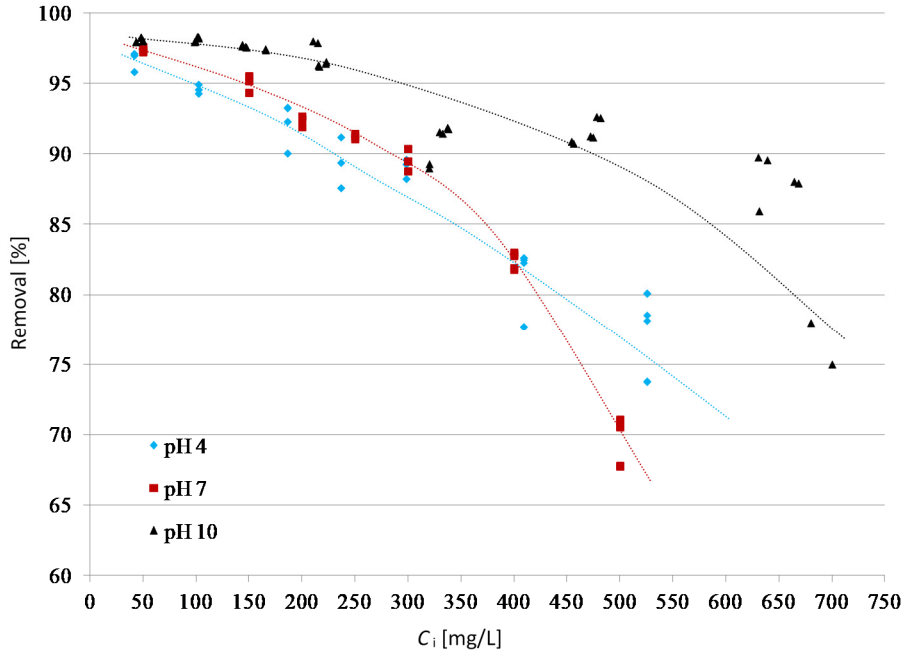


Figure 4. Experimental dosage curves obtained (the lines drawn are just to guide the view)

Adsorption isotherms allow to evaluate the adsorbent capacity and to understand how the process is carried out. Figure 5 shows the experimental equilibrium curves obtained by plotting the retained amount (q_e) [eq. (2)] vs. the equilibrium concentration (C_e) [31]:

$$q_e = \frac{C_i - C_f\ [\frac{mg}{L}]}{\text{adsorbent mass [mg]}}\ \text{Vol [L]} \tag{2}$$

Langmuir [32], Freundlich [33] and BET [34] models were used to evaluate the MB adsorption process. The mathematical expression of the linearized Langmuir isotherm is presented in eq. (3):

$$\frac{C_\mathrm{f}}{q_\mathrm{e}} = \frac{1}{b\,Q_\mathrm{m}} + \frac{C_\mathrm{f}}{Q_\mathrm{m}} \tag{3}$$

The mathematical expression of the linearized Freundlich isotherm is presented in eq. (4):

$$\ln q_\mathrm{e} = \ln k_\mathrm{F} + \frac{1}{n} \ln C_\mathrm{f} \tag{4}$$

The mathematical expression of the linearized Brunauer-Emmett-Teller (BET) isotherm is presented in eq. (5):

$$\frac{C_\mathrm{f}}{q_\mathrm{e}\,(C_\mathrm{i} - C_\mathrm{f})} = \frac{1}{K\,X_\mathrm{m}} + \frac{K-1}{K\,X_\mathrm{m}} \times \frac{C_\mathrm{f}}{C_\mathrm{i}} \tag{5}$$

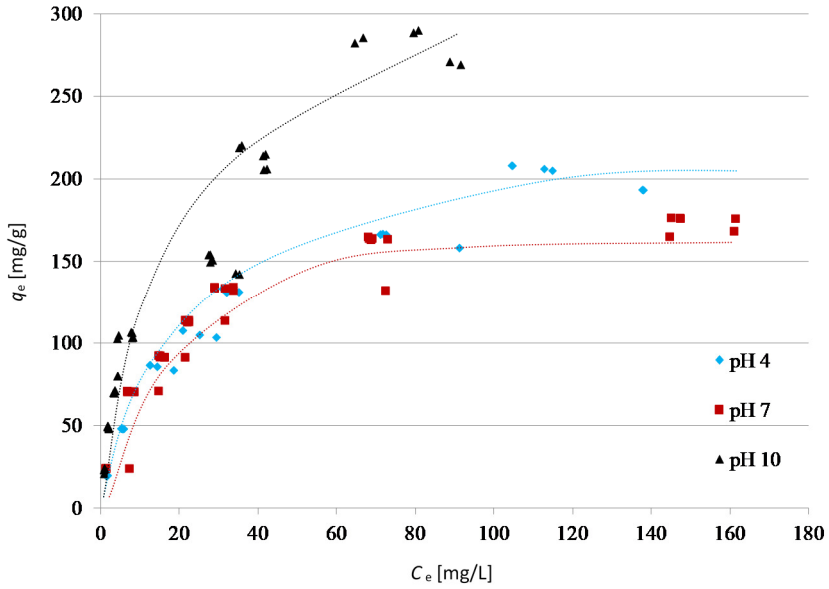


Figure 5. Experimental isotherms obtained from MB adsorption onto A (the lines drawn are just to guide the view)

Table 2 shows the obtained parameters from the different models. The Langmuir model has the better correlation and describes the adsorption of MB on CA, which is indicative of the process that could be associated with chemisorption. This equation is derived by assuming that there is no interaction between the adsorbed molecules and it predicts an adsorptive capacity of a monolayer [35].

For the kinetic studies the pseudo-first order [36] and pseudo-second order [37] models were used. Eq. (6) is the linearized equation for the pseudo-first model and eq. (7) for the pseudo-second one:

$$\ln(q_\mathrm{e} - q_\mathrm{t}) = \ln q_\mathrm{e} - k_1 t \tag{6}$$

$$\frac{t}{q_\mathrm{t}} = \frac{1}{K_2 q_\mathrm{e}^2} + \frac{1}{q_\mathrm{e}} t \tag{7}$$

Table 2. Adsorption parameters from the different models tested

Model	pH	R^2	Q_m X_m [mg MB/g ads.]	b, K_F K	N
Langmuir	4	0.9689	227	0.0445	-
	7	0.9966	189	0.0803	
	10	0.9177	303	0.0710	
Freundlich	4	0.9716	-	19.468	1.959
	7	0.9357		0.0008	0.453
	10	0.9438		32.660	1.994
BET	4	0.0463	435	1.9167	-
	7	0.8157	156	12.800	
	10	0.9689	227	0.0449	

Table 3 shows the results obtained from the fit of kinetic models to the experimental data. The pseudo-second order model best explains the kinetics of MB adsorption on CA, since the correlation coefficient R^2 is close to 1 and the q_e parameter is similar to the experiment. The pseudo-second order model assumes that adsorption capacity is proportional to the number of active centers of the adsorbent surface and the adsorption rate is controlled by chemical adsorption [38].

Table 3. Kinetic parameters at 25 °C

Model	pH	R^2	k_1 or k_2	q_e (experimental) [mg MB/g ads.]	q_e [mg MB/g ads.]	t_e [min]
Pseudo first order	4	0.8992	0.0076	175	155	1,380
	7	0.9735	0.0034	164	57.4	1,140
	10	0.9534	0.0037	282	269	1,320
Pseudo second order	4	1	0.0002	175	185	1,380
	7	1	0.0059	164	164	1,140
	10	0.9837	0.0019	282	313	1,320

CONCLUSIONS

In this work, a process of adsorption of a dye, MB, on residues of cotton fibrils was studied. In this way, it is intended to contribute to the use of a difficult-to-dispose residue and, at the same time, offering to the textile industries the possibility of a low-cost treatment of their effluents.

Washing with boiling water is considered the most appropriate conditioning method for these adsorbents. This technique gives the opportunity of elimination of the natural color from the material and removes the undesirable contaminants. Also, it is one of the procedures that causes less environmental impact.

Considering the zero charge point equal to 7, it can be estimated that the cationic dyes, such as MB, would have a higher adsorption in alkaline medium. This was verified on the results obtained in the adsorption studies at different pH.

The Langmuir model was the best for describing the adsorption of MB onto the waste cotton fibrils. It is an indicator of the phenomenon which could be associated with chemical adsorption.

The pseudo-second order model best explains the kinetics of this process, this model assumes the adsorption capacity is proportional to the number of active centers of the adsorbent surface and the adsorption rate is controlled by chemical adsorption. This is consistent with the results obtained from the adsorption isotherms.

Further studies on filled reactors and the corresponding scale-up will be made. It is also very important to study the possibilities of reusing the adsorbent in several cycles and its final disposal in some useful ways for the planet, taking into account the circular economy principles.

Desorption adsorption cycles should be studied for adsorbent recovery. It is also necessary to study the different existing technologies to dispose the saturated adsorbents, as well as studying their alternative use in the manufacture of new materials for construction, such as cement floors.

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NOMENCLATURE

b	Langmuir parameter related to the energy of adsorption	[L/mg]
C_e	concentration of the solution at equilibrium state	[mg/L]
C_f	concentration of the solution at final times	[mg/L]
C_i	concentration of the solution at initial times	[mg/L]
K	BET parameter related to the molar energy of adsorption	[-]
K_F	Freundlich parameter related to the adsorption capacity	[-]
k_1	velocity constant in the pseudo-first order model	[1/min]
k_2	velocity constant in the pseudo-second order model	[1/min]
n	Freundlich parameter related to the intensity of adsorption	[-]
t	time	[min]
q_e	amount of adsorbed species per unit mass of adsorbent at the equilibrium	[mg/g]
q_t	amount of adsorbed species per unit mass of adsorbent at the time t	[mg/g]
Q_m	Langmuir parameter related to the maximum capacity of the adsorbent	[mg/g]
X_m	BET parameter related to the maximum capacity of the adsorbent	[mg/g]

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