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A regenerable microporous adsorbent based on microcrystalline cellulose for organic pollutants adsorption

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ABSTRACT

The adsorption properties of highly homogeneous microcrystalline cellulose pellets were investigated. The removal of the cationic dye Methylene Blue from aqueous solutions using a batch adsorption technique was studied as a typical application. Equilibrium and kinetic adsorption processes are studied. Equilibrium data were best fitted by Langmuir isotherm with an adsorption capacity about 82 mg/g. The model that best describes the kinetics of adsorption process is the pseudo-second order. Microcrystalline adsorbent regeneration using acetic acid or sulphuric acid was shown to be promising. Finally, microcrystalline cellulose pellets as a regenerable adsorbent can lead to viable application in environmental ecotechnology.

Keywords: Microcrystalline cellulose; Adsorption kinetics; Cationic dye; Adsorption thermodynamics; Regenerable adsorbent

1. Introduction

Dyestuffs represent the main pollutants of wastewater in many industries, ranging from textile, paper, and textile chemical finishing, to leather or chemical synthesis. Besides the unpleasant aesthetic effect given to the industrial effluents, it must be considered that many dyes are highly toxic, mutagenic and carcinogenic. Therefore, the removal of these pollutants from wastewater has a significant importance from both environmental and human health considerations, and it is, therefore, an important step in the treatment of industrial effluents before discharge in the natural environment [1].

Various methods are currently employed for dye removal; among them, one can cite: coagulation/flocculation, membrane processes, photolysis, and adsorption using different adsorbents, chemical oxidation and biological treatment [2–7]. The main drawbacks of these methods are connected with the high costs associated with the used products, and moreover, these methods generate bulky sludge.

Adsorption represents one of the most efficient and less expensive methods to be considered for the removal of dyes. One of the main advantages is the possibility of using a wide range of materials as adsorbents: from synthetic and engineering materials (resin and cellulose ion exchange, different

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copolymers, nanocrystalline cellulose) [8–16], to some low-cost adsorbents, such as natural materials (algae, seashell, peat, cypress cone chips, orange waste and sawdust) [17–20], agricultural by-products, or/and industrial wastes [21–30].

Among the numerous kinds of adsorbents, cellulosic materials have acquired an important place due to their physical, mechanical and chemical characteristics dependent on the technological process used to produce them. Moreover, the abundance of cellulose in nature and its renewable feature are other elements worth considering. Cellulose as an adsorbent can be found in many forms and types ranging from fibers, linters, microcrystalline powders, softwood pulp, bacterial cellulose, orange waste and many others [11,31–41]. Cellets are one type of cellulose versatile product which combines different properties, such as perfect sphericity, narrow particle size distribution, low friability, low solubility and inertness [42]. Very recently, an extensive work has been devoted to produce pellets of Cellets 200 by a continuous mode of operation, using a Wurster fluidized bed, in contrast with the batch-wise technique, to reduce the production costs and to improve the process control [43]. The authors found that the particle size distribution of the obtained Cellets 200 pellets is narrow, ranging from 200 to 400 µm [43]. The coordination number for Cellets 200, which is a basic attribute that influences many properties of products made of particulate materials, has been determined as 8.1±1.5 using DBSCAN (density-based spatial clustering of applications with noise) for segmentation of X-ray micro-tomographic images [44].

The main applications of microcrystalline cellulose Cellets are in the biomedical field. Due to outstanding mechanical properties that give them resistance to repeated manipulations (such as repeated cycles of adsorption–desorption), cellulose pellets were tested as an adsorbent material for adsorption of persistent organic pollutants, such as organic dyes with a relatively low molecular weight, up to 400 g/mol, which are usually poorly adsorbed, due to the porous structure of Cellets [42]. The morphological properties and the physicochemical characteristics of this natural adsorbent allow the use of large volumes of wastewater per mass of solid, which is an advantage for situations where the pollutant is found highly diluted or dispersed in large volumes of influent or effluent of sewage treatment plants because it makes both removal and concentration of the pollutant possible at the same time.

Starting from the conclusions of our previous studies [42,45], this paper investigates the adsorption process of a cationic dye onto cellulose Cellets 200 in order to acquire valuable information regarding the thermodynamics and kinetics of dye removal to facilitate the estimation of the quantitative characteristic parameters, thermal effect, rate limiting step and to assess the mechanism of adsorption. To achieve this objective, our work reports the experimental results using pellets of microcrystalline cellulose Cellets 200 as a potential adsorbent for the removal of cationic dye Methylene Blue (MB) from aqueous solutions using batch adsorption experiments. In this context, the adsorption equilibrium and kinetic data were analyzed using different equilibrium and kinetic models in order to determine the prevailing adsorption mechanism of the dye molecules on the proposed adsorbent, the nature of the physical or chemical interactions between adsorbent and adsorbate and their characteristic thermodynamic and kinetic properties.

2. Materials and methods

2.1. Adsorbent

Pellets of microcrystalline cellulose Cellets 200 (donated by *Synthafarm*, Germany) were used as the adsorbent. The cellulosic material displays both weak base and weak acid components bound to the same matrix, depending on the pH, and they can retain cationic and/or anionic species [42]. The morphology and surface of Cellets 200 pellets were previously investigated by means of environmental scanning electron microscopy (ESEM) microscopy and Fourier-transform infrared spectroscopy (FTIR) [42]. The FTIR spectra for the Cellets, the studied dye, and the dye attached to the Cellets spheres were obtained using a Vertex 70 instrument (Bruker, Romania). All the spectra were the results of 256 co-added scans at a resolution of 4 cm^{-1} in KBr pills, in the working range 400–4,000 cm^{-1} [42]. The structural characterization of the microcrystalline cellulose spheres, before and after dye attaching, was performed by ESEM. The ESEM studies were performed on Quanta 200 instrument, in which the samples were fixed by means of colloidal silver on copper supports and were covered with a thin layer of gold, by sputtering (K550x, Emitech Ltd., UK). The coated surface was examined by using an Environmental Scanning 200, operating at 5 kV with secondary electrons in high vacuum mode.

2.2. Dye solution

The cationic dye MB (Fig. 1, Mw = 320 g/mol, λ_{max} = 660 nm) was used as a commercial salt. The stock solution (430 mg/L) was prepared in distilled water and the working solutions were obtained by proper dilution.

2.3. Adsorption equilibrium studies

The adsorption of the dye on this adsorbent was studied in a batch system with established operational parameters

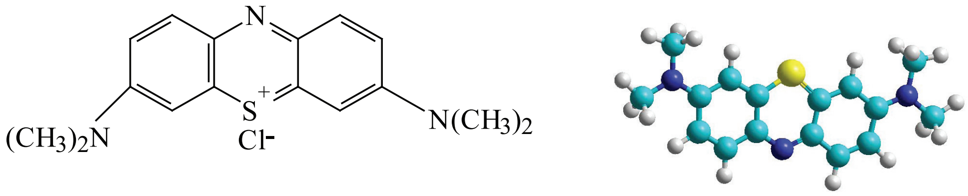


Fig. 1. Structure of cationic dye Methylene Blue (MB).

[42]: contact time (24 h), solution pH 11.4 and 2 g/L adsorbent dose. Known volumes of dye solutions (25 mL) with different initial dye concentrations (17–103 mg/L) and well-defined pH value, were brought into contact with an established dose of adsorbent for 24 h at three temperatures of 10, 25°C and 60°C, respectively (Fig. 2).

After the equilibrium has been attained, the concentration of the dye in the residual solution was spectrophotometrically determined using a UV–VIS Digital Spectrophotometer, model S 104D/WPA.

The adsorption capacity q of the cellulose (mg of dye/g of cellulose) was calculated by using Eq. (1):

$$q = \frac{C_0 - C}{G} \cdot V \tag{1}$$

where C_0 and C are the concentrations (initial and at the equilibrium) of the dye, in solution (mg/L), G is the amount of adsorbent (g) and V is the volume of solution (L).

2.4. Adsorption kinetic studies

The "limited bath" technique was employed to study the influence of the contact time on the adsorption of cationic dye onto Cellets 200 microcrystalline cellulose. A sample of 0.05 g adsorbent was added under intermittent stirring to 25 mL solution of dye at pH 11.4 using two initial concentrations: 43 and 60.2 mg/L, respectively. The temperature of solutions was strictly maintained with a thermostatic bath at 20°C. Several samples of supernatant were taken at different times (5–360 min), for spectrophotometric measurements to estimate the dye content. It was calculated the fraction of solute adsorbed at any time t, F (Eq. (2)), which may reach the equilibrium value 1.

$$F = \frac{q_t}{q_{eq}} \tag{2}$$

where q_t and q_{eq} (mg/g) are the amounts of dye adsorbed at time t and at equilibrium (24 h), respectively.

2.5. Regeneration studies

In order to clarify the nature of adsorption of MB dye on the cellulose Cellets 200, desorption studies were performed in accordance with literature data [14]. The desorption of dye on cellulose was studied in a batch system, when 0.04–0.05 g of adsorbent were brought into contact with 25 mL of elution reagent for established time of contact at 20°C. After the equilibrium has been reached, the concentration of the dye in the residual solution was spectrophotometrically determined using a UV–VIS Digital Spectrophotometer, model S 104D/WPA.

3. Results and discussion

3.1. Characterization of the CELLETS celluloses beads before and after dye adsorption

Our study allowed identification in the FTIR spectrum (Fig. 3) a broad peak in the 3,600–3,100 cm^{-1} band is due to the OH-stretching vibration. Also, a sharp peak at 2,922 cm^{-1} corresponds with C–H stretching vibration, and the peak at 1,645 cm^{-1} is attributed to the OH bending of absorbed water,

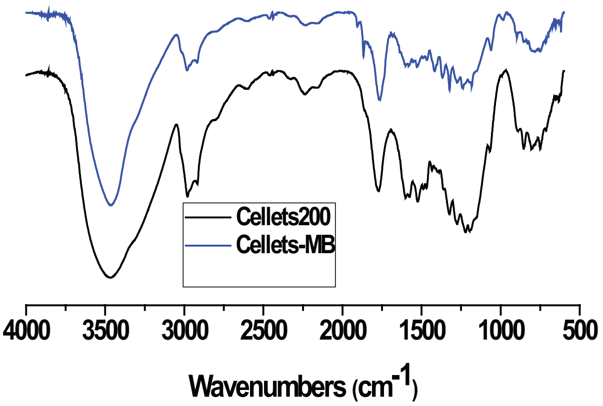


Fig. 3. Typical FTIR spectrum of Cellets 200 before and after dye adsorption.

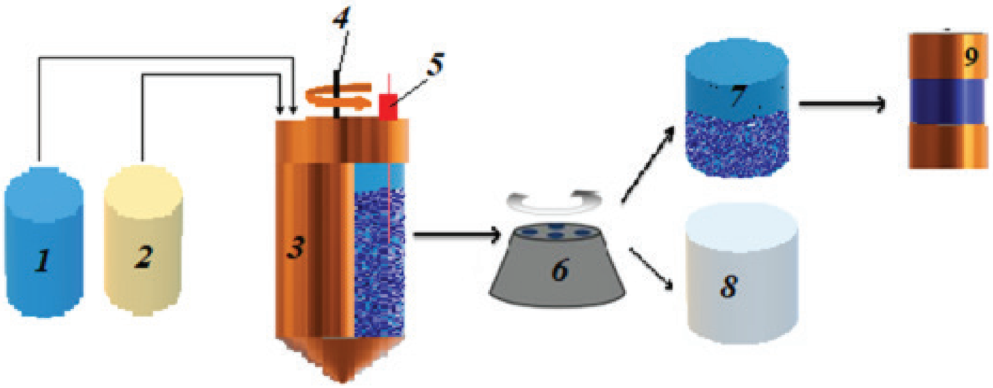


Fig. 2. Schematic diagram of the lab-scale adsorption system. (1) Storage tank for the dye solution; (2) storage tank for the adsorbent; (3) adsorption system equipped with heating/cooling and stirring device; (4) stirrer; (5) temperature control system; (6) centrifugal device; (7) storage tank for the exhausted adsorbent; (8) storage tank for the dye solution after adsorption; (9) adsorbent regeneration column.

since the region between 1,200 and 1,000 cm^{-1} comprised the totality of the C–O–C symmetric stretching, OH plane deformation, C–O–C asymmetrical stretching and C–C, C–OH, C–H ring and side group vibrations [14].

Also, Fig. 4(a) presented the ESEM images of the initial Cellets 200 and from the images it was observed the structure of the original cellulose beads which consists on small size spheroids, in the range of 200–350 μm. The integrity and the particles size remain mostly unchanged after the dye adsorption [14].

After the dye adsorption, some small changes in the cellulosic adsorbent structure were identified by studying the FTIR spectra and the ESEM images (Figs. 3 and 4(b)).

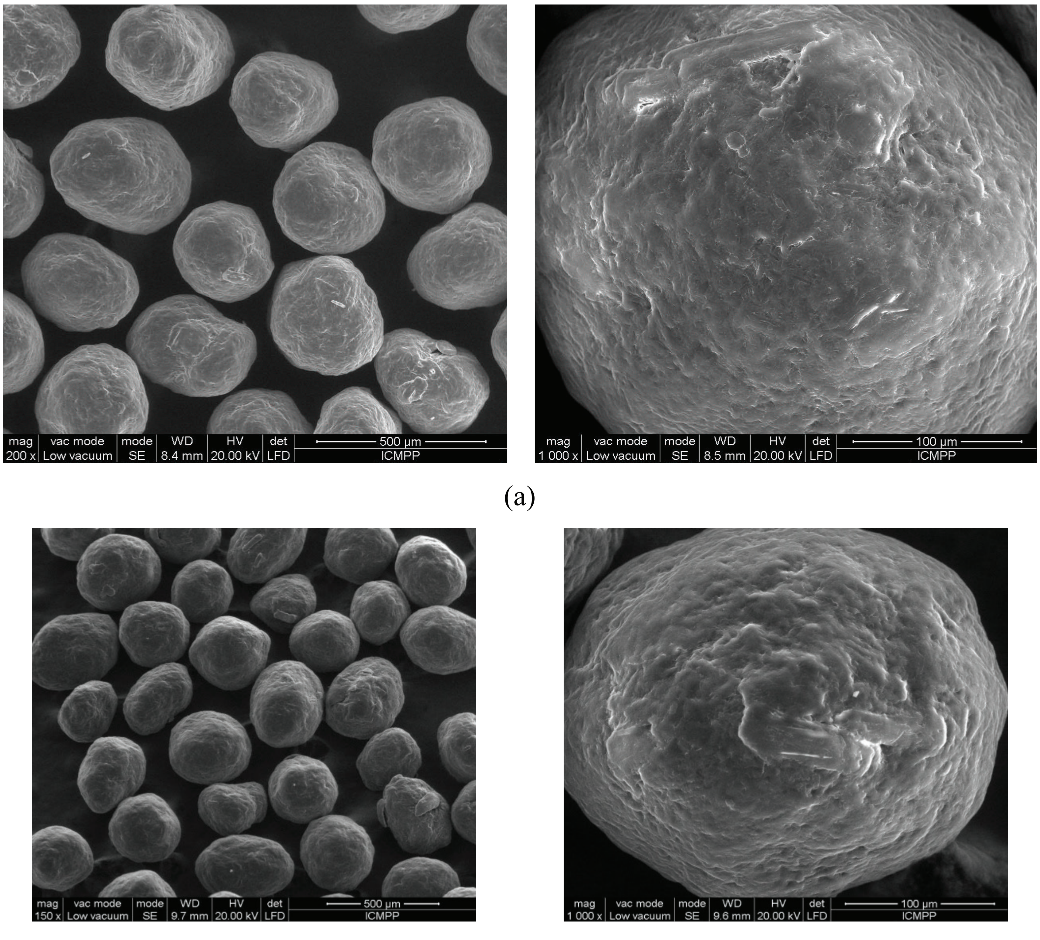
The FTIR spectra of Cellets beads modified with MB dyes are different to a small extent, with representative peaks of the cellulosic structures located around 4,000–2,995 cm^{-1} (hydrogen-bonded OH stretching), and 2,891 cm^{-1} (CH stretching mode) [14]. The differences are visible in the range of 1,000–2,000 cm^{-1}, when a shoulder peak located around 1,780 cm^{-1} appears after adsorption processes. Also, there are some shifts and reduction of the intensity of the peaks originated from cellulose structure, located at 1,645 cm^{-1}. These changes clearly evidenced the dye adsorption on the cellulose structure.

In the same time, the ESEM images of the initial and modified Cellets reveal that they have regular spherical shapes, with a compact structure within the size range of 200–350 μm, as Fig. 4(b) shows. The modified samples reveal insignificant modification as compared with the original materials [14].

It can be concluded that the dye adsorption did not influence the cellulose structure because even at the surface level, there are not any observable effects of the Cellets beads after adsorption, therefore the cellulosic materials might be proper for being used for multiple adsorption stages.

3.2. Adsorption equilibrium

Our previous study [42] revealed that the two Cellets types of microcrystalline cellulose analyzed (Cellets 200 and 350, respectively), exhibited different behaviours in the adsorption processes of the dyes. Cellets 200 showed better adsorption due to its higher specific surface area (up to 75%). This was verified in the case of the cationic dye, MB, which has a low molecular weight (Mw = 320 g/mol) compared with Brilliant Red, a reactive dye (Mw = 1,460 g/mol), which has a larger molecule.



(a)

(b)

Fig. 4. ESEM images for initial Cellets 200 (a) and after adsorption of MB dye (b).

In this study, it was started from the optimum pH conditions of retention of the MB dye from aqueous solutions onto cellulose Cellets 200 established [42].

The equilibrium adsorption of cationic dye MB on Cellets 200 from aqueous solutions was measured at 10°C, 25°C and 60°C using aqueous dye solutions with different initial concentrations: from 17 to 103 mg/L. The adsorption isotherms are presented in Fig. 5.

Scientific literature [46] describes a wide variety of equilibrium isotherm models such as Langmuir [47,48], Freundlich [49], Brunauer–Emmett–Teller [50], Redlich–Peterson [51], Dubinin–Radushkevich [52], Temkin [53], Toth [54], Koble–Corrigan [55], Sips [56], Hill isotherm [57], etc.

Though the relationship between the amount of dye adsorbed and the equilibrium dye concentration could be modelled by different adsorption isotherm equations, three of the most known and used models were compared in this paper: Freundlich, Langmuir, and Dubinin–Radushkevich isotherms.

The Freundlich isotherm assumes the surface heterogeneity and the exponential distribution of active sites of the adsorbent:

$$q = K_F \cdot C^{1/n} \tag{3}$$

where K_F ((mg/g)(L/mg)$^{1/n}$) is a parameter related to the adsorption capacity and n is a measure of adsorption intensity. The constants K_F and n are calculated from the linearized equation:

$$\log q = \log K_F + \frac{1}{n}\log C \tag{4}$$

According to the Langmuir model, there is a monolayer of adsorbate on the homogeneous surface, which means that all sites are equivalent and have the same adsorption enthalpy:

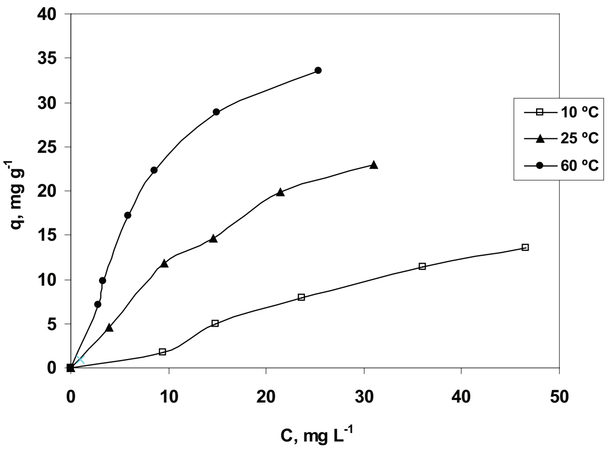


Fig. 5. Adsorption isotherms of the cationic dye MB on microcrystalline cellulose Cellets 200. Conditions: 10°C, 25°C and 60°C; pH 11.4; 2 g/L adsorbent dose; 24 h contact time.

$$q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C} \tag{5}$$

where constant K_L (L/g) is the equilibrium constant related to the energy of adsorption and q_0 (mg/g) is the maximum adsorption capacity of the monolayer.

The constants K_L and q_0 were calculated from the plot of the linearized Langmuir equation:

$$\frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L \cdot q_0} \cdot \frac{1}{C} \tag{6}$$

The Dubinin–Radushkevich (DR) equation describes adsorption on microporous solids with a quasi-Gaussian distribution of adsorption enthalpy. This is defined as follows:

$$\ln q \ = \ \ln q_0 - B\varepsilon^2 \tag{7}$$

where q_0 (mg/g) is the maximum adsorption capacity, B (mol^2/kJ^2) is the activity coefficient related to mean adsorption energy and ε is the Polanyi potential, equal to:

$$\mu = RT\ln\left(1 + \frac{1}{C}\right) \tag{8}$$

The adsorption energy, E (kJ/mol) can be determined using the following equation:

$$E = \frac{1}{\sqrt{2B}} \tag{9}$$

The parameters related to each isotherm equation, calculated from the intercepts and slopes of the corresponding linear plots (Figs. 6(a)–(c)) together with their correlation coefficients (R^2) are presented in Table 1.

It can observed from Table 1 that the values of Freundlich quantitative parameters, K_F and n increase with increasing the temperature, showing that the adsorption process is favourable at high temperature. The values of the correlation coefficients higher than 0.99 illustrate that the Langmuir model was more suitable to describe the adsorption process. The values of q_0, which reflect the accessibility of adsorption sites, present a reduced variation with the temperature, as expected on a monolayer, while the Langmuir constant K_L reflecting the binding energy between cationic dye molecules and cellulose increases with increasing temperature and suggesting that adsorption is an endothermic process.

The value of adsorption capacity at 25°C was found to be 81.9 mg dye/g of cellulose, comparable with those reported in the literature for some other cellulose materials used as adsorbent (Table 2). It is observed that the value of the adsorption capacity of the adsorbents based on cellulose depends primarily on the method used to prepare them and on the existing functional groups, and second on the structure and properties of dyes studied (molecular weight, functional groups, etc.).

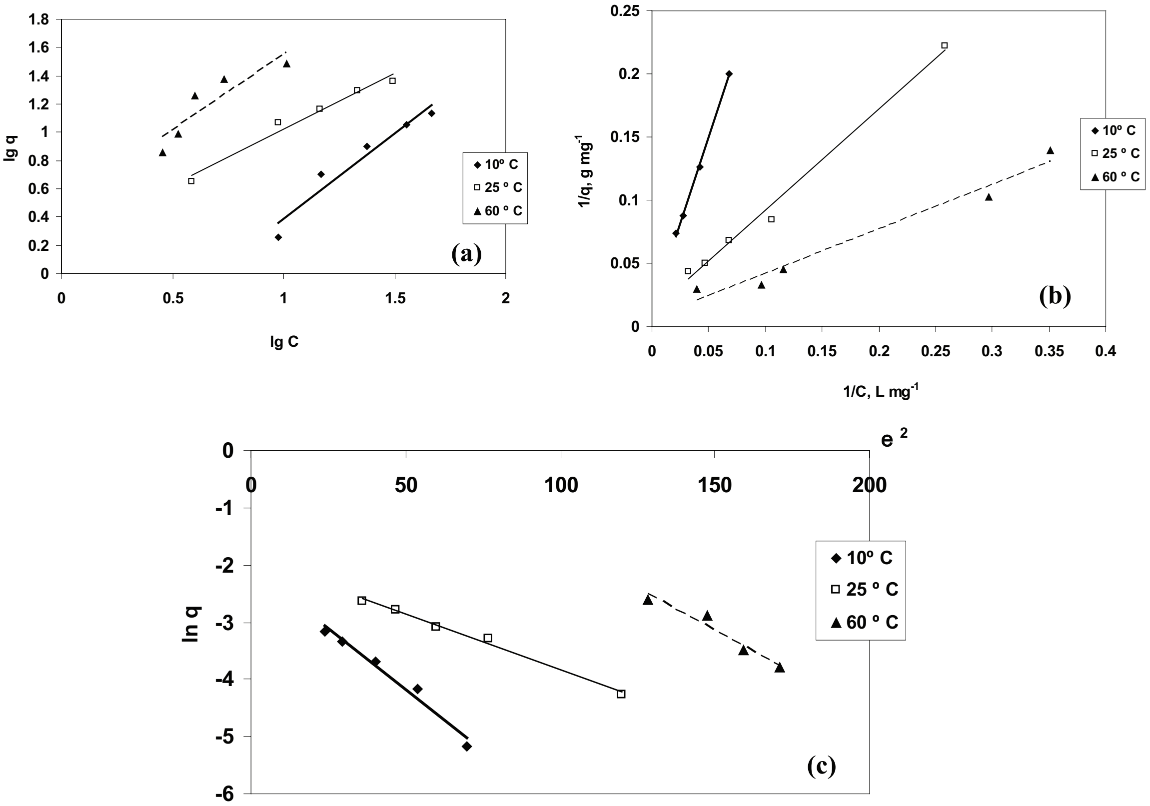


Fig. 6. Freundlich (a), Langmuir (b) and DR (c) plots for the adsorption of the cationic dye MB on microcrystalline cellulose Cellets 200 at three temperatures. Conditions: 10°C, 25°C and 60°C; pH 11.4; 2 g/L adsorbent dose; 24 h contact time.

Table 1
Characteristic quantitative parameters for the adsorption of cationic dye Methylene Blue (MB) onto cellulose Cellets 200

Type of isotherm	T (K)		
	283	298	333
Freundlich			
K_F ((mg/g)(L/mg)$^{1/n}$)	0.1516	1.7123	2.962
N	0.828	1.267	0.925
R^2	0.9407	0.9713	0.814
Langmuir			
q_0 (mg/g)	80.645	81.967	117.65
K_L (L/g)	0.00449	0.01526	0.0257
R^2	0.9990^a	0.9917^a	0.9794^a
Dubinin–Radushkevich (DR)			
q_0 (mg/g)	40.96	48.48	1102.59
B (mol^2/kJ^2)	0.0427	0.0195	0.0292
E (kJ/mol)	3.422	5.064	4.138
R^2	0.9722	0.9928	0.9378

[a] Best values.

DR and Langmuir equations are not contradictory, but DR usually describes adsorption on high energy sites in microporous regions, while Langmuir equation describes adsorption up to a complete monolayer. In practice, Table 1 shows that DR cannot fit efficiently dye adsorption at 60°C because high coverage is achieved at lower equilibrium concentrations than at lower temperature. Thus, the adsorption energy can be estimated from the DR equation (Table 1) at 10°C and 25°C. The calculations reveal a physical mechanism for the cationic dye adsorption on cellulose, the adsorption energy being less than 8 kJ/mol [63,64]. This suggests that MB binding onto microcrystalline cellulose may be due to relatively weak Van der Waals forces, hydrogen bonding, dipole–dipole interactions and strong electrostatic interactions between the negatively charged surface of the cellulose and the cationic dye.

3.3. Thermodynamic parameters

In order to evaluate the effect of temperature on the MB dye adsorption on microcrystalline cellulose Cellets 200 and to understand the nature of adsorption process (that could be physical or chemical but without a clear demarcation [63]), thermodynamic parameters were determined (Table 3) from the values of Langmuir constant, K_L (L/mol), and the following equations [63,64]:

$$\Delta G^0 = -RT \ln K_L \tag{10}$$

$$\ln K_L = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{11}$$

where $\Delta G°$ is free Gibbs energy, kJ/mol, $\Delta H°$ is adsorption enthalpy, kJ/mol and $\Delta S°$ is adsorption entropy, J/mol K,

Table 2
Comparison of performance of MB dye adsorption by various adsorbents based on cellulose

Sorbents based on cellulose	Dye	Adsorption capacity, (mg/g)	Reference
Acrylic acid–grafted cellulosic Luffa cylindrical fiber	MB	65.15	[58]
Carboxymethyl cellulose – g poly(2-(dimethylamino) ethyl methacrylate) hydrogel B	Methyl Orange	1,825	[59]
Carboxymethyl cellulose	MB	369–652	[60]
Ion exchanger cellulosic materials	Acid Clue 25/Acid Yellow 9/ Reactive Yellow 23/Acid Blue 79	294/333/175/127	[8]
Cellulose multicarboxyl	Malachite Green/Basic fuchsine	458.72/1,155.76	[36]
Carboxylate – functionalized cellulose from waste cotton fabrics	MB/Rhodamine 6G	185.63/118.21	[38]
Cellulose nanocrystal – alginate hydrogel beads	MB	256.41	[40]
Cellulose nanocrystal	MB	118	[61]
Cellulosic biomass carbon–based montmorillonite composites	MB	93.5	[62]
Microcrystalline cellulose Cellets 200	MB	81.967	Present paper

R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature, K.

Analyzing the data from Table 3, some conclusions can be highlighted:

- The negative values of Gibbs free energy, $\Delta G°$, indicate that the cationic dye adsorption on studied cellulose is spontaneous. The positive value of adsorption enthalpy ($\Delta H°$) computed from the slope of linear dependence $\Delta G°$ vs. T confirms the endothermic nature of dye adsorption.
- The value obtained for $\Delta H°$ is relatively low, insufficient for chemical adsorption (which should be in the order of –40 to –800 kJ/mol [63]). Scientific information in the field specifies that both the physical and chemical forces can be involved in the adsorption process on a solid surface, but the energy requirement is different (thus, for physical forces as Van der Waals: 4–10 kJ/mol, hydrophobic bond: 5 kJ/mol, coordination bond: 40 kJ/mol, dipole bond forces: 2–29 kJ/mol and for chemical forces the need would be >60 kJ/mol [64]. Therefore, the value obtained for the adsorption of dye MB on Cellets 200 cellulose adsorbent suggests, in agrees with adsorption energy at low coverage deduced from DR equation, that the process is more physical than chemical.
- The positive value of adsorption entropy ($\Delta S°$) characterizes the increased randomness at the solid–solution interface during the adsorption of dye, and some structural changes in the adsorbate and the adsorbent.

3.4. Adsorption kinetics study

The effect of the contact time on MB cationic dye removal from solutions of initial concentrations 43 and 60.2 mg/L, respectively, at pH 11.4 by adsorption onto cellulose Cellets 200 is shown in Fig. 7.

Table 3
Thermodynamic parameters of the adsorption of MB dye onto cellulose Cellets 200

T (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)
283	–0.853	24.371	91.606
298	–3.929		
333	–5.833		

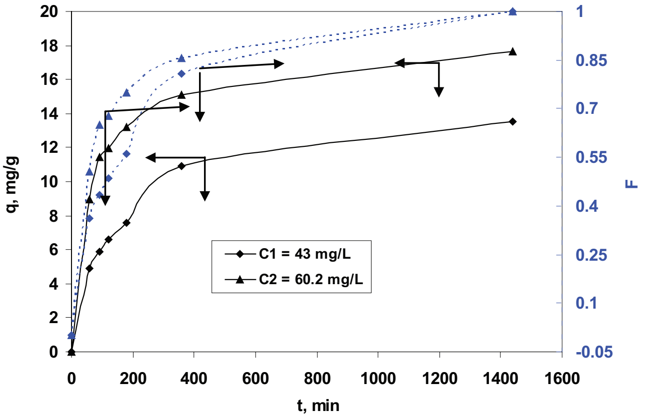


Fig. 7. Effect of contact time on the adsorption of the cationic dye MB on cellulose Cellets 200: the fractional attainment of equilibrium, F, and the amount of dye adsorbed, q vs. time.

The plots in Fig. 7 show that the time period required for maximum removal of cationic dye was lower than 6 h; however, the adsorption half-times ($t_{1/2}$) were between 1.0 and 1.5 h. In order to study the mechanism of adsorption and establish the rate controlling step, the kinetic data were analyzed and interpreted on the basis of three kinetic models: Lagergren, Ho and Elovich models [65–68]. The Lagergren model (pseudo-first order), traditionally used for describing adsorption kinetics, is expressed as follows:

$$\log(q_0 - q_t) = \log q_0 - k_1.t \tag{12}$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first order mechanism, evaluated from the slope of the log (q_0–q_t) vs. t plot (Fig. 8(a)).

According to Ho's model (pseudo-second order), the dye adsorption kinetics is described by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_0^2} + \frac{t}{q_0} \tag{13}$$

where k_2 is the rate constant of pseudo-second order adsorption (g/mg min) and $h = k_2 \cdot q_0^2$ is the initial adsorption rate (mg/g min). By plotting t/q_t vs. t (Fig. 8(a)), a straight line should be obtained and q_0, k_2 and h could be estimated.

The Elovich equation was used in case of chemical adsorption on heterogeneous surfaces:

$$q_t = \frac{1}{\beta}\ln(\alpha \cdot \beta) + \frac{1}{\beta}\ln t \tag{14}$$

where β is the desorption constant (g/mg) and α is the initial adsorption rate (mg/g min), which can be obtained from the slope and intercept of a straight line plot of q vs. ln t (Fig. 8(b)).

The kinetic parameters related to each model, calculated from Eq. (12) to Eq. (14), are reported in Table 4. The fitting of each model to the experimental data was estimated using linear regression, the quality of which is deduced from the correlation coefficient, R^2.

It can be observed from Table 4 that the experimental data are best represented by the pseudo-second order reaction model. Consequently, increasing the initial dye concentration has a favourable effect on the rate of adsorption by increasing the concentration gradient between the solutions and adsorbent.

This is confirmed by data plots using the equations reported previously for kinetic models. As can be seen from Fig. 8(a), the log(q – q_t) vs. t plots gives a straight line which does not pass through the origin and also, the $q_{e\,\mathrm{exp}}$ values do not agree with the calculated $q_{e,\mathrm{exp}}$. So, the results for both dye concentrations suggest that the pseudo-first order model does not fit the kinetic data. Conversely, the linearity of the t/q_t vs. t plots (Fig. 8(a)), and the q_0 calculated values are much closer to the experimental values, suggest that adsorption kinetics for both dye concentration follows a pseudo-second order kinetic model. Several mechanisms correspond to a pseudo-second order kinetics, among which chemical adsorption or chemisorption involving valence forces through sharing or exchange of electrons between the two phases involved. However, this seems to contradict thermodynamic data and this kinetic model may describe any surface reaction or more complex mechanisms involving also mass transfer limitation.

The analysis of thermodynamic data is also in agreement with the results obtained from the Elovich equation which describes a specific kinetics of chemical adsorption. Since the R^2 values are close to 0.96 for the studied adsorption system

Table 4
Kinetic parameters of cationic dye MB adsorption onto cellulose Cellets 200

Kinetic model	C_o = 43 mg/L	C_o = 60.2 mg/L
	$q_{0,\mathrm{calc}}$ = 13.53 mg/g	$q_{0,\mathrm{calc}}$ = 17.62 mg/g
Pseudo-first order kinetic model		
k_1 (min^{-1})	0.0039	0.0037
q_0 (mg/g)	11.19	9.34
R^2	0.9908	0.9543
Pseudo-second order kinetic model		
k_2 (g/mg min)	0.00448	0.0011
h (mg/g min)	0.104	0.329
q_0 (mg/g)	14.81	17.27
R^2	0.9729	0.9988
Elovich kinetic model		
α (mg g^{-1} min^{-1})	0.2173	1.0264
β (g mg^{-1})	0.3026	0.3086
R^2	0.9643	0.961

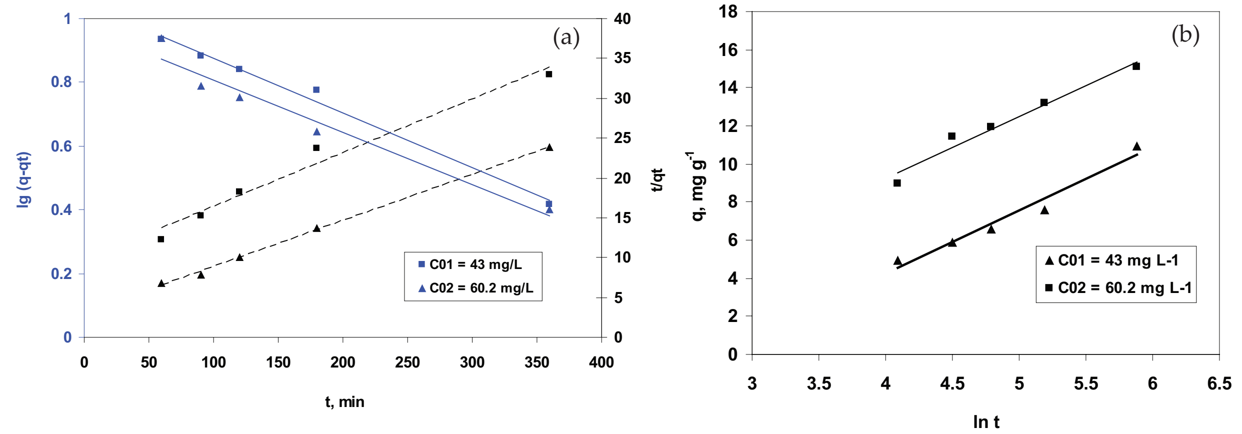


Fig. 8. Applicability of the pseudo-first and pseudo-second order kinetic models (a) and of the Elovich model (b) to cationic dye MB adsorption on cellulose Cellets 200. Conditions: 20°C, 2 g/L adsorbent, 24 h contact time and pH 11.4.

in Table 4, the linear representation q vs. ln$t$ does not perfectly fit experimental data, which also emerges from Fig. 9(b) and confirms that chemisorption cannot be the only step that controls the studied adsorption processes. The conclusion is in accordance with Langmuir parameters previously calculated [42], the fact that diffusion process could be the step that could control the adsorption dye onto cellulose must be investigated.

3.5. Adsorption diffusion mechanism

In order to accurately determine whether the diffusion mechanism may limit the rate of adsorption process, experimental data were analyzed using two models [65,66]:

- the intraparticle diffusion model proposed by Weber and Morris (where k_d is the rate constant for intraparticle diffusion, mg/g min$^{1/2}$; c is intercept to the y axis):

$$q_t = k_d t^{1/2} + c \tag{15}$$

This model suggests that the intraparticle diffusion is involved in the adsorption process if the plot q_t vs. $t^{1/2}$ (Fig. 9(a)) is linear. In this case, intraparticle diffusion is the rate-limiting step if the line passes through the origin, as c accounts for external mass transfer across the boundary layer.

- film diffusion model proposed by McKay (where k_f is the rate constant for film diffusion, min^{-1}; F is the fractional attainment):

$$\ln(1-F) = k_f t \tag{16}$$

This model specifies that the film diffusion could be involved in the adsorption process if the plot ln$(1–F)$ vs. t (Fig. 9(b)) is linear, and becomes the rate-limiting step if the line passes through the origin.

From Fig. 9(a), it can be observed that the plots are linear, but none pass through the origin, and this could underline the conclusion that both diffusion mechanisms are involved in the adsorption processes of MB dye onto cellulose Cellets 200, and these might be the rate determining steps. In the graphical representation of the dye amount retained by microcrystalline cellulose vs. $t^{1/2}$ (Fig. 9(a) – initial concentration C_{02} = 60.2 mg/L), two line segments emerge: the first part is generally associated with the external mass transfer (film diffusion), while the second linear part indicates intraparticle diffusion into the porous structure of the adsorbent. From Fig. 9(b), it can be also concluded that the film diffusion is not the only rate-limiting step of the adsorption process.

3.6. Adsorbent regeneration studies

The desorption capacity of the cellulose was evaluated by means of the amount of dye desorbed (q_{des}, mg of dye/g of cellulose) (Eq. (17)) and by percentage of dye desorbed (R %) (Eq. (18)):

$$q_{\text{des}} = \frac{C_{\text{des}}}{g} \cdot V \tag{17}$$

$$R,\% = \frac{C_{\text{des}} \cdot 100}{C_{\text{ads}}} \tag{18}$$

where C_{ads} and C_{des} are the concentrations (adsorbed on cellulose and after desorption in solution at the equilibrium) of the dye (mg/L), g is the amount of adsorbent loaded with dye (g) and V is the volume of solution (L).

The results are reported in Table 5. These indicate that acetic acid could be a better reagent for desorption and also the possibility of efficient desorption of MB dye with mineral acids (such as H_2SO_4, HCl).

An excellent phenomenon expressed by Table 5 is that the R% of CH_3COOH is higher but it decreased after mixed with HCl, and still higher than that of group of HCl only, the fact that opens up new perspectives in elucidating the desorption process mechanism.

From the point of view of the adsorption mechanism, the adsorption equilibrium data reveals that MB binding onto microcrystalline cellulose may be due to relatively weak Van

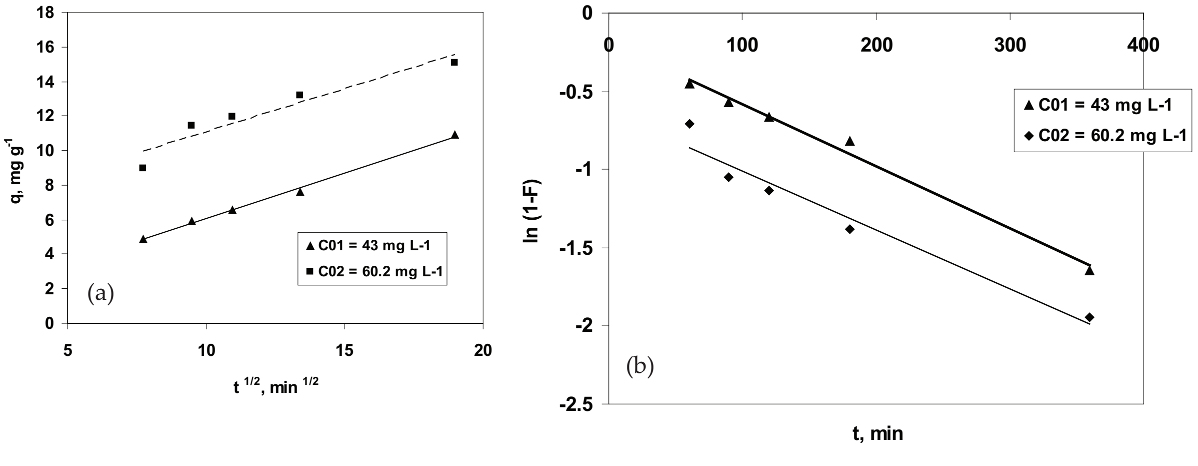


Fig. 9. Applicability of intraparticle diffusion kinetic model (a) and film diffusion model (b) in MB dyes adsorption on cellulose Cellets 200. Conditions: 20°C, 2 g/L adsorbent, 24 h contact time and pH 11.4.

Table 5
Results of regeneration study of MB dye from cellulose Cellets 200

Desorption conditions		Cellulose Cellets 200		
		q_{ads}, mg/g[a]	q_{des}, mg/g	R, %
1M HCl, 24 h, 20°C		17.112	2.791	16.31
1M CH_3COOH, 24 h, 20°C		15.652	3.77	24.1
1M HCl: 1M CH_3COOH (1:1), 24 h, 20°C		16.915	3.074	18.18
4M H_2SO_4	4 h, 20°C	15.209	2.391	15.72
	24 h, 20°C		3.182	20.92

[a]Represents the adsorption capacity of studied cellulose obtained in batch conditions by contacting 0.05 g of Cellets with 25 mL dye solution with initial concentration of 43 mg/L and 24 h contact time at 20°C.

der Waals forces, hydrogen bonding and electrostatic interactions between the negatively charged surface of the cellulose and the cationic dye.

Further work is still necessary to optimize the regeneration, to elucidate the desorption mechanism and to define the techno-economic conditions in which are effective. In the experiments of Table 5, it must be pointed out that the water-to-adsorbent mass ratio was maintained the same, which impaired R %, but did not require more water than the amount treated in the adsorption experiments. The opportunity to reuse the Cellets in a new adsorption process will not only depend on R % but also on the amount of water, the nature and the concentration of the acid needed.

4. Conclusions

The results of this study show that the tested microcrystalline cellulose *Cellets 200* are worthy to be considered as a potential adsorbent for the removal of MB cationic dye from aqueous solutions at pH 11.4.

- The Cellets, owing to their morphological and mechanical properties, are ready to be used as a viable adsorbent in industrial applications. They present the advantages to be regenerable and commercial products for ecosystem rehabilitation.
- The equilibrium adsorption data, analyzed with Freundlich, Langmuir and Dubinin–Radushkevich models, are better described by Langmuir isotherm model. The obtained adsorption capacity value of 81.9 mg g^{-1} at 25°C. This adsorbent can, therefore, be efficient even when the pollutant is highly diluted or dispersed in large volumes of influent or effluent of sewage treatment plants because they can make both removal and concentration of the pollutant possible at the same time.
- The values of the mean free energy of adsorption (E) obtained from the Dubinin–Radushkevich model between 3 and 4 kJ/mol revealed a physical mechanism for the cationic dye adsorption on cellulose.
- The values of thermodynamic parameters confirm also the feasibility and the endothermic behaviour of the adsorption process. The order of magnitude of adsorption enthalpy shows that chemisorption is unlikely to occur.
- The experimental data processing using different kinetic models (pseudo-first order, pseudo-second order, intraparticle and film diffusion) indicate the applicability of pseudo-second order model in predicting the kinetics of MB adsorption by microcrystalline cellulose Cellets 200. Also, the diffusion models suggested that the intraparticle diffusion (pore diffusion), and the external mass transfer (film diffusion) influence the adsorption rate.
- The adsorbent based on microcrystalline cellulose Cellets 200 could be regenerated using acetic acid or sulphuric acid 4M at 20°C for 24 h, which represents a major advantage for this type of adsorbent.
- The obtained results provide additional valuable information about the possibility to use microcrystalline cellulose Cellets 200 as an adsorbent to retain the textile dyes with low molecular weight from aqueous solutions and also inspire the expansion of these studies in order to investigate dynamic processes and real industrial effluents.
- Also, the results obtained in the present paper combined with those obtained in previous studies [43,45] suggests that we can extend the adsorption studies using this type of material to persistent organic micropollutants, such as drug residues with a molecular weight up to 400–500 g/mol and for heavy metal ions present in various aqueous environments.

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