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Removal of an Anionic Dye from Aqueous Solution by A Chemically Treated Vegetable Biomass: Batch and Dynamic Study

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***Abstract*:** *The purpose of this study is to investigate the capacity of a biosorbent (bamboo stalks), treated chemically, to uptake a dyestuff (*cibacron green (RG12)) *from aqueous solution in batch and dynamic modes. A series of batch experiments were performed in order to identify the appropriate adsorption isotherm. Kinetic study showed that the pseudo-second order model represents well the biosorption phenomenon. Both Langmuir and Freundlich equilibrium isotherms were analyzed according to the experiment data and related parameters were estimated. For dynamic study, a fixed bed in column was used. The breakthrough curves were plotted by varying initial concentration of pollutant (RG12) and flow rate of the aqueous solution. The experimental breakthrough curves were modeled by the Thomas model and the Yoon-Nelson model, the results obtained show that the two models fit the experimental data well with correlation coefficients R^2 ranging from 0.97 to 0.98.*

***Keywords*:** *Biosorption, Breakthrough curve, Cibacron green, Thomas model, Yoon-Nelson mode, Fixed-bed column*

1. Introduction

Water is a vital resource that is widely used in industrial processes, particularly in the textile industry. On a daily basis, large volumes of wastewater are discharged into the aquatic environment causing an imbalance in the ecosystem. The development of new water purification technologies is essential for the preservation of this resource. Several purification techniques are currently used such as membrane filtration, ion exchange columns or adsorption columns, but these technologies have certain technical constraints that limit their use for the treatment of large volumes containing various types of contaminants, in particular toxic substances such as dyes. This study focuses on the development of a saline chemically modified plant material for the adsorption of Cibacron green in aqueous solution in batch and fixed bed column mode. The treatment of effluents containing dyestuff is challenged by the choice of the removal process, in this context, adsorption is the most used process to treat water polluted by dyestuffs. The choice of an adequate adsorbent depends on its efficiency and preparation cost, without forgotten the environment aspect that must be considered. The present study was undertaken to develop a plant biomass chemically activated, to eliminate an anionic dye (methylene blue) from aqueous solution. The bibliography reveals that most studies, associated with the use of bamboo as a precursor, have been limited to its transformation into activated carbon [1-3]**.** Furthermore, biosorption is an economical, viable and competitive process compared to other conventional processes and has proven its effectiveness in recent years [4].

2. Materials and Methods

Bamboo stems, used as an adsorbent in this study, were collected from Algiers green space development establishment, which were cut to desired sizes, washed first with hot water, then with distilled water in order to remove all impurities and water-soluble materials, then dried in an oven at 105 ± 2°C for 24 h. The dried mass was crushed and then sieved to obtain a mean particle size of 0.8 mm.

The agent of activation is an electrolytic solution formed by a homogeneous mixture of water and salts dissolved in the form of aqueous species. The washed and dried bamboo stalks were chemically activated using this solution. *Cibacron green (RG12)* was used without purification. Stock solution of RG12 (1.00 g. L^{-1}) was prepared by dissolving an appropriate mass of RG12. The desired concentration of dye was obtained by dilution of the RG12 solution in distilled water.

Adsorption experiments were carried out, firstly in batch mode, and then in dynamic mode. In a double-walled batch reactor was introduced a known amount of biosorbent into 100 ml of RG12 solution. After a known contact time, the colored solution was separated from the adsorbent by centrifugation. The absorbance of the supernatant solution was measured using UV-Visible spectrophotometer. RG12 concentrations were determined from the calibration curve for different concentrations of RG12 solutions.

The yield of RG12 elimination Y_e (%) and the absorption amount of RG12 at equilibrium (q_e) in $mg.g^{-1}$ are calculated using Equations (1 and 2), respectively.

$$Y_e(\%) = \frac{C_0 - C_t}{C_0} .100 \qquad (1)$$

$$q_e = \frac{(C_0 - C_t).V}{m} \qquad (2)$$

Where C_0 is the initial concentration of methylene blue ($mg.L^{-1}$), C_t is the residual concentration of Cibacron green at time t ($mg.L^{-1}$), V is the volume of the solution (L) and m is the mass of absorbent (g). C_e is the concentration of MB adsorbed at equilibrium.

3. Results and Discussion

3.1. Effects of operational parameters on the RG12 elimination

3.1.1. Effect time contact

The equilibrium time of RG12 removal by bamboo stalks was determined, it corresponds to the saturation of the biomass by the dye. Fig.1 shows that the removal of RG12 by adsorption is a relatively fast phenomenon, which can be reached in 60 min. The maximum amount of RG12 adsorbent is 0.39 $mg.g^{-1}$.

According to the Fig.2, the adsorption of RG 12 exhibits two phases, the first one very fast which can be explained by the availability of sorption sites easily accessible to RG12 present in the solution; then, a second one, less fast, where sorption reaches the equilibrium stage therefore, no more sorption sites are available or accessible to RG12 molecules.

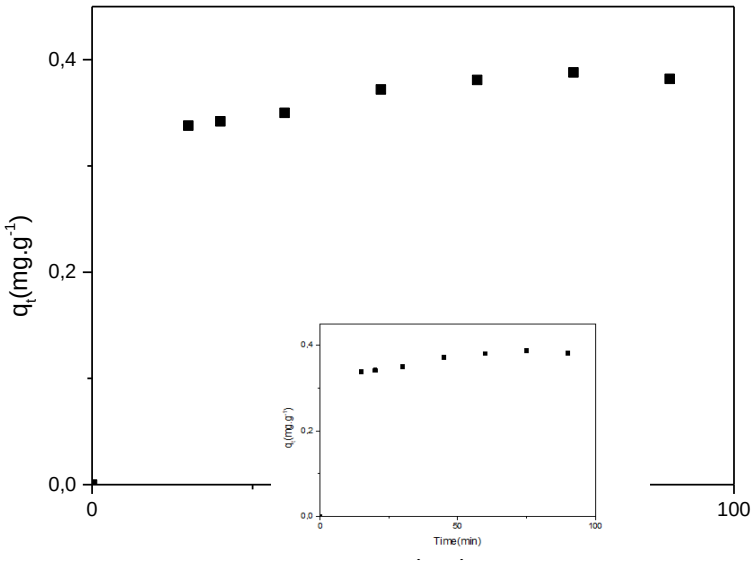


Fig 1**.** Variation of RG12 adsorbed amount versus time
(T = 20 ± 2 °C, pH = 5.93, [RG12] = 50 mg.L^{-1}, m_{ads} = 45 g.L^{-1})

3.1.2. Effect of Initial Solution pH

The ionic character of the dye and the charge on the surface of adsorbent are two very important parameters in the adsorption process. These two properties are strictly linked to the pH value. Thus, it is necessary to investigate the effect of the initial pH of the solution on the adsorption [5].

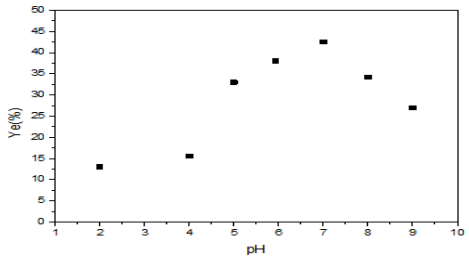


Fig. 3. Effect of the initial pH on the RG12 elimination
(T = 20 ± 2 °C, pH = 5.93, [RG12] = 50 mg.L^{-1}, m_{ads} = 45g.L^{-1})

The effect of RG12 degradation by varying the pH of the solution can be interpreted based on the surface charge of the elaborate adsorbent, and the ionization state of the dye (pKa values). We observe for pH<7 (interval containing the pHzc) a notable increase in the yield of dye reduction (figure.2). A positive charge is developed on the surface of the biomass attracts the negative charges of the sulphonate groups of the dye. This charge becomes neutral then negative, the dye is supposed to be positively charged thanks to the secondary amine functions and imine groups. When pH>7 (deviating from pHzc), the net positive charge of the dye is greatly reduced and becomes negative. It then induces a decrease in biosorption.

3.1.3. Effect of adsorbent dose

In order to determine the optimal dose of adsorbent, amounts between 15.0 and 55.0 g.L^{-1} of adsorbant were used, the RG12 concentration of initial solution was 50 mg. L^{-1}, no pH adjustment has been done. The decrease in the biosorption capacity of adsorbent (Fig.3) can be explained by the fact that increasing of adsorbent dose, used to adsorb approximately the same amount of RG12, leads to a decrease in the equilibrium adsorption capacity of adsorbent (q_e), because on the one hand, (q_e) is inversely proportional to the adsorbent dose, and on the other hand, the relatively high number of free

sites available on the adsorbent to hold the RG12 molecules **[6]**. The curve (q_e) versus of dose shows that when a biomass dose is equal to 45.00 g.L^{-1}, the maximum biosorbent adsorption capacity is reached so, no change in this quantity will be noted, then this value can be considered as optimum. This can be attributed to the agglomeration of biomass particles above this dose causing a decrease in active sites **[7]**.

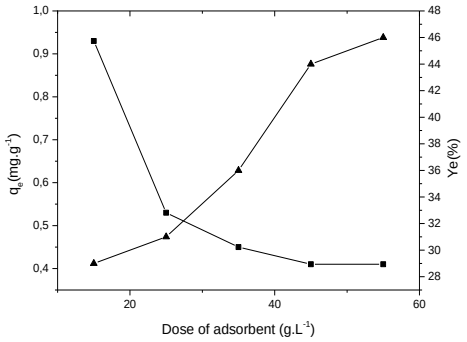


Fig. 3. Effect of adsorbant dose on RG12 adsorption **:** q_e (▲) , Y_e (■)
(T = 20 ± 2°C, pH = 5.93, [RG12] = 50 mg.L^{-1}).

3.1.4. Effect of initial dye concentration

The effect of this parameter on the adsorption capacity of adsorbent was investigated in the range 10-50 mg.L^{-1}. Runs were performed under the following conditions, contact time (= 60 min), dose of adsorbent (= 45 g/L), without pH adjustment, at a temperature of 20 ± 2 °C and at a stirring speed of 400 rpm. Fig.4 shows a dependence between the quantity of dye adsorbed and its initial concentration. In the study range of initial concentration of dyestuff, the adsorbed amount (q_e) varies from 0.10 to 0.47 mg.g-^{1}. The increase of (q_e) with the increase in initial concentration can be explained by the increase in driving force caused by a high concentration gradient for large concentrations of solute in water [8].

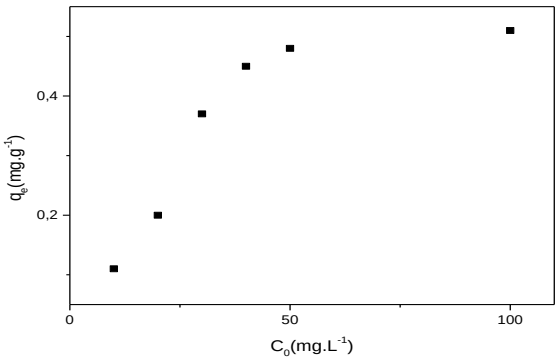


Fig. 4. Effect of the initial concentration of RG12on the adsorption capacity
(T = 20 ± 2 °C, pH = 5.93, m_{ads} =45g.L^{-1}).

3.1.5. Temperature effect

This investigation was performed at 20, 30 and 40 °C. The RG12 concentration and the adsorbent dose used were 50 mg.L^{-1} and 45 g. L^{-1}, respectively. Fig.5 shows that the temperature variation has no impact on the elimination of RG12, whatever the operational temperature, the yield of MB reaches 46% at equilibrium. Thus, in this biosorption process no input of energy for its implementation is required.

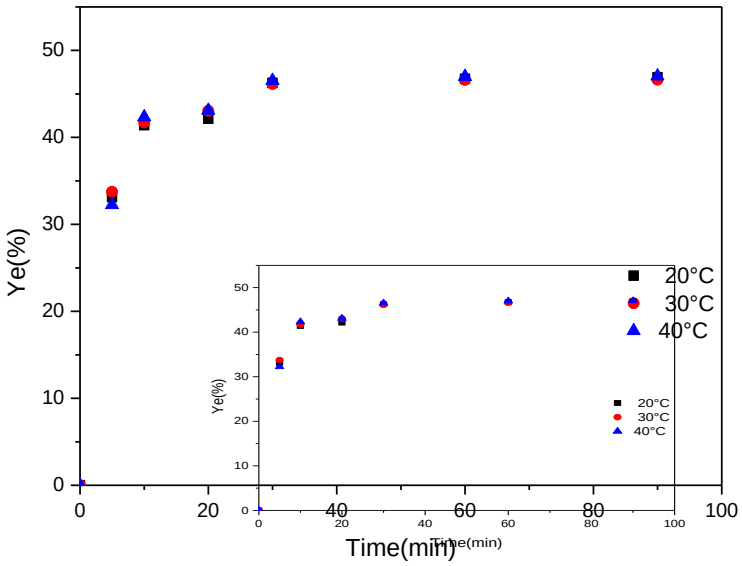


Fig. 5. Effect of temperature variation on yield elimination of RG12
(pH = 5.93, [RG12] = 50mg.L^{-1}, m_{ads} =45g.L^{-1}).

3.2. Nonlinear regression analysis of isotherms models

Adsorption isotherms provide a better understanding of the adsorption mechanism, and give an indication of surface properties, adsorption capacity of adsorbent, adsorbent/adsorbate affinity and adsorption energy. As mentioned above, different mathematical models have been proposed to represent the adsorption equilibrium of MB on the biosorbent, these are the models of Langmuir, Freundlich, Temkin, Sips, Toth and Redich -Peterson. To determine the most adequate parameters values of the models, the non-linear regression method was applied using the Origin Pro8 software. Table 1 gathers the obtained results.

TABLE I**.** Values of isotherm model parameters

Model parameters		Error function			
	Two parameters model	R^2ajust	EABS	χ^2	HYBRID
Langmuir	K_L(L.mg^{-1}) = 0.059 q_m (mg.g^{-1}) = 0.746	0.940	0.797	0.687	13.742
Freundlich	K_F (mg.g^{-1})(L.mg^{-1})$^{1/n}$ = 0.093 1/n = 0.475	0.888	0.383	0.138	2.760
Temkin	A_T(L.mg^{-1}) = 0.192 b_T(kJ.mol^{-1}) = 0.410	0.943	0.241	0.045	0.905
	Three parameters model				
Spis	q_m (mg.g^{-1}) = 0.518 a_S(L.mg^{-1}) = 0.006 1/n = 2.245	0.983	0.122	0.014	0.274
Toth	K_T(L.mg^{-1}) = 7.7 E-14 mt = 9.347 q_m (mg.g^{-1}) = 0.487	0.998	0.031	0.001	0.196
Redich-Peterson	K_{R-P} (L.mg^{-1}) = 4.85 a_{R-P} = 0.026 b_{R-P} = 2.723	0.996	0.110	0.041	0.820

Based on the error functions, the models can be classified as follows: Toth> Sips> Redlich – Peterson >Temkin> Langmuir>Freudlich hence it can be concluded that three parameter models describe better the biosorption of RG12, with regression coefficients >0.98, in parallel for the two-parameter model, it can be seen that the Temkin model satisfactorily adjusts the biosorption of RG12 with a regression coefficient of 0.943.

3.3. Kinetic study

Adsorption kinetic of RG12 on elaborate adsorbent is investigated using the different models. For this purpose, results obtained for different initial concentrations (10–50 mg L^{-1}) at 298 K, are utilized.

The linear form of the pseudo-first order model is used to fit the experimental data (plots not shown). The values of R^2 obtained vary between 0.829-0.922, These findings suggest that the pseudo first order model does not allow a satisfactory description of the adsorption of RG12 on adsorbent. However, the parameters of the pseudo-second order model (k_2, q_e) are determined by plotting the t/q_t versus time (t) (figure 6), the values of the coefficients of determination are between (0.990 and 0.999) and the values of qe_{cal} and qe_{exp} are roughly equal, thus this model describes perfectly this adsorption kinetic.

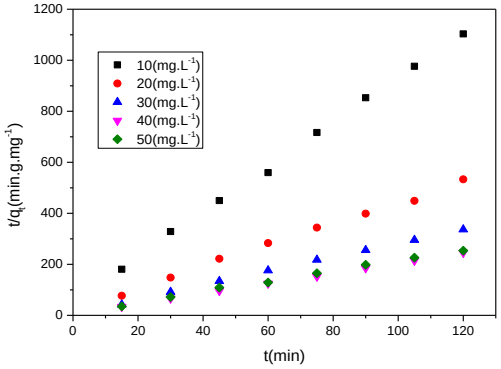


Fig. 6. Plot of the pseudo-second order kinetic model

In order to highlight the importance of the diffusion phenomena, which are not taken into account in the previous kinetic models, the intra-particle diffusion model was applied.

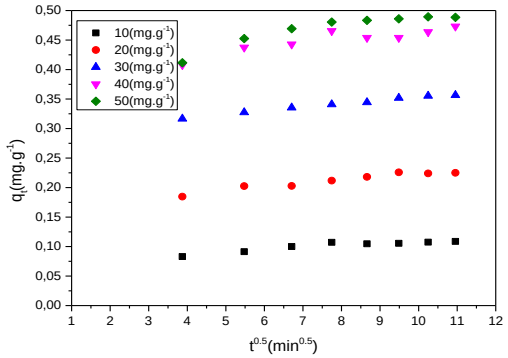
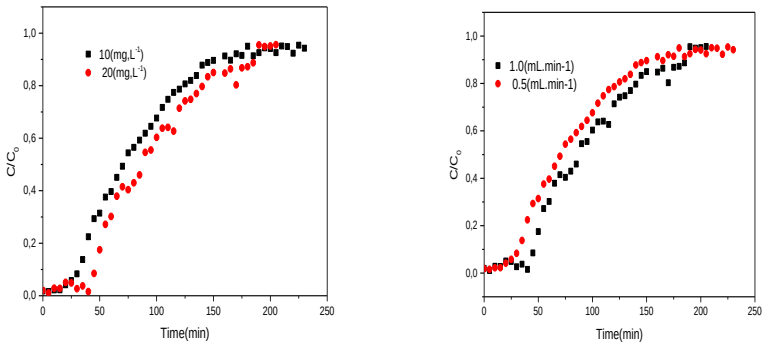


Fig. 7. intra-particle model for adsorption of RG12 on adsorbent

According to the plot of the experimental results (fig.7), two straight line sections can be observed, which means that only two stages involved in the adsorption process, corresponding to the intraparticule diffusion and the equilibrium, furthermore the first sections straight line does not pass through the origin, this finding suggests that the adsorption is not controlled by the step of the intra-particle diffusion [9].

4. Breakthrough Curve Modeling

The experimental data relating to the variation of the initial concentration of RG12, and the feed rate are modeled using the Thomas and Yoon-Nelson models. The experimental data relating to the variation of the initial concentration of RG12 as well as the feed rate are plotted (figure.8).



(a) **(b)**

Fig. 8. Breakthrough curves of : (a) RG12 initial concentration, (b) Flow rate and

The fit goodness of these models is assessed by calculating the adjusted correlation coefficient (R^2_{adj}). The model parameters are determined and given in Table 3.

From the values of R^2_{adj} (>0.970), both models fit very well to the breakthrough curves regardless the parameter studied. Based on the Thomas model assumptions, the adsorption process follows reversible second –order kinetics, which can be governed by the Langmuir isotherm without axial dispersion. Note that the model constant (K_{th}) decreases with increase feed rate.

The modeling of the experimental data by the YOON-Nelson model also makes it possible to obtain a remarkable adjustment of the breakthrough curves, and this whatever the variation of the parameter considered (initial concentration and flow rate).

The Yoon-Nelson constant (K_{YN}) decreases, With increasing initial concentration, on the other hand, it increases with the increase in the feed rate

TABLE II. Parameters of Thomas and Yoon-Nelson models.

Operating parameters	Thomas model parameters			Yoon-Nelson model parameters		
	K_{Th} (mL.min^{-1}.mg^{-1})	q_{Th} (mg.g^{-1})	R^2_{adj}	K_{YN} (min^{-1})	τ (min)	R^2_{adj}
			C_0 (mg/L)			
10.0	**3.328**	**0.051**	**0.982**	**0.0332**	**91**	**0.982**
20.0	**1.111**	**0.192**	**0.974**	**0,0019**	**87**	**0,980**
			Q (ml.min^{-1})			
0.50	**1.111**	**0.192**	**0.974**	**0,0019**	**87**	**0,980**
1.00	**1.671**	**0.088**	**0.980**	**0,0222**	**77**	**0,970**

5. Conclusion

This study demonstrates the ability of the biomaterial developed to eliminate RG12 in batch and in dynamic system. It can be used in the treatment of colored water

Breakthrough modeling results are satisfactory and demonstrate the ability to adsorb azo dye in a dynamic system at low concentrations.

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