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MICROCRYSTALLINE CELLULOSE AS ADSORBENT FOR REMOVAL OF DYES FROM WASTEWATERS

BY

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Abstract. Batch adsorption studies were carried out for the adsorption of some dyes (Brilliant Red HE-3B, Orange 16, Rhodamine B and Methylene Blue) onto a new versatile cellulose-based product (Cellet), to be a new adsorbent. Studies were shown that the adsorption process is influenced by the chemical structure of dyes and experimental working conditions, *i.e.* pH, initial dye concentration, cellulose dose, phases contact time and temperature. The obtained results were shown that this cellulose-based product (Cellet) can be use as an adequate adsorbent in discoloration of textile effluents.

Keywords: adsorption; aqueous medium; microcrystalline cellulose; organic dye.

1. Introduction

Dyes are organic compounds used in a few industries to finish the final aspect of some commercialized products: textiles, papers, packages, shoes, cosmetics, etc. The wastewaters resulted from these processes contain variable

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loads of residual dyes which can modify clearly the esthetic aspect but also the composition and the character, caused in specific conditions from the decomposition process of dyes' molecules can result species with toxic character, even carcinogen (*i.e.* amines, benzidines).

There are many methods used to retain dyes from industrial effluents (oxidative destruction via UV/ozone treatment, photocatalytic degradation, extraction, precipitation-coagulation), choosen mainly in accordance with the concentration of dyes in the aquatic environment and destination of treated wastewater (Zaharia and Șuteu, 2012; Gupta *et al*., 2015; Zaharia *et al*., 2012; Sharma *et al*., 2016; Ravi *et al*., 2016). These methods have certain efficiency but relative high initial and operational costs, and for this reason, the *adsorption* is positioned as an attractive alternative (Ravi *et al*., 2016; Seow and Lim, 2016; Yagub *et al*., 2014; Chindoli *et al*., 2014; Dawood *et al*., 2014), being characterized by the following advantages: increasing of processing sensibility and selectivity; reducing of matrix effects and possibility of simultaneous achievement the pre-concentration and proper estimation. But a particular advantage of this method is given by the fact that it can be used as adsorbent in the wastewater treatment a great category of materials: materials with ion exchange properties, activated charcoal, celluloses, lignin-cellulose-based materials which are presented in nature, different kind of industrial or agriculture wastes (Zaharia and Șuteu, 2012; Chindoli *et al*., 2014; Dawood *et al*., 2014; Panic *et al.*, 2013; Adeyemo *et al*., 2017; Anastopoulos *et al*., 2017; Razi *et al*., 2017; Șuteu *et al*, 2014; Șuteu *et al*., 2015a; Zaharia and Șuteu, 2013).

Cellulose represents a great aspirant as efficient class of adsorptive materials, being one of the most abundant natural polysaccharides having a high specific surface area. Furthermore, it represents a renewable resource and, depending on the technological process used to produce them, celluloses may be found in such many forms and types to be utilized ranging from fibers, linters, microcrystalline powders, softwood pulp, bacterial cellulose and many others (Șuteu *et al*., 2015b; Silva *et al*., 2015).

A versatile cellulose product which combines different properties such as perfect sphericity, narrow particle size distribution, low friability, low solubility and inertness is represented by *Cellets*. *Cellets* are microcrystalline cellulose beads, produced exclusively by certified microcrystalline cellulose and purified water, without any additive. These possess high spherical starter cores with extreme stability and low friability. *Cellets* combine the known advantages of multiple dosage forms with the unique features of microcrystalline cellulose, being capable to be an efficient excipient respecting the increasing demanding regulatory needs for industrial processes. The manufacturing process of *Cellets* (under GMP-rules) is considered a new and very economic process.

That is why, the aim of this paper is to present a review of our results performed in study of a new versatile cellulose-based product (*Cellets 200*), which has interesting properties (*e.g.*, perfect sphericity, narrow particle size distribution, low friability, low solubility, and inertness), as adsorbent for removal of some dyes (Brilliant Red HE-3B, Methylene Blue, Orange 16, Rodhamine B) from their aqueous solutions. Operating variables (initial dye concentration, adsorbent dose, dye concentration, pH, temperature) were studied in batch conditions, in order to establish the adequate conditions of adsorption process onto *Cellets* and its mechanism in order to get high dyes removal performance and/or discoloration efficiency.

2. Experimental

Materials

Adsorbent material is represented by microcrystalline cellulose *Cellets 200*, donated by *Synthafarm*, Germany, being characterized by white or almost white colour, hard and nearly spherical particles (>85%, 200-355 µm), loss on drying ≤ 7.0%, bulk density of 0.80 ± 5%, pH of 5.0-7.0, degree of polymerization ≤ 350, insoluble in water, ethanol, acetone and toluene, diluted acids and sodium hydroxide solution (50 g/L). The cellulosic material reveals both weak base and acid components bounded to the same matrix, depending on the pH value, and they can remove cationic and/or anionic species (Șuteu *et al*., 2015b). The morphology and surface of *Cellets 200* pellets were previously investigated by means of ESEM microscopy and FTIR spectroscopy (Șuteu *et al*., 2015b). The four selected dyes were used as commercial salts and characterized in Table 1.

Table 1
Characterization of the Selected Dyes

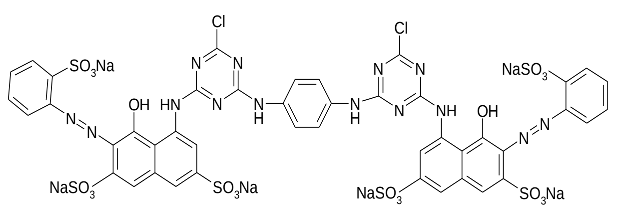
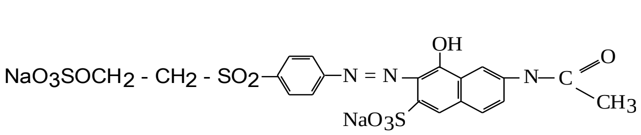
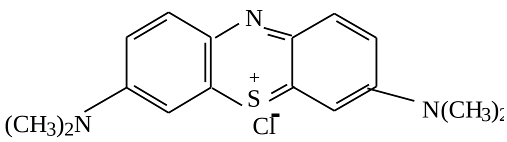
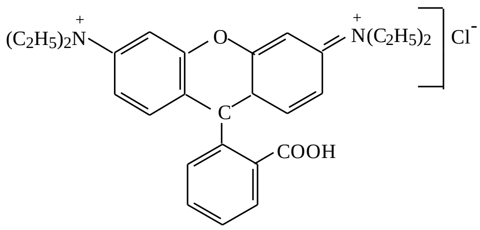
Structure	Characteristics
	**Brilliant Red HE-3B** (Reactive Red 120) C.I. 25810; anionic, bifunctional reactive dye; MW = 1463 g/mol λ_{max} = 530 nm; concentration of the stock solution = 500 mg/L
	**Orange 16** (Reactive anionic dye) C.I. 18097; anionic, MW = 735.6 g/mol; λ_{max} = 560 nm; concentration of the stock solution = 715 mg dye /L

Table 1
Continuation

Structure	Characteristics
	**Methylene Blue** (Basic Blue 9); C.I. 52015; cationic, phenothiazine dye; MW =319.85 g/mol; λ_{max} = 660 nm; Concentration of the stock solution=320 mg/L
	**Rhodamine B** (Basic Violet 10) ; C.I. 45170; xantenic dye, MW = 479.2 g/mol; λ_{max} = 550 nm; Concentration of the stock solution – 479 mg/L

Note. Abbreviations: Bred - Brilliant Red HE-3B; O16 - Orange 16; MB – Methylene Blue; RhB – Rhodamine B

Adsorption Experiments

The adsorption experiments were conducted in the batch system, where samples of 0.06-0.15 g of cellulose *Cellets 200* were contacted with 25 mL of aqueous dye solutions of established initial concentration in 150 mL Erlenmayer flasks placed in a thermostated bath at particular temperature. The initial solution pH was adjusted to the necessary value using HCl 1N or NaOH 1N solutions, and determined with a Radelkis OP-271 pH/Ion analyzer. After a contact time of 24 h, concentration of the dye in supernatant was determined spectrophotometrically with an UV-VIS Digital Spectrophotometer, model S 104D /WPA. The adsorption capacity of the adsorbent was evaluated by the Eq. (1).

$$q = \frac{C_0 - C}{G} \cdot V \text{ [mg of dye (g of cellulose)}^{-1}\text{]} \qquad (1)$$

where: C_0 and C are the initial and the equilibrium (residual) concentration of dye in solution, [mg L^{-1}], G is the amount of adsorbent, [g] and V is the volume of solution, [L].

3. Results and Discussions

For appreciation of the adsorptive potential of the selected material it will be used the *Cellets* as adsorbent for a series of dyes from aqueous solutions, thus being studied the influence of some operational parameters (aqueous solution pH, concentration of dye, dose of adsorbent, contact time between the phases, temperature) towards the adsoption process. Also, the establishment of some adequate/corresponding values for these operational parameters permits the continuing of the investigations by studying of the adsoption equilibrium and mechanism, process kinetics and establishing of the rate determining step and also process optimization.

Effect of solution pH, contact time and dye type

The solution pH is an extremely important operational parameter in the study of adsorption process, because its value depends both of the adsorption onto the adsorbent surface and of the availability in a certain ionic form of the species to be adsorbed. The effect of initial solution pH towards the adsorption of dyes onto cellulose *Cellets 200* was investigated, and the results are presented in Fig. 1. The variation of the amount of dye adsorbed (q, mg g^{-1}) as a function of initial pH of aqueous solution, presented in Fig. 1, shows that the anionic dye could be better retained from acidic media (around of pH ≤ 2) (Șuteu *et al*., 2015b;) and for cationic dyes, it is efficient the adsorption from slightly alkaline media.

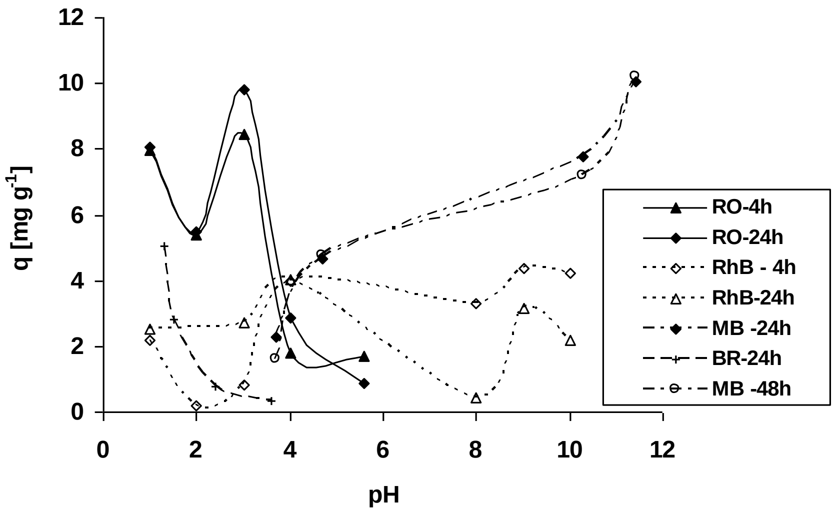


Fig. 1 – Effect of pH on the adsorption of dyes by microcrystalline cellulose Cellets 200: Bred - 50 mg L^{-1}, MB - 51.2 mg L^{-1}, RhB - 29.04 mg L^{-1}; cellulose dose- 2 g L^{-1}, 24 h of adsoption, T = 20^{0}C.

Also, regardless of the pH is observed that the amount of dye increases with contact time and depends on the type of dye (anionic or cationic) and how great is the colorant (for example red and orange dye).

Effect of adsorbent dose and contact time

It was investigated the effect of adsorbent dose, meaning of the microcrystalline cellulose pellets amount on the removal capacity of dyes from aqueous solutions. For this purpose, selecting a concentration for each dye and a favourable pH value, adsorption experiments were carried out using different adsorbent amounts. The phases were kept in contact for 5, or 24 hours. The results, presented in Fig. 2, showed that the amount of dyes adsorbed per mass unit of cellulose pellets decreases, indicating a relative lower adsorptive capacity of the cellulose pellets. An amount of 2.4 g adsorbent L^{-1} for RO and 4.4 g L^{-1} in case of RhB assures adequate adsorption capacity, and was chosen for subsequent experiments. Also, an increase in the amount of adsorbed dyes with the increase of phase contact time is also observed.

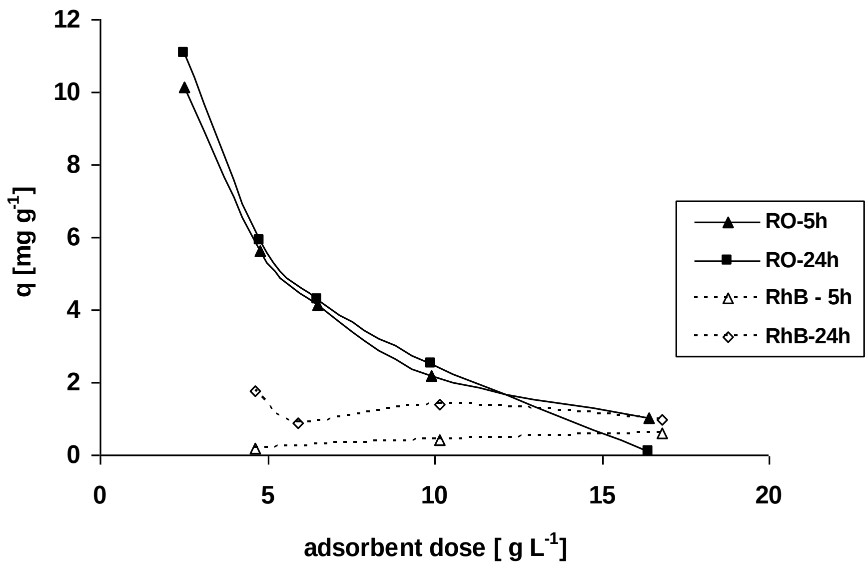


Fig. 2 – Effect of adsorbent dose on the adsorption of RO and RhB dyes onto microcrystalline cellulose pellets CELLETS 200: RO: C_0= 30.6 mg L^{-1}; pH = 3; 24 h; T = 25^{0}C; RhB: C_0=29.04 mg L^{-1}; pH=9; 24 h; T = 25^{0}C.

This behaviour may be correlated with the variation of the cellulose surface charge in function of the solution pH.

Effect of initial dye concentration and the studied dye type

The capacity of microcrystalline cellulose *Cellets 200* to retain by adsorption the anionic and cationic dyes at the favorable pH was determined from aqueous solutions of various initial dyes concentrations', and the results are presented in Fig. 3. It can observe an increase in adsorption capacity with the increase of the initial dyes concentration, but also a clear difference in the adsorption capacity behavior, depending on the dye type and its molecular weight. Thus, for example, between the two reactive dyes it was better retained Orange 16 dye, less voluminous and capable of shedding on the pore size of the adsorbent material.

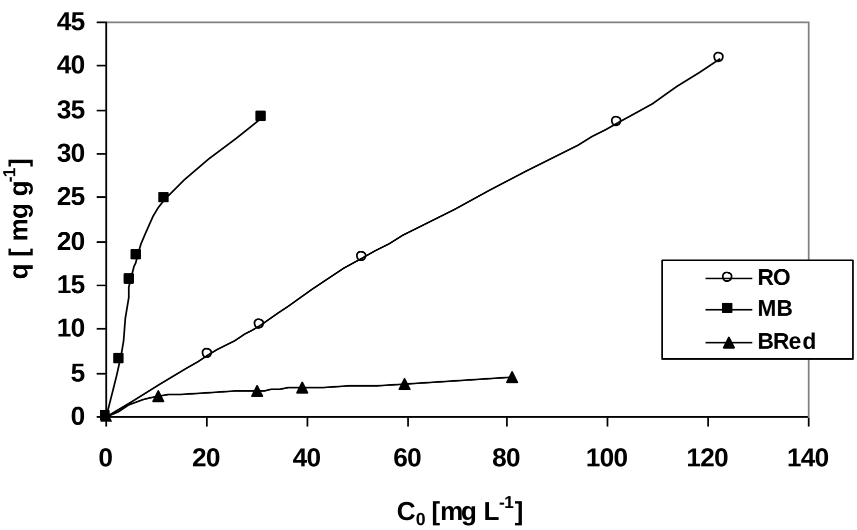


Fig. 3 – The effect of initial dye concentration on the adsorption by microcrystalline cellulose Cellets 200 of: MB- pH=11.5; adsorbent dose=2 g L^{-1}; RO- pH=2, adsorbent dose =2.4 g L^{-1}: Rred- pH=2, adsorbent dose=4 g L^{-1}, 24 h, T = 25^0C.

Effect of temperature

The adsorption of dyes onto microcrystalline cellulose pellets (*Cellets 200*) is temperature dependent. Decreased adsorption capacity with the temperature increasing for Brilliant Red HE-3B dye, suggests an exothermic process in which the lower temperatures favor the dyes' molecules diffusion in the internal porous structure of adsorbent (Fig. 4). Also, increasing the amount of dye adsorbed along with the increase in temperature (Fig. 4) suggests that adsorption is an endothermic process.

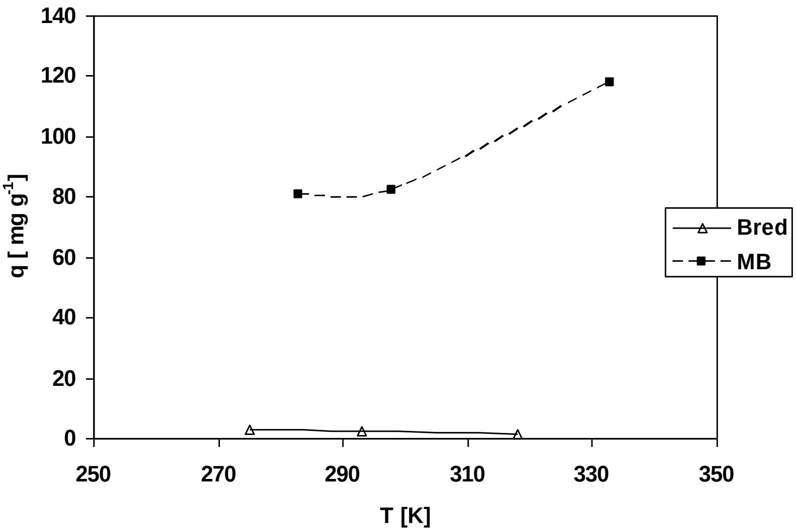


Fig. 4 – The effect of temperature on the adsorption of dyes: MB: C_O= 51.2 mg L^{-1}, pH=11.5; adsorbent dose =2 g L^{-1}, 24 h; Rred: C_O = 50 mg L^{-1}, pH=2, adsorbent dose = 4 g L^{-1}, 24 h.

3. Conclusions

The experimental results lead to a few final comments:

❑ The adsorption of Brilliant Red HE-3B and Orange 16 reactive dyes, Methylene Blue phenotiazine dye and Rodhamine B xanthenic dye from aqueous solutions was investigated using microcrystalline cellulose pellets *Cellets 200* as a new type of cellulose-based absorbent.

❑ The results indicated that the amount of adsorbed dyes depends of the dyes type, and solution pH; it increases with the increasing of initial dye concentration, phases contact time and adsorbent dose, and it decreases with the increasing of temperature.

❑ Also, these preliminary results suggest the possibility to use the microcrystalline cellulose pellets (*Cellets*) for adsorption of textile dyes with low molecular weight from aqueous solutions with good results in the case of low flows.

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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ADSORBANT PE BAZĂ DE CELULOZĂ MICROCRISTALINĂ PENTRU REŢINEREA COLORANŢILOR DIN APE UZATE

(Rezumat)

S-a studiat adsorbţia în condiţii statice a unor coloranţi (Brilliant Red HE-3B, Orange 16, Rhodamine B şi Methylene Blue) pe un nou tip de adsorbant pe bază de celuloză (Cellet). Studiile au arătat că procesul de adsorbţie este influenţat de structura chimică a coloranţilor şi condiţiile experimentale de lucru (pH, concentraţia iniţială a colorantului, doza de celuloză, timpul de contact al fazelor şi temperatura). Rezultatele obţinute sugerează că acest tip de material pe bază de celuloza (Cellet) poate fi utilizat în bune condiţii pentru decolorarea efluenţilor textili.