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FIXED-BED-COLUMN STUDIES FOR METHYLENE BLUE REMOVAL BY CELLULOSE CELLETS

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Abstract

The *Cellets* product represents a cellulose material, which combines different properties such as the perfect sphericity, fine particle size distribution, low friability and solubility, and inertness. The experiments were carried out with *Cellets 200* granulated celluloses used as a filling material for a laboratory glass column, using diluted dye solution (9-10 mg of dye /L of solution) at adequate initial pH (4.7). The effect of flow rate was investigated, and the modeling of experimental data for dynamic adsorption of Methylene Blue organic dye from aqueous solution in a fixed bed column was studied based on Thomas, and Yoon-Nelson models. The optimal volume of working dye solution per adsorbent mass was determined as higher than 0.01368 m^3/day and the adsorption capacity of *Cellets 200* celluloses in fixed-bed column study for Methylene Blue dye removal was in the range of 1.375-3.303 mg/g. The obtained results confirm that the tested granulated cellulose can be considered as a good adsorbent into dynamic operating systems, which can be used in the treatment of wastewater containing organic dyes.

Key words: cellulosic adsorbent, cationic dye, dynamic adsorption, flow rate effect, Thomas and Yoon-Nelson model

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1. Introduction

Although a wide variety of strategies have been developed for removal of colored species, dyes are an inevitable presence in all areas of everyday life, being still considered as major pollutants in the water resources. They are generally present in the effluents of different industries, highlighting the textile, paper and pharmaceutical industries.

The aesthetic aspect but also the toxic effects (possible carcinogenicity) of dyes and their degradation products (i.e. benzidine), as well as damage to aquatic life by blocking the light penetration and aeration, have determined that their removal be a subject of increasing attention and concern for the environmental specialists (Zaharia and Șuteu, 2012).

Nowadays, a large number and various types of methods for dyes removal, such as chemical oxidation, ion exchange, electrochemical reduction, ozonation, reverse osmosis, membrane technologies, adsorption, photocatalytic degradation have certain efficiency (but their initial and operational costs are too high) (Gupta et al., 2015; Madi et al., 2019; Muthusaravananet al., 2019; Sivarajasekar et al., 2017; Subashini et al., 2020; Zaharia and Șuteu, 2012). It is worth noting that there is a continuous diversification of these simple but especially combined treatment methods, which ensure an increased efficiency of the wastewater cleaning treatments with adequate cost-efficient investments.

One method of interest in the industrial practice is *adsorption*, but using innovative materials as adsorbents, along with improved and/or optimized

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operating techniques (Adeyemo et al., 2017; Anastopoulos et al., 2018; Chiucholi et al., 2014; Dawood and Sen, 2014; Kharat, 2015; Nacu et al., 2019; Panic et al., 2013; Salahshoor and Shahbazi, 2014; Seow and Lim, 2016; Tomczak and Tosik, 2017; Vital et al., 2016).

Being a renewable resource, cellulose still remains a serious candidate for obtaining various biomaterials, such as numerous materials for water and/or wastewater depollution due to their good adsorptive properties, availability and easiness of use in different forms as granules, fibers, filters etc. (Wang, 2019). Among its advantages are noticed: the possibility of processing in different forms, the large specific surface, the ease of physical and chemical functionalization and regeneration, the tolerance to biological structures, and the relative fast adsorption (Lazzari et al., 2019). One of such material is the *Cellets* product, which combines different properties, for instance the perfect sphericity, the narrow particle size distribution, the low friability, the low solubility and inertness (Șuteu et al., 2019). The satisfactory results obtained with this cellulosic material, as an adsorbent for retaining dyes (Methylene Blue) in terms of static retrieval (Șuteu et al., 2015) and its regeneration (Mazouz et al., 2016; Șuteu et al., 2019), have led us to expand our works to the dynamic adsorption studies for establishing the optimal operating parameters as one of the finishing cleaning step in the study of real systems, *i.e.* wastewaters with variable contents of dyes, associated with its adequate modeling and specific corresponding design.

The study of adsorption into dynamic regime has permitted the establishing of a few correlations between the adsorbent properties, the characteristics of pollutant (Methylene Blue cationic dye), and the profile of flowing regime through the fixed bed of adsorbent, information which will permit to identify the optimal operating conditions for the implementation of such system at the industrial scale setup.

The paper presents our results on the adsorption study into a fixed-bed column for the removal of Methylene Blue (MB) cationic dye from aqueous solutions (low concentration of cationic dye, < 10 mg of dye/L of solution). The experiments were carried out using granulated *Cellets 200* celluloses. The adsorption modeling of experimental data in dynamic regime was based on Thomas and Yoon-Nelson models. For complete description of dye-cellulose adsorption system behavior and performance, all findings in this fixed bed column study were compared with our results performed in the batch adsorption studies which were carried out for description of mechanism, especially from the equilibrium isotherms and estimated adsorption capacity of *Cellets 200* cellulose for MB cationic dye. The information from only batch adsorption studies was not enough to design an effluent treatment system in continuous operating regime.

The obtained results reconfirmed that the studied celluloses can be considered as a good candidate as adsorbent in static but also dynamic operating system in order to be applied in the treatment of effluents containing organic dyes.

2. Material and methods

2.1. Materials

Adsorbent. The Cellets 200 cellulose is used in this experimental work, being purchased from Synthafarm Company from Germany, and some of its main physical-chemical characteristics are shown in Table 1 (Șuteu et al., 2015).

Dye. It was selected *Methylene Blue* dye (Basic Blue 9; C.I. 52015 – MB, chemical formula: $C_{16}H_{18}ClN_3S$), used as commercial salts. This is a cationic phenothiazine dye, with molecular weight of 319.85 g/mol and maximum wavelength (λ_{max}) at 660 nm considered as the most commonly used reference material for dyeing cotton, wool and silk. The dye stock solution was of about 468 mg of dye /L of solution concentration, and the working solutions were prepared by appropriate dilution, such as to be ranged in the concentration domain of 9-10 mg of dye/L of solution.

2.2. Analytical methods for physicochemical and quantitative characterization of dye removal

The residual dye concentration in the aqueous samples periodically collected was determined spectrophotometrically by measuring the absorbance at the maximum dye wavelength of 660 nm (MB dye) with a JK-VS-721N VIS spectrophotometer, using a calibration curve method (range of working concentrations selected in the Lambert-Beer region). The solution pH value was measured directly on a Hanna high precision KL-009(I) pH-meter, the pH adjustment being performed specifically with 0.1N NaOH or 0.1N HCl solution. Usually, the initial pH of the dye solution is a key factor in all reported adsorption studies, but if the adequate pH was found for the system of adsorbent (*Cellets 200*) - adsorbate (MB dye), all experiments can be focused on other different operating factors, or designing parameters and norms at the known pH value for dye adsorption. For this adsorption study in dynamic regime, it was selected the corresponding pH from the batch adsorption study for this system, meaning pH of 4.7 which permitted to estimate an adsorption capacity of 81.968 mg of MB dye/g of *Cellets 200* adsorbent (Suteu et al., 2019). The adsorption capacities of this cellulosic adsorbent (q_e) were evaluated by means of the amount of adsorbeddye (Eq 1):

$$q_e = \frac{C_0 - C_e}{G} \cdot V \quad (1)$$

where: C_0 and C_e are the initial and equilibrium concentration of dye in solution (mg of dye/L of solution); G is the amount of cellulose (g), and V is the volume of treated solution (L).

The *Cellets 200* cellulose behavior in the MB dye adsorption (dynamic regime) was analyzed considering the shape of its breakthrough curve for each selected flowrate which represents the plotting of dye concentration in effluent (C_t), or normalized dye concentration in effluent (C_t/C_0) as a function dependent of time (t), or treated volume (V). These breakthrough curves are significant in evaluation of operation performance and dynamic response of a fixed bed in an adsorption column (Tofan et al., 2013). Usually, when C_t approaches 90% of its initial concentration (C_0), the adsorbent is closed to its exhausted form, and can be considered as essentially exhausted (C_{exh}) (Mazouz et al., 2016). The breakthrough concentration (C_b) is chosen arbitrarily beginning with a low value (e.g., the C_t value when approaches 10% of its initial concentration, or a legislative norm for the dye concentration in water resource, i.e. the maximum admissible concentration of MB dye in treated effluent (M.A.C.=1 mg of dye/L of effluent), or other imposed value). The total adsorption time (t_{ads}) is considered as the adsorption time after which the adsorbent is exhausted ($C_t=C_0$), meaning that the analyzed samples has the dye concentration value equal or a little bit (no more than 10%) higher than the initial dye concentration.

2.3. Characterization of adsorbent

FT-IR analysis: Infrared spectra were recorded on a Fourier transform infrared spectroscopy (FTIR) Bruker Vertex 70 Spectrophotometer (Bruker, Ettlingen, Germany) in the transmission mode, using KBr pellets, and the spectra were acquired by accumulation of 32 scans with a resolution of 2 cm^{-1}, recorded in the range of 400–4000 cm^{-1}.

Polarized Light Microscopy (PLM): PLM observations were carried out with an Olympus BH-2 polarized light microscope (Olympus, Hamburg, Germany), under crossed polarizers with a Linkam THMS 600/HSF9I heating stage and a TMS91 control unit (Desy, Hamburg, Germany). The sample was prepared by pressing around 1 mg of adsorbent between two lamellae.

2.4. Dynamic adsorption procedure

Dynamic adsorption working methodology. Dynamic adsorption studies were performed in a glass column of 1.5 cm in inner diameter and 21 cm in length. The column was filled with a known varying amounts of *Cellets 200* cellulose (4 - 8 g) providing a packed bed height of adsorbent between 3 - 7 cm. A dye solution of known concentration (commonly 9.04 mg of dye/L of solution) was introduced on the top of the column by means of a feeding funnel to ensure uniform continuous flow. The passing of the dye solution through the column was done freely, gravitationally, and the effluent was collected from the bottom for further analyzing and control. At specified time intervals (5, or 10 min depending on the selected flowrate), samples of 5 mL of effluent were taken from outlet (the bottom of the column) at different time intervals and analyzed with the UV-VIS Digital Spectrophotometer, model S 104D /WPA, especially for the residual dye concentration in the treated effluent.

In order to evaluate the proposed adsorption model, all experiments had to be performed considering the following operating parameters: (1) the feed temperature and pH were stabilized at 25°C and 4.7 (normal pH of aqueous dye solution), based on the best results performed in the batch adsorption study (Șuteu et al., 2019); (2) three different flowrates (F_{vi}, i=1…3) of dye-containing solutions with the same dye concentration were passed through the fixed adsorbent bed in the column: 5.5, 9.5 and 13.0 mL/min, corresponding to the mass of celluloses (m) equal to 7.63, 4.06 and 5.14 g, respectively. All experiments were stopped when saturation was achieved and further control (at least three samplings after the saturation point establishment, meaning the point where the final dye concentration had equal or higher value than the initial dye concentration in the collected treated samples).

Adsorption designing in the fixed bed column. Some operating parameters necessary to design the fixed bed column adsorption were determined, i.e. (i) the mean flowrate per adsorbent mass (b_i) for establishment of the optimal volume of treated dye solution (V_{opt}); (ii) the adsorption time (t_{ri}) till attaining of a maximum admissible dye concentration in the treated effluent, and also (iii) the sizes of a proposed adsorption tank, or reactor (H_{ads}, D_R, H_R), working with granulated *Cellets 200* celluloses. Thus, the optimal volume of treated dye solution per adsorbent mass (V_{opt}) was determined experimentally by using a number (i) of identical columns with fixed bed of adsorbent inside, working at different flowrates (F_v= 5.5, 9.5 or 13.0 mL/min). In each column, it was stabilized the mean flowrate of dye-containing solution per adsorbent mass (b_i, mL/g.min) as follows (Eq. 2):

$$b_i = \frac{V_n + n_i \cdot v}{m \cdot t_{ni}} \qquad (2)$$

where, $V_n$is the volume of dye solution passed through the fixed adsorbent bed, collected at the bottom of the column (mL); n_i- the number of samples periodically analyzed for the dye content; v - the volume of each analyzed sample (v=5 mL); m - the mass of adsorbent (g) and $t_{ni}$is the total adsorption time till attaining the maximum residual dye concentration in the treated effluent (min).

Moreover, it was determined for each treatment experiment, the adsorption time (t_{ri}) after which the solution passing through each fixed bed in the column attained the maximum admissible limit (M.A.C.) of dye concentration (1 mg of dye/L of solution). Accordingly, there were obtained three values for t_{r1}, t_{r2} and t_{r3} for each tested flowrate (F_{v1}, F_{v2} and F_{v3}).

After that, it was calculated the volume of solution treated per adsorbent mass till attaining of the maximum admissible concentration of dye in the treated effluent (V_i, mL/g) (Eq. 3) as:

$$V_i = b_i \cdot t_{ri} \quad (3)$$

There were calculated three values (V_1, V_2 and V_3) which were interpreted considering the graphical representation, $V_i = f(b_i)$, in order to determine the optimal volume of dye solution (V_{opt}) passed through the fixed bed of adsorbent in the column till the maximum admissible concentration of MB dye in the treated effluent (dynamic regime) attained. The V_{opt} value corresponds to the inflexion point of the above mentioned graphical representation. Further, the main sizes of an adsorption tank or column reactor are calculated based on adsorbent mass (M_{ads}) and corresponding adsorbent volume in the fixed bed column (V_{ads}), bulk density of adsorbent (ρ_{ads}), estimated flowrate (F_{Vi}), estimated adsorption time (t_{ni}), uniformity distribution coefficient (β) of adsorbent in the fixed bed (β=1-3), and free space above the fixed bed of adsorbent (λ corresponds to (0.3–1)·V_{ads}, or (1-3)·H_{ads}), mainly considering the correlations presented in Table 2 (Musteret et al., 2014).

2.5. Modeling of adsorption experimental data into dynamic regime

For determination of the characteristic adsorption parameters in the dynamic adsorption system, a few well-organized experimental data must be processed using a few of the most known models from the scientific literature, i.e. Thomas and Yoon-Nelson models. These selected models are briefly described in table 3 (Bulgariu and Bulgariu, 2013; Gopal et al., 2016; Smaranda et al., 2017; Tofan et al., 2015), and applied specifically for the investigated adsorption system retaining the MB dye onto the fixed bed of adsorbent in continuous dynamic regime. The specific parameters are determined from the slope and intercepts of the graphical representation of the linearized form of these two kinetic models, considering the specific theoretical assumptions for each one.

Table 1. The main characteristics of microcrystalline *Cellets 200* cellulose spheres

Physical-chemical characteristic	***Value***
Particle size distribution (μm) (size fraction %)	200 – 355 (≥ 85 %)
Loss on drying (%)	≤ 7.0
Bulk density (g/cm^3)	0.80 ± 0.05
Sphericity degree (average)	0.90 ± 0.05
Degree of polymerization	≤ 350
pH value	5.0 – 7.0
Conductivity (μS /cm)	≤ 75

Table 2. Correlations for the experimental design of an adsorption tank (column reactor)

Adsorbent mass (kg)	***Adsorbent volume, (m^3)***	***Internal diameter of adsorption tank, (m)***	***Height of fixed bed, (m)***	***Height of adsorption tank, (m)***
$M_{ads} = \frac{F_{vi} \cdot t_{ni}}{V_{opt}}$	$V_{ads} = \frac{M_{ads}}{\rho_{ads}}$	$D_R = \sqrt[3]{\frac{4 \cdot M_{ads}}{\beta \cdot \pi \cdot \rho_{ads}}}$	$H_{ads} = \beta \cdot D$	$H_R = \lambda \cdot H_{ads}$

Table 3. Adsorption models in dynamic regime applied for fixed-bed column reactor

Model	***Characteristic model, linearized form***	***Observations***
Thomas	$\ln(\frac{C_0}{C_t} - 1) = \frac{k_T \cdot q_{0(T)} \cdot m}{F_V} - \frac{K_T \cdot C_0}{F_V} \cdot V_t$ (4) where: C_0 and C_t - the dye concentration at initial moment (t=0) and time t (mg/L); k_T - the Thomas constant (L/min mg); F_V - the volumetric flowrate (L/min); $q_{0(T)}$ - the maximum adsorptive capacity (mg/g), m – the weighted adsorbent mass (g) and V_t - the treated volume at time t (L). The linear model corresponds to the graphical representation of $ln(C_0/C_t-1)$ versus V_t.	The model does not rely on the internal and external mass transfer resistance and omits the axial dispersion phenomenon (Tomczak and Tosik, 2017).
Yoon-Nelson	$ln(\frac{C_t}{C_0 - C_t}) = k_{YN} \cdot t - t_{1/2} \cdot k_{YN}$ ..... (5) where, k_{YN} - the Yoon-Nelson rate constant (min^{-1}); $t_{1/2}$ - the time required for 50% dye breakthrough; t - the adsorption time (min). The linear model corresponds to the graphical representation of $ln [C_t/(C_0-C_t)]$ versus t.	The model stated on the assumption that the decrease of adsorption rate for each adsorbate molecule is proportional with probability of adsorbate breakthrough onto adsorbent bed (Chowdhury et al., 2013).

The most general and widely used adsorption model in fixed bed column studies is considered to be the Thomas model which is based on the assumption of Langmuir kinetics of adsorption-desorption without axial dispersion, and the hypothesis of rate driving force corresponding to second-order reversible reaction kinetics (Tofan et al, 2013).

A less complicated model is proposed by the Yoon-Nelson model based on the assumption that the dye amount adsorbed in a fixed bed is half of the total initial dye amount entering the fixed bed within $t_{1/2}$ period (Gupta et al., 2000).To compare the models with experimental data, it was used the linear regression method, where the linear regression coefficients (R^2) must be as closed as possible to unity for best accordance of calculated model values with the experimental ones.

3. Results and discussions

3.1. Characterization of the Cellets cellulose

Characterization of the Cellets 200 before and after adsorption. For completing the already known physicochemical characteristics of *Cellets 200* cellulose adsorbent, before and after adsorption (Șuteu et al., 2019), it was used the new data resulted from IR spectrometry (FT-IR) and Polarized Light Microscopy (PLM) of the *Cellets* 200. Fig. 1a shows the FTIR spectra of *Cellets* samples before and after adsorption of MB dye. The spectra of *Cellets* and *Cellets* with MB dyeshows similar chemical composition, with representative peaks located at around 4000 – 2995 cm^{-1} (hydrogen-bonded OH stretching), 2891 cm^{-1} (CH stretching mode). The other two typical peaks for cellulose are present at 1430 cm^{-1} (“crystalline” adsorption band) and 900 cm^{-1} (“amorphous” adsorption band). The band from 1645 cm^{-1} is attributed to the OH bending of absorbed water, since the region between 1200 - 1000 cm^{-1} summarizes the totality of the C-O-C symmetric stretching, OH plane deformation, C-O-C asymmetrical stretching, and as well as the C-C, C-OH, C-H ring and side group vibrations.

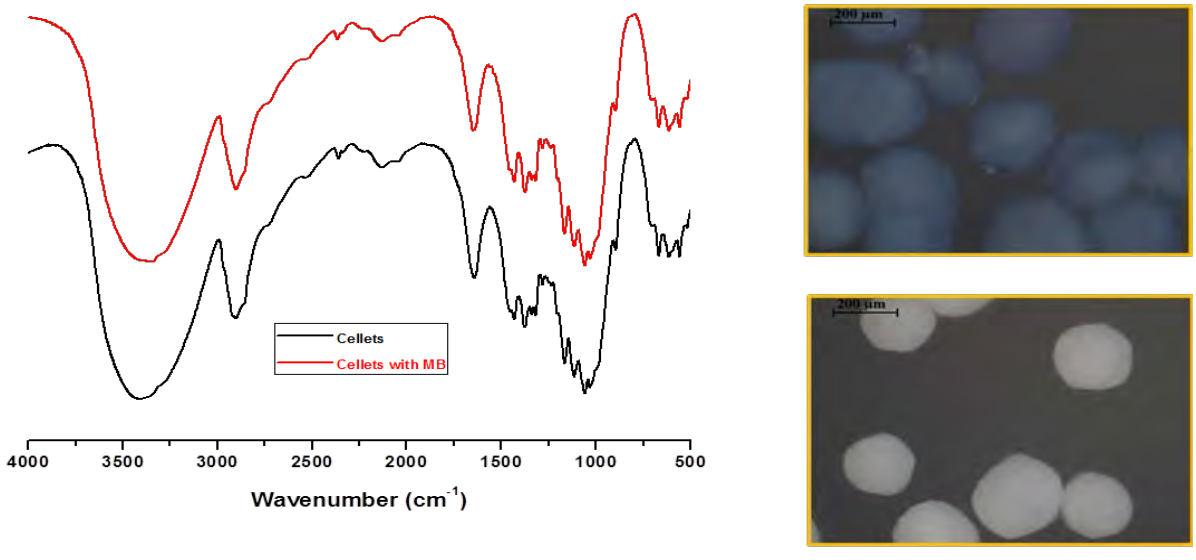
The PLM of the *Cellets 200* samples are presented in Fig. 1b. Cellulose samples have a uniform aspect, after adsorption the sample reveals also a homogeneous aspect, which are explained by a good incorporation of MB dye into the cellulose matrix.

3.2. Fixed bed column adsorption study in dynamic regime

3.2.1. Breakthrough curves

The breakthrough curve for retaining of MB dye onto a column filled with granulated*Cellets200* adsorptive cellulose, represented in coordinates: dye concentration at t time (C_t, mg of dye/L of solution) versus profile of adsorption time (t, min), is illustrated in Fig. 2. Its shape offers preliminary information on the nature of the studied adsorption process and the loading behavior of the dye in the continuous column. Also, there are calculated a series of characteristic parameters of adsorption models presented in Table 4, from the slope and intercepts of the breakthrough curves.

From Fig. 2, it can be observed that the breakthrough curves had a shape assimilated to “S” type, being the result of some competitive interactions between the adsorbed dye molecules, in which the significant role is possessed by the mass transfer processes (Chowdhury et al., 2013; Tofan et al., 2013).



(a) **(b)**

Fig. 1. FTIR spectra (a)and PLM microphotographs(b) of *Cellets 200* before and after adsorption

In case of "S" type breakthrough curve, these interactions usually cause the stabilization for adsorbate species onto the fixed adsorbent bed and thus is produced a surface affinity for adsorbate species such as the surface excess withadsorbate species increases. Moreover, at low initial dye concentration, the breakthrough curve is commonly dispersed. This finding was noting in the same line of conclusions resulted from the adsorption study in static regime (Şuteu et al., 2019). Also, it is shown that the increase of flowrate (F_V) leads to the decrease of breakthrough time (t_b), fact that induces the idea that the cellulose saturation achieves much faster. This fact is confirmed also by the value of breakthrough time (t_b) (Table 4) that is reduced with the increase of working solution flowrate, and also the volume of treated solution till breakthrough point (V_b) that is decreased from 786 mL (F_v= 5.5 mL/min) to 299 mL (F_v=13 mL/min). A similar behavior is registered for the saturation time (t_s)and the saturation volume (V_S), i.e. the saturation time (t_s) reduced from 143 min (F_v=5.5 mL/min) to 111 min (F_v= 13 mL/min), as well as the breakthrough volume (V_b) decreases from 1,619 mL (F_v=5.5 mL/min) to 1,443 mL (F_v= 13 mL/min).

The calculated data suggest that the adsorption of MB dye onto *Cellets 200* celluloses placed in a vertical column depends of the flowrate of working dye solution through the filled column. The highest volume of working dye solution (V_t) and adsorption time till the maximum admissible concentration of MB dye in treated solution (t_{ri}) was performed for the lowest flowrate (F_v=5.5 mL/min). Caused lower adsorption time till a residual dye concentration in treated effluent equal with the recommendedmaximum admissible dye content in water resources (from environmental legislation)was performed in case of higher flowrate, and also a lower volume of working dye solution is passed through the fixed adsorbent bed in the column, a compromise between the volume of working dye solution and adsorption time in dynamic regime must be proposed, and the optimal volume of treated working solution per adsorbent mass must be determined (V_{opt}).

The plotting of b_i values (mL/gmin) versus V_i (mL/g) permits to determine the corresponding value of optimal volume per adsorbent mass as V_{opt}= 150.384 mL/g =$150.384 \cdot 10^{-3}$ m^3/kg, in accordance with Fig. 3. The optimal volume of working solution per adsorbent mass (V_{opt}=150.384 m^3/kg) is corresponding to a flow rate of 0.01368 m^3/day (9.5 mL/min). In further experiments, it is indicated to work in all adsorptive treatments in dynamic regime for MB dye - *Cellets 200* system with a flowrate of 13.68 L/day, or higher (but no more than 100 L/day).

For a common flowrate of 50 m^3/day (2.083 m^3/h) in the fixed bed column reactor and an adsorption time corresponding to a day (24 h) (or to a working shift, 8 h), considered as the reference for the textile wastewater treatment by adsorption in dynamic regime, the sizes/ dimensions of a column reactor (adsorption tank) filled with a packed bed of *Cellets 200* cellulose (ρ_{ads}=800 kg/m^3)used for MB dye removal from working influent solution, considering the determined optimal value of V_{opt}= $150.384 \cdot 10^{-3}$ m^3 kg^{-1}, and also β=1.5, λ= 2, are estimated as in Table 5.

3.2.2. Modeling the experimental column data

In order to determine the characteristic parameters in dynamic adsorption system, the experimental data were processed using a few of the most known models from the literature: Thomas and Yoon-Nelson models (Table 6). The experimental data are plotted considering the linearized form of the two models selected for adsorption study in dynamic regime as in Fig. 4 for the Thomas model and Fig. 5 for the Yoon-Nelson model, respectively.

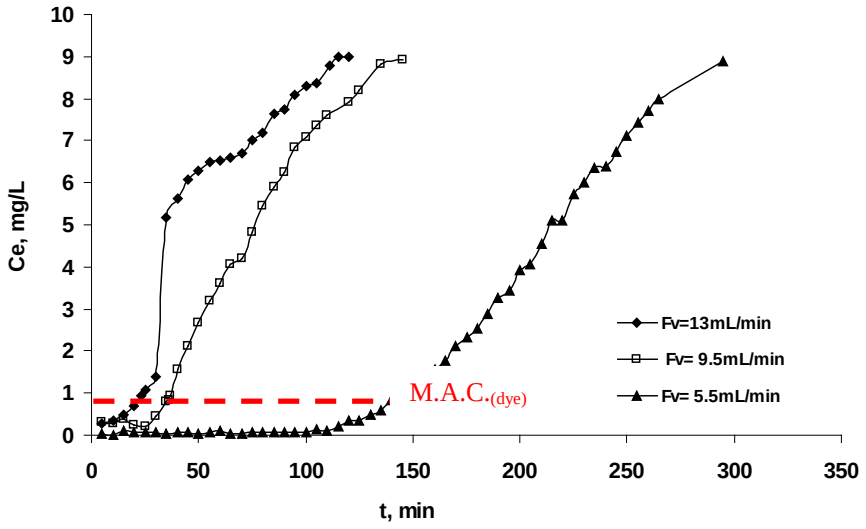


Fig. 2. Breakthrough curve of Methylene Blue dye adsorption in a fixed-bed column filled with granulated *Cellets 200* cellulose. Operating conditions: T = 20^0C, C_0 = 9.04 mg/L

Table 4. Characteristic parameters of the breakthrough curves

Parameter	***Significance and characteristics***	***Experimental values for each studied flowrate (F_V), (mL/min)***		
		5.5	***9.5***	***13***
Adsorbent bed height – h (cm)	Height in column of each added adsorbent amount	7.0	3.0	4.0
Breakthrough time - t_b(min)	Time required for attaining the breakthrough point, when the dye concentration has the value of $0.1C_0$ (C_b)	142.4	36.5	22.6
Saturation time - t_s (min)	Time required for attaining the saturation point, where dye concentration has a value of $0.9C_0$ (C_s)	294.4	135	111
The length of mass transfer zone – L(MTZ) (cm)	$L(MTZ) = h \cdot \left(1 - \frac{t_b}{t_S}\right)$ where, h - the heigth of adsorbent bed (cm)	3.609	2.189	3.185
Breakthrough volume – V_b (L)	Volume of working solution at breakthrough point, calculated as $V_b = F_V \cdot t_b$, where $F_V$is the volumetric flowrate (L/min).	0.78	0.347	0.294
Saturation volume – V_s (L)	Volume of working solution at saturation point, calculated as $V_S = F_V \cdot t_S$, where $F_V$is the flowrate (L/min)	1.617	1.282	1.443
Breakthrough capacity - q_b (mg/g)	Amount of MB dye retained per adsorbent mass at breakthrough point. $q_b = \frac{(C_0 - C_b) \cdot V_b}{m}$ where, m - adsorbent mass, g.	0.8015	0.602	0.467
Saturation capacity - q_S (mg/g)	Amount of MB dye retained per adsorbent mass at saturation point. $q_S = \frac{(C_0 - C_S) \cdot V_S}{m}$ where, m - adsorbent mass, g.	0.0322	0.072	0.073
Rate of exhaustion - R_{AE} (g/L)	Amount of exhausted adsorbent (g) per volume of working solution at the breakthrough point. $R_{AE}\ (g/L) = \frac{\text{mass of exhaused adsorbent}}{\text{volume of working solution}}$	2.47	1.351	1.392

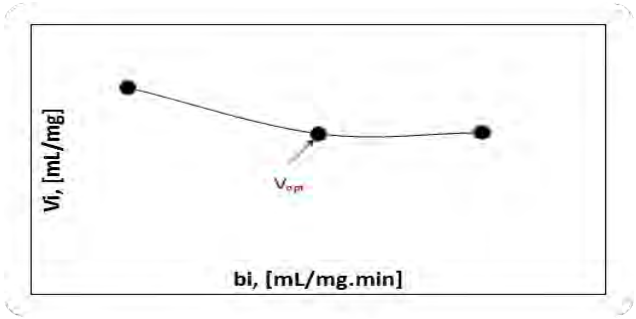


Fig. 3. Graphical representation of b_i versus V_i

Table 5. The estimated characteristic operating dimensions of packed bed column reactor

Characteristic operating dimensions	***Notation***	***Measured units***	***Value***
Adsorbent mass	M_{ads}	(kg)	332.482
Adsorbent volume	V_{ads}	(m^3)	0.416
Internal diameter of reactor, or adsorbent bed diameter ($D_R = D_{bed}$)	D_R	(m)	0.707
Height of fixed bed	H_{ads}	(m)	1.060
Height of adsorption reactor (H_R= 2 H_{ads})	H_R	(m)	2.120

Table 6. Thomas and Yoon-Nelson model applied for dynamic MB dye – *Cellets 20* adsorption system

Model	***F_V, Initial flowrate (mL/min)***	***k_T (L/min.mg)***	***$q_{0(T)}$ (mg/g)***	***R^2***	***k_{YN} (min^{-1})***	***$t_{1/2}$ (min)***	***$q_{0(YN)}$ (mg/g)***	***R^2***
Thomas	5.5	1.82 x10^{-3}	2.7552	0.9589				
	9.5	2.86 x10^{-3}	3.2442	0.9567				
	13.0	2.25 x10^{-3}	3.3034	0.9604				
Yoon-Nelson	5.5				0.0340	211.065	1.375	0.9645
	9.5				0.0490	74.900	1.585	0.9730
	13.0				0.0407	73.852	1.688	0.9604
$q_{0\ (Langmuir)}$*(mg/g)	81.968*							

* *(Suteu et al., 2019)*

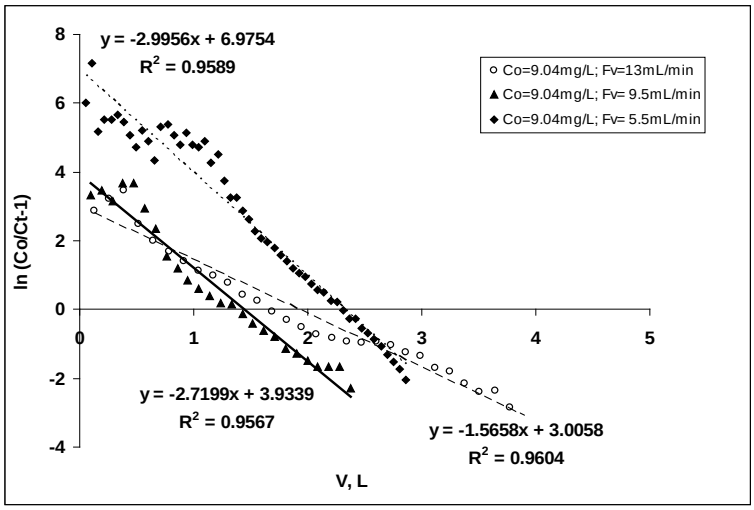


Fig. 4. Graphical representation of linearized form of dynamic Thomas adsorption model/min to 3.303 mg/g at 13.0 mL/min

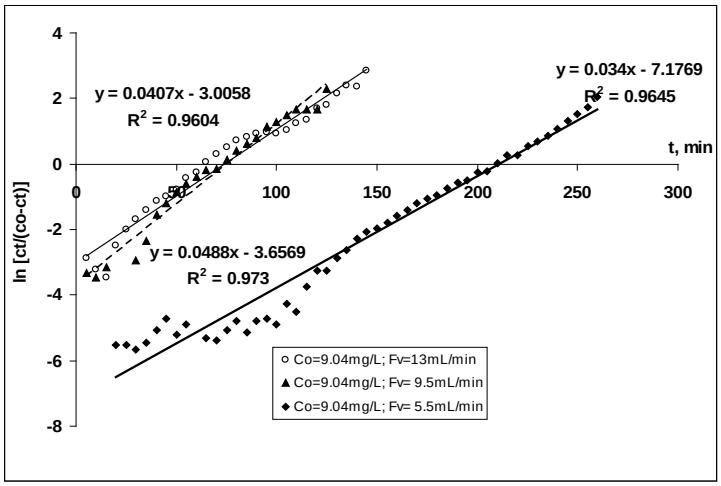


Fig. 5. Graphical representation of linearized form of dynamic Yoon-Nelson adsorption model

After the analysis of the processed experimental adsorption data from Table 6, and also the linear regression coefficient (R^2) values, it seems that the experimental data provided by the dynamic fixed bed column adsorption of MB dye from aqueous solution (low concentration) were verified better the Yoon-Nelson model due to its higher R^2 value referring to Thomas model. This finding complies with the results of batch study which pointed that the MB dye adsorption onto *Cellets 200* cellulose is very well described by the Langmuir isotherm model and follows a pseudo-second order kinetics (Șuteu et al., 2019). For the same concentration of the working dye solution passing through the adsorbent bed in the column (dynamic regime), the breakthrough time (t_b) and adsorption removal capacity (q_0) depends on the adsorbent amount fixed in the packed bed of the column (m) and the flowrate (F_V).

The values of Thomas rate constant (k_T) are varied in the range of (1.825 – 2.837) x 10^{-3} L/min.mg, and the *Cellets 200* maximum adsorption capacity ($q_{0(T)}$) is increasing as the flowrate increases from 2.755 mg/g at 5.5 mL/min to 3.303 mg/g at 13.0 mL/min.

It is clear shown in Table 5 that the values of the Yoon-Nelson rate constant (k_{YN}) are ranged of 0.0340-0.0407 min^{-1}, and the *Cellets 200* maximum adsorption capacity ($q_{0(YN)}$) increases as the flowrate increases from 1.375 mg/g at 5.5 mL/min to 1.688 mg/g at 13.0 mL/min.

Moreover, the *Cellets 200* maximum adsorption capacity (q_0) for MB cationic dye in this fixed-bed column study is higher when it was applied Thomas model than Yoon-Nelson model by more than 1.957-2.004 times in the selected flowrate range (5.5-13.0 mL/min). For the same dye concentration (9.04 mg/L) and adsorption pH (4.7), the adsorption capacity of *Cellets 200* cellulose for MB dye was highest in all batch adsorption study (81.968 mg/g) than in this dynamic fixed bed column adsorption study (1.375-3.303 mg/g), more than 24.813-59.613 times.

3.2.3. Column regeneration and comparison of Cellets 200 adsorption capacity with other adsorbents

The column with fixed adsorbent bed of 3 - 7 cm in depth and flowrate in range of 5.5 – 13.0 mL/min saturated with 9.04 mg of MB dye /L of solution was regenerated by successive desorption carried out with deionized water, acetic acid (CH_3COOH 1N) or sulphuric acid (H_2SO_4 4 N) till a constant pH value of washing/regeneration solution. It was observed that the 1st desorption cycle was almost finished after at least 24 h, after which further desorption was not significant. The adsorption efficiency of regenerated cellulose adsorbent in the fixed bed column study for MB dye removal working with diluted dye solution (9.04 mg of dye/L of solution) at a flowrate of 5.5-13.0 mL/min decreases with more than 30-50%, and also the breakthrough time (t_b) and saturation time (t_s). The values of dye adsorption capacities in batch and fixed bed column systems are compared in Table 7. It was found that the adsorption capacity of batch system performed better than that of fixed bed column system. The increased capacity of batch adsorption system may be attributed to a long continuous contact between the two phases (adsorbent-dye solution), high specific surface of adsorbent, while the gradient concentration decreases with time.

It is well known that a direct comparison between different absorbents is difficult to be performed due to the utilization of different experimental conditions for maximum adsorption capacity establishment. Data from Table 7 shows that dye adsorption capacity of cellulose adsorbent is significant and comparable, the *Cellets 200* celluloses being considered as a valuable adsorbent for treatment of industrial effluents containing organic dyes.

4. Conclusions

The dynamic adsorption system, Methylene Blue cationic dye – *Cellets 200* cellulose, was studied in fixed bed column, and the main working parameters were established in terms of adequate flowrate and adsorption time (breakthrough and saturation time) for dye removal till its maximum admissible concentration (1 mg of dye/L of solution) in water resources. It was worked with diluted dye solution (9-10 mg of dye/L ofsolution) at adequate initial pH (4.7) for highest MB dye adsorption onto Cellets celluloses. The optimal volume of working dye solution per adsorbent mass was determined as higher than 0.01368 m^3/day.

The adsorption kinetics for dye removal from aqueous solution were described by Thomas and Yoon-Nelson models, being associated with their characteristic parameters and coefficients, the best fitting corresponding to Yoon-Nelson model for packed bed adsorption column. The slope of the obtained breakthrough curves is deeper as influent flowrate decreases.

Table 7. Dye adsorption capacities of cellulose-based adsorbents in fixed bed column study

Adsorbent	***Type of adsorbed dye***	***q_{exp}, mg/g***	***Reference***
Chitosan impregnated with cetyl tri-methyl ammonium bromide (CTAB)	Brilliant Black (BBN) azo dye	0.16 - 1.89 (4-8 cm bed height, 0.8-1.5 mL/min, 20-100 mg/L of dye)	Rouf and Nagapadma, 2015
Rubber leaf powder	MB cationic dye	85.0 - 96.0 (5-10 cm bed height, 20 mL/min, 50-100 mg/L of dye)	Chowdhury et al., 2016
Granulated slag *Arcelor-Mittal, Algeria)	MB cationic dye	0.296 (15 cm bed height, 2 mL/min, 10 mg/L of dye)	Mazouz et al., 2016
Coffee residues	MB basic dye	104.5 (15 cm bed height, 20 mL/min, 800 mg/L of dye)	Kopsidas, 2016
Can Papyrus	MB cationic dye	0.0213 - 0.2044 (1-3 cm bed height, 12.5 mL/min, 5-15 mg/L of dye)	Saed et al., 2014
Carbon-alumina composite pellet	Acid fuchsin	2.185 - 3.89 (2.5-7 cm bed height, 5-15 mL/min, 20 mg/L of dye)	Dutta and Basu, 2014
Acid activated sawdust	Malachite Green dye	4.5 - 10.06 (7.5-15 cm bed height, 100 mL/min, 500 mg/L of dye)	Singh et al., 2015
TES fixed-bed (NaOH Treated Eggshell)	AO7 azo dye	0.567 - 17.111 (5-15 cm bed height, 2-6 mL/min, 5-30 mg/L of dye)	Chafi et al., 2015
Chitosan-glutaraldehyde	Direct Blue 7lAzo dye	343.59 (3-12 cm bed height, 1-3 mL/min, 50 mg/L of dye)	Lopez-Cervantes et al., 2018
Cellets 200 cellulose	MB cationic dye	1.375 - 3.3037 (3-7 cm bed height, 5-13.5 mL/min, 9.04 mg/L of dye)	This study

The adsorption capacity of Cellets 200 celluloses in fixed-bed column study for MB dye removal (1.375-3.3034 mg/g) was much lower than that of dye-cellulose batch system (81.968 mg/g).

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