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CELLULOSE CELLETS AS NEW TYPE OF ADSORBENT FOR THE REMOVAL OF DYES FROM AQUEOUS MEDIA

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Abstract

In the current study, the structural and adsorptive properties of the micro crystalline cellulose beads, Cellets 200 and 350, as well as the possibility to use them as adsorbents for removal of reactive dye Brilliant Red HE-3B and cationic dye Methylene Blue from aqueous solutions have been investigated. Batch experiments were conducted to study the effect of adsorbent particles size (200-500 μm), initial solution pH (1-11), adsorbent dose, dye concentration, temperature (2-45^{0}C) and contact time (30 min – 24 hours). It was observed that the optimum values of experimental parameters and the maximum amount of dye adsorbed onto cellulose were dependent on the type of dye. The results of the study suggest the adsorption capacity of the investigated materials for removal of dyes from aqueous environment strongly depends on the structure of dyes and the working conditions. At the same time, further research regarding the study of adsorption equilibrium is encouraged in order to gain useful information for extending the process at a large scale, and also for applying the process for adsorption of some inorganic species, such as metallic ions.

Key words: adsorption, aqueous medium, cationic dye, cellulose CELLETS, operating variables, reactive dye

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1. Introduction

Removal of textile dyes from wastewater constitutes an important topic of study for environmental protection specialists, considering the impact of these pollutants on the waters where they are discharged. Thus, the presence of dyes in surface waters leads to problems related to esthetics, inhibition of aquatic flora and fauna development, occurrence of different byproducts with carcinogenic effect formed by dyes degradation.

Different techniques have been developed and applied for treatment of textile wastewater, which is characterized by color, high values of pH, considerable amounts of suspended solids, different and unacceptable COD levels, and the presence of non-biodegradable chemical compounds (Ding et al., 2010; Pereira and Alves, 2012; Sulak and Yatmaz, 2012; Zaharia and Suteu, 2012). Physical methods, such as mechanic separation (coagulation, flocculation, precipitation) or membrane processes, physico-chemical processes (adsorption, chemical precipitation, coagulation-flocculation, and ionic exchange), chemical process (advanced oxidation with ozone, H_2O_2, UV), biological process (biological processes in connection with the activated sludge processes and membrane bioreactors) or combination of those can be applied in order to ensure the efficiency of dye containing wastewater treatment process (Allen and Koumanova, 2005; Anjaneyulu et al., 2005; Ding et al., 2010; Kanawade, 2014; Kasperchik et al., 2012; Kharub,

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2012; Latif et al., 2011; Mohamed et al., 2014; Ozdenir et al., 2011; Ramesh et al., 2007; Saraswathy et al., 2013; Suteu et al., 2009a; Zaharia et al., 2009, 2012; Zaharia and Suteu, 2012). Adsorption remains one of the techniques that have been successfully applied for dyes removal (Kanawade, 2014; Rashed, 2013). This is the result of the fact that adsorption is an easy and feasible technology that can use a variety of materials as adsorbents. These materials can be classified as follows (Abbas, 2013; Bharathi and Ramesh, 2013; Kyzas et al., 2013; Ouasif et al., 2013; Sharma et al., 2011; Suteu et al., 2009b, 2012; Sulak and Yatmaz, 2012):

a) *synthetic and engineered materials*, including synthetic resins, polyamides, ion exchange (celluloses, functionalized polymers (with chelating group, textile dyes), activated charcoal and ash;

(b) *unconventional materials,* such as: (b1) synthetic, (ashes, different charcoals both in the presence or absence of biodegradable polymers such as polyelectrolytes); (b2) natural, cellulosic and/or lignocellulosic materials (pumpkin core, hemp fibres, cellolignin, sawdust, peat); (b3) agriculture and seafood industry wastes.

Recently, researches regarding the materials used as adsorbents for textile dyes have been focused again on synthetic and engineered materials probably due to several advantages that include (1) ease of use in dynamic systems, (2) increased adsorption efficiency, (3) possibility of being employed in several consecutive cycles of adsorption - desorption and (4) high performance in terms of degree of discoloration and treatment of aqueous effluents (Greluk and Hubicki, 2011; Suteu et al., 2014; Wawrzkiewicz and Hubicki, 2010).

Cellets represents a versatile product of cellulose type, which combines different properties such as perfect sphericity, narrow particle size distribution, low friability, low solubility and inertness. Cellulose, a natural carbohydrate polymer consisting of β-D-glucose repeating units (Klemn et al., 2005) is considered the most abundant renewable polymer resource available on Earth (Kaplan, 1998). Depending on the technological process used to produce them, celluloses may be found in many forms and types ranging from fibers, linters, microcrystalline powders, softwood pulp, bacterial cellulose and many others.

Cellets are microcrystalline cellulose beads, produced exclusively by microcrystalline cellulose and purified water, without any additive. They possess high spherical starter cores with extreme stability and low friability.

The aim of this paper is to investigate the structural and adsorptive properties of Cellets 200 and 350 and the possibility to use them as adsorbents in order to remove reactive dye *Brilliant Red HE-3B (BRed)* and cationic phenotiazine dye *Methylene Blue (MB)* from aqueous solutions under batch conditions. The dyes adsorption potential of *Cellets 200* and *350* was evaluated as a function of adsorbent particles size, initial solution pH, adsorbent dose, dye concentration, temperature and contact time. The results confirm the moderate adsorption capacity of studied celluloses beads -*Cellets 200* and *350*- and suggest the necessity to complete the data with equilibrium, thermodynamic and kinetic studies in order to elucidate the mechanism and the rate-limiting step.

2. Experimental

2.1. Materials

2.1.1. Adsorbent types

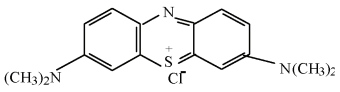
Two sorts of Cellets, differing on their particle size, namely Cellets 200 and Cellets 350 were used in our work. Table 1 shows the main physical and chemical characteristics of Cellets.

Table 1. Physical and chemical parameters of microcrystalline cellulose spheres

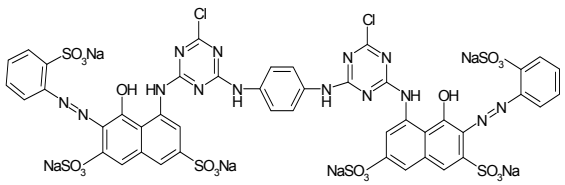
	Cellets 200	***Cellets 350***
Particle size distribution	***200 – 355 μm (≥ 85 %)***	***350 – 500 μm (≥ 85 %)***
Loss on drying	≤ 7.0 %	
Bulk density (g cm^{-3})	0.80 ± 5 %	
Sphericity degree (average)	0.90 ± 0.05	
Degree of polymerization	≤ 350	
pH value	5.0 – 7.0	
Conductivity/μS cm^{-1}	≤ 75	

2.1.2. Dye

Methylene Blue (Fig. 1a), and *Brilliant Red HE-3B* (Fig.1b) were selected as dyes for experimental studies. The selected dyes were used as commercial salts and are characterized in Table 2. The working solutions were obtained by appropriate dilution of a stock solution.



(a)



(b)

Fig. 1. (a) Structure of the Methylene Blue dye; **(b)** Structure of the Brilliant Red HE-3B dye

2.2. Dye adsorption procedure

The adsorption experiments were performed through batch method by contacting different amounts of adsorbent with 25 mL of solution containing various amounts of dye.

Table 2. Summary data on dyes studied

Name	*Classification*	*C.I.*	*MW, g/mol*	λ_{max} *nm*	*Concentration of solutions, mg/L*	
					Stock	*Working*
Brilliant Red HE-3B (Procion Red HE-3B ; Reactive Red 120; C.I. 25810)	anionic reactive	25810	1463	530	500	25 - 400
Methylene Blue (Basic Blue 9; C.I. 52015)	cationic phenothiazine	52015	319.85	660	320	19 -102

Note. Abbreviations: BRed - Brilliant Red HE-3B; MB- Methylene Blue

The pH of the solution was adjusted to the required value using NaOH and HCl aqueous solutions (1N and 0.1 N, respectively). Concentrations were measured with a RADELKIS OP-271 pH/Ion analyzer. The system was maintained at constant temperature in a thermostatic bath, under stirring. After reaching the equilibrium time (24 hours), the amount of unretained dye was determined using a spectrophotometric method. The adsorption capacities of the cellulosic adsorbent were evaluated by means of the amount of dyes adsorbed according to Eq. (1) and by percent of dye removal (Eq. 2), where: C_0 and C are initial and the equilibrium concentration of dye in solution in mg/ L, G is the amount of cellulose (g) and V is the volume of solution (L).

$$q = \frac{C_0 - C}{G} \cdot V \quad (1)$$

$$R,\% = \frac{(C_0 - C) \cdot 100}{C_0} \quad (2)$$

2.3. Analytical methods for quantitative determinations and physicochemical characterization

The concentrations of unretained dyes were determined spectrophotometrically at the maximum wavelengths (Table 1) and using a JK-VS-721N VIS spectrophotometer.

2.3.1. Fourier transforms infrared spectroscopy (FTIR)

The FT-IR spectra for the Cellets, the studied dye and the dye attached to the Cellets beads were obtained using a Bruker Vertex 70 instrument with 4 cm^{-1} resolution in KBr pills.

2.3.2. Environmental Scanning Electron Microscopy (ESEM)

The structural characterization of the microcrystalline cellulose spheres, before and after dye attaching, was performed by environmental scanning electron microscopy (ESEM). The ESEM studies were performed on Quanta 200 instrument. Samples were fixed by means of colloidal silver on copper supports.

The samples were covered with a thin layer of gold, by sputtering (EMITECH K 550x). The coated surface was examined by using an Environmental Scanning 200, operating at 5 KV with secondary electrons in High Vacuum Mode.

3. Results and discussion

3.1. Characterization of the CELLETS celluloses beads before dyes adsorption

Before the adsorption experiments, the Cellets beads were structurally and morphologically characterized by using FTIR and SEM analyzes. The FTIR spectrum of Cellets beads consist on absorption bands characteristic for any cellulosic materials: a broad band in the 3600 – 3100 cm^{-1} region due to the OH-stretching vibration and a sharp band at 2922 cm^{-1} which corresponds to the C-H stretching vibration.

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 cellulosic materials exhibit both weak base and weak acid components bound to the same matrix and, depending on solution pH, they can remove cationic and/or anionic species. The morphology and surface of Cellets beads were also investigated by means of ESEM microscopy (Fig. 2).

The structure of the original cellulose beads, presented in Fig. 2, consists on small size spheroids, in the range of 200 – 350 μm for Cellets 200 and 350 – 500 μm for Cellets 350 respectively.

3.2. Effect of solution pH and type of cellulose on adsorption efficiency

The pH value determines the surface charge of the adsorbent and the ionic form of the dyes molecules, both influencing the amount of dye adsorbed by unit weight of adsorbent. The surface charge of the adsorbent is a function of the solution pH. The solution characteristic pH value is in the range 5-7 (Table 1). At pH values lower than this range, the adsorbent surface is positively charged, exhibiting affinity for anionic dye. At pH higher than 7, the surface of Cellets is negatively charged and this is available to electrostatic interactions with cationic dyes. The effect of initial solution pH on the adsorption of dyes onto microcrystalline cellulose beads (Cellets) was examined and the results are presented in Fig. 3.

The variation of dyes uptake (q, mg/g) as a function of initial pH of solution, presented in Fig. 3, shows that the anionic dye is adsorbed from acidic media with pH of about 1.3 (lower than 5), while cationic dye is adsorbed from basic solutions with pH of about 11.5 (higher than 7). This behaviour may be the consequence of the availability of dyes exchange positions and also of the variation of the adsorbent surface charge as a function of the solution pH.

Thus, when the cellulose surface is positively charged, it is susceptible to electrostatic interactions with the polar fractions of Brilliant Red HE-3B (reactive dye) molecule (dissociated sulphonic groups), whereas when the surface is negatively charged, it is not able to bind anionic dyes, but is available to electrostatic interactions with Methylene Blue (cationic dye) molecules.

3.3. Effect of adsorbent dose and dye structure on adsorption efficiency

Aiming at establishing the optimum dose of the microcrystalline cellulose beads, different amounts of material were contacted with solutions containing the studied dyes in certain concentrations, at the selected initial pH, for 24 hours.

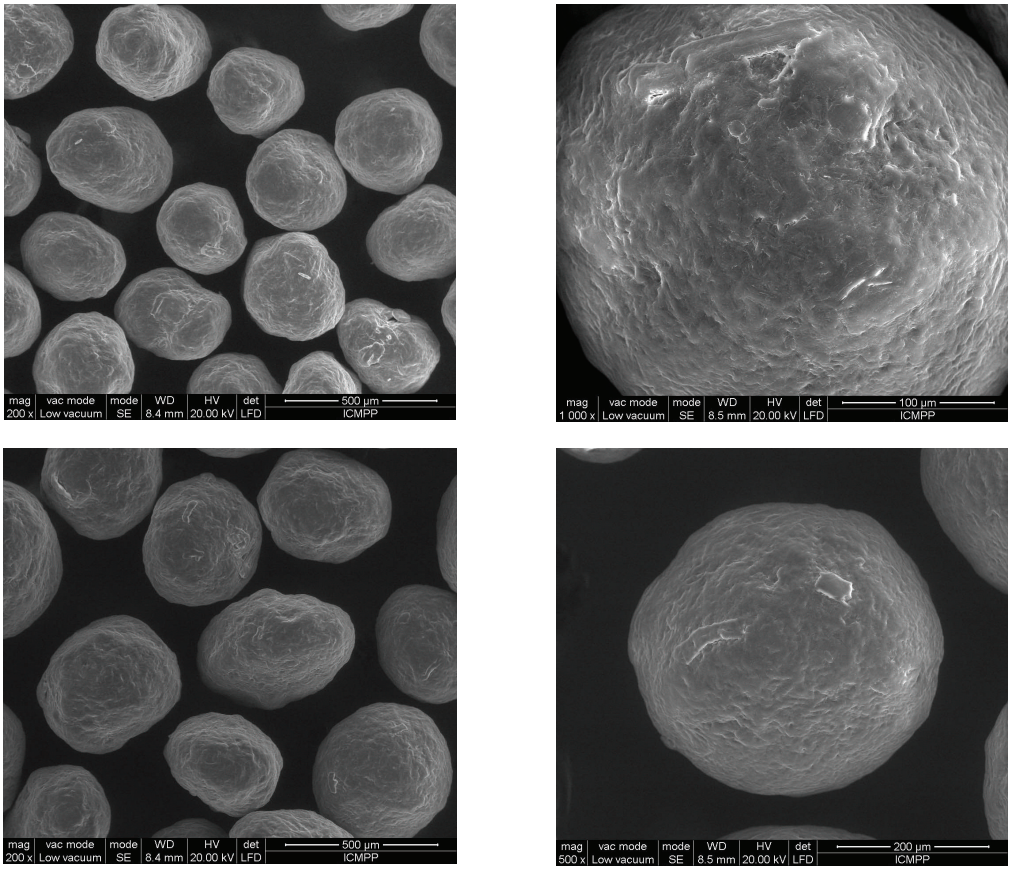


Fig. 2. ESEM images for Cellets 200 (top) and Cellets 350 (bottom)

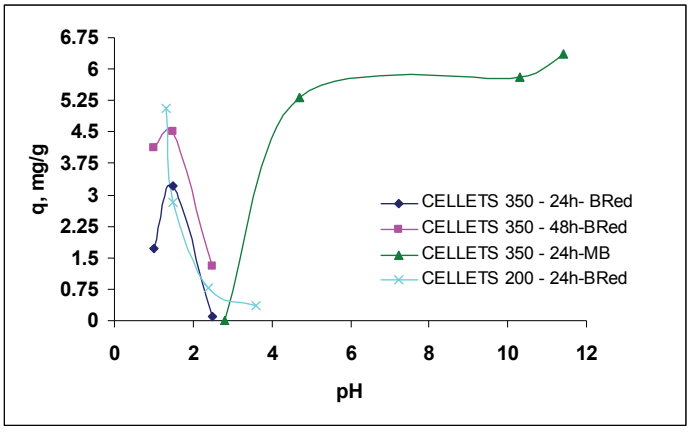
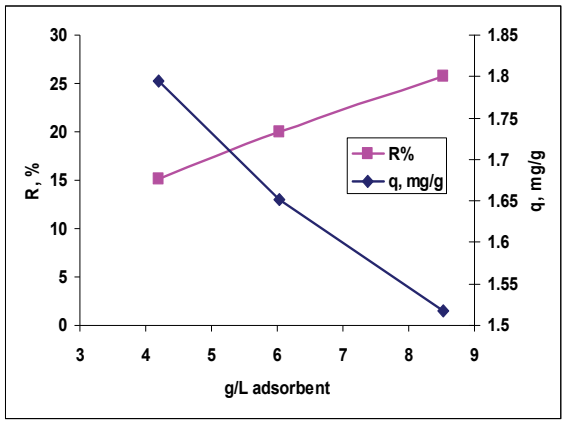
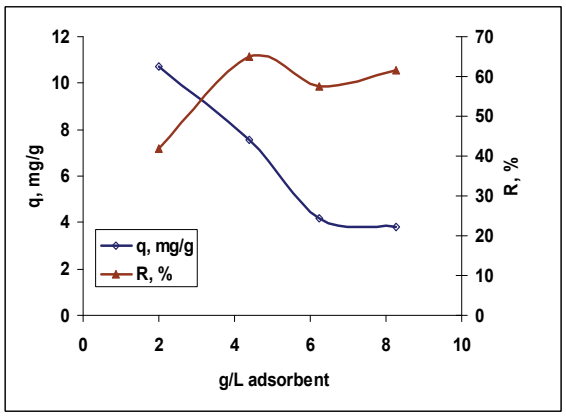


Fig. 3. Effect of pH and type of celluloses on the adsorption of BRed dye onto microcrystalline cellulose pellets: C_0= 50 mg/L; adsorbent dose- 2 g/L, 24 h, T = 25 ^{0}C and MB dye: C_0= 51.2 mg/L; adsorbent dose- 2 g/L, 24 h, T = 25 ^{0}C

The results presented in Fig. 4, show that the dye uptake decreases with the increase in adsorbent dose (from 1.682 mg/g to 1.517 mg/g for BRed and from 10.69 mg/g to 3.8 mg/g for MB). At the same time, the percent of dye removal increases from 7.26 % to 25.8 % in the case of MB, and from 41.76 % to 61.45 % in the case of BRed. The adsorbent dose which results in a higher removal percent is dependent on size of dye molecule: 2 g/L for Methylene Blue and 4 g /L Brilliant Red HE-3B.



(a)



(b)

Fig. 4. Effect of adsorbent dose on the adsorption of dye onto microcrystalline cellulose pellets Cellets 350: (a) BRed - C_0= 50 mg/L; pH = 1.5; 24 h, T = 25 ^{0}C; (b) MB - C_0= 51.2 mg/L; pH = 11.4; 24 h, T = 25 ^{0}C

Moreover, the results show a completely different behaviour of the celluloses toward the studied dyes. It is obvious that the material has a much greater affinity for MB dye compared with BRed dye, fact which could be explained by the reduction of dispersion inside the solid powder mass due to the dye steric effect and preservation of anionic dye with more voluminous molecule only at the outside of the adsorbent.

3.4. Effect of temperature and initial dye concentration on adsorption efficiency

Adsorption of Brilliant Red HE-3B dye onto cellulose powder is dependent on the solution temperature. In order to assess this influence, experiments were performed using aqueous solutions of dyes with concentration of 50 mg/L which were contacted with a dose of 4 g/L adsorbent materials at pH=1.5 and at three temperature values (2, 20 and 45 ^{0}C). The experiments reveal that the dyes adsorption onto microcrystalline cellulose beads depends on temperature value.

Adsorption capacity decreased with increase of temperature from 2.984 mg/L at 2^{0}C to 1.49 mg/L at 45 ^{0}C (for Brilliant Red HE-3B dye), suggesting an exothermic process in which the lower temperatures favors the dyes molecules diffusion in the internal porous structure of adsorbent.

3.5. Effect of contact time on adsorption efficiency

The influence of phases contact time on the dyes adsorption upon microcrystalline cellulose has been investigated for solution with 50 mg/L BRed dye, at pH =1.5 and 20 ^{0}C.

The experimental data from Figs. 3 and 5 show that dye removal rate has increased with time up to 2000 min, after that remaining constant as a result of the fact that the equilibrium was reached.

The extent of adsorption could be expressed by the fractional attainment of equilibrium, *F,* according to Eq. (3), where q_t and q_e (mg/g) are the amounts of dye adsorbed at time t and at equilibrium (24 h).

$$F = q_t/q_e \qquad (3)$$

The $t_{50\%}$ (F= 0.5) values correspond to about 250 min for an initial dye concentration of 50 mg/L.

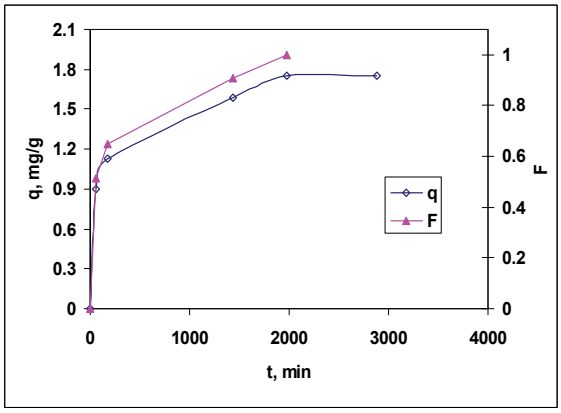


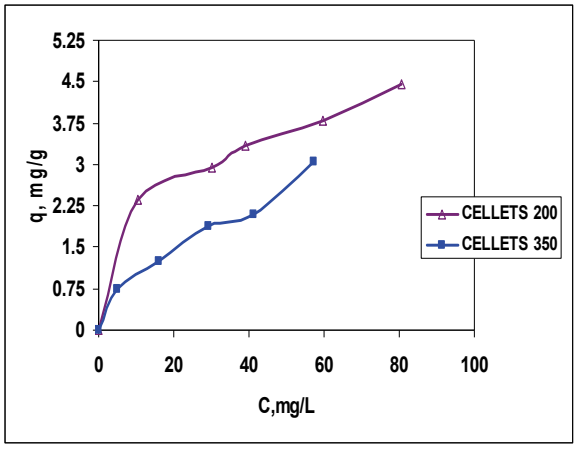
Fig. 5. Effect of contact time on BRed dye adsorption onto microcrystalline cellulose Cellets 350: C_0= 50 mg/L; 4g adsorbent/L, 24h, T = 20 ^{o}C

3.6. Effect of initial dye concentration, type of cellulose and dye structure on adsorption efficiency

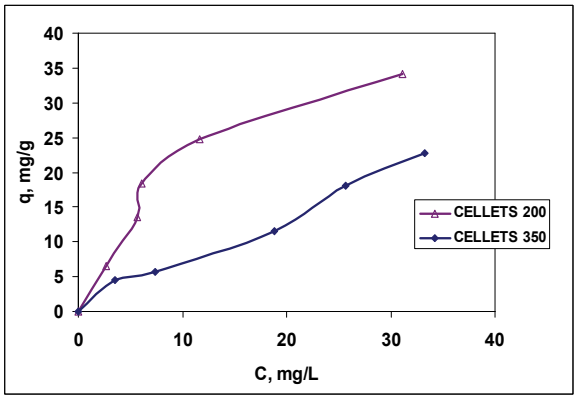
The adsorption capacity of cellulose beads for selected dyes was determined in solutions with different initial dyes concentrations and corresponding values of pH. The results presented in Fig. 6 a, b show that the dyes uptake (q, mg/g)

increases with the increase in initial dye concentration. Therefore, for BRed adsorption onto *Cellets* 350, the dye uptake has increased from 2.35 mg/g to 4.455 mg/g when the dye initial concentration increased from 8 to 100 mg/L. At the same time, increase in the initial MB dye concentration from 13.6 mg/L to 81.6 mg/L led to increase in adsorption capacity of the celluloses from 6.49 mg/g to 34.1 mg/g.

The relative low value of adsorption capacity for BRed may be attributed to the large size of dye molecule, which inhibits adsorption in the porous structure of adsorbent. Also, one can observe a different behavior of the two celluloses. This can be attributed to the different pore size: the smaller pore size in case of *Cellets* 200 provides a higher specific surface area (up to 75%) and therefore a higher adsorption capacity.



(a)



(b)

Fig. 6. The effect of initial dye concentration on dye adsorption on microcrystalline cellulose: (a) BRed - pH=1.5; adsorbent dose- 4 g/L, 24 h, T = 25 ^{0}C ; (b) MB - pH=11.5; adsorbent dose- 2 g/L, 24 h, T = 25 ^{0}C

The greater adsorption capacity of the adsorbent in the case of MB dye (Molecular weight = 320 g/moles) may be a consequence of smaller size of the dye molecule, compared with BRed (Molecular weight = 1460 g/mole), whose larger molecules inhibit the adsorption process onto the material with relatively small pores.

3.7. Characterization of celluloses after dyes adsorption

The FT-IR spectra of the original *Cellets* beads (C200 µm), but also of the beads modified with dyes (BRed and MB) are shown in Fig. 7. These spectra are different in a small extent, with representative peaks of the cellulosic structures located around 4000 – 2995 cm^{-1} (hydrogen-bonded OH stretching), and 2891 cm^{-1} (CH stretching mode). The differences are visible in the spectra of Cellets-MB and Cellets-BRed, especially in the range of 1000 – 2000 cm^{-1}, when a shoulder peak located around 1780 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 1645 cm^{-1}. These changes clearly evidenced the dye adsorption on the cellulose structure.

Microphotographs of the original and modified Cellets reveal that they have regular spherical shapes, with a compact structure within the size range of 200–350 µm, as Fig. 3 shows. The modified samples reveal insignificant modification as compared with the original materials, (Fig. 8). One can assume that the dyes structures have no effect on the cellulose structure.

Even at the surface level, there are not visible any damages or defects of the Cellets beads after adsorption, therefore the cellulosic materials might be suitable for being used for multiple adsorption stages.

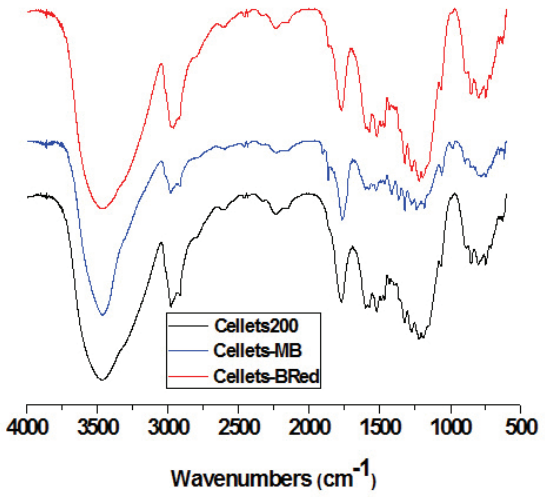


Fig. 7. FT-IR spectra of starting (C200 µm) and modified (B and R) materials (spectra were vertically shifted for better comparison)

4. Conclusions

Adsorption of both Brilliant Red HE-3B reactive dye and Methylene Blue cationic dye from aqueous environment onto microcrystalline cellulose was investigated as a function of initial solution pH, cellulose dose, dye concentration, temperature, contact time, dye structure and cellulose type.

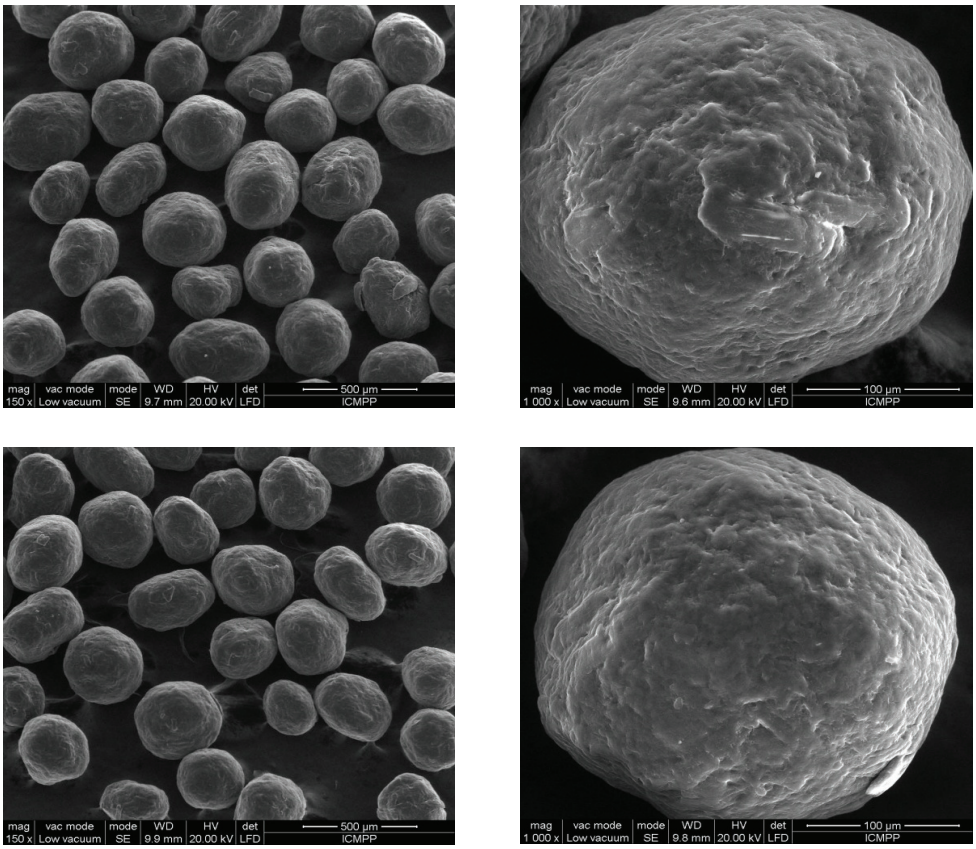


Fig. 8. ESEM images of MB adsorbed on Cellets 200 µm (top), and BRed adsorbed on Cellets 200 µm (bottom)

The results indicated that adsorption depends on the dye structure (molecular weight) and cellulose type (pore size distribution). Moreover, the adsorption capacity increases with increase in dye concentration, adsorbent dose, contact time and decreases with increase in temperature. The initial solution pH is an important factor and the selection of the optimum value depends upon the dye type: anionic or cationic.

The results lead to conclusion that the microcrystalline cellulose, cellets, can be considered as a new and valuable adsorbent for the removal of dyes with relatively low molecular weight from aqueous solutions. Further studies should be performed regarding the equilibrium, thermodynamics and kinetics of the adsorption process in order to determine the quantitative characteristic parameters, thermal effect, rate limiting step and to assess the mechanism of adsorption.

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