ORIGINAL PAPER

METHYLENE BLUE REMOVAL FROM RESIDUAL WATER USING FIR WOOD SAWDUST AS ADSORBENT

MIHAELA-LUMINITA UDREA[1], CARLA-CEZARINA PADURETU[1*],
IOANA-RALUCA SUICA-BUNGHEZ[1], SANDA-MARIA DONCEA[1],
RODICA-MARIANA ION[1,2]

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Abstract. *Methylene blue is generally used as dyeing agent in textile, printing and pharmaceutical industries, which leads to the obtaining of large amounts of wastewater. The purpose of this study is to remove methylene blue dye from aqueous solutions using fir wood sawdust waste as low cost biosorbent material. In order to evaluate the adsorption process, analyses for determination of micrometric properties, infrared spectroscopy, optical microscopy and colorimetry were performed. To increase the efficiency of the process and the adsorption surface, the fir wood sawdust was grinded and sieved. Some specific parameters were varied in the experimental part in order to study the influence of the adsorbent support dose, concentration, temperature, contact time, volume and stirring rate. The removal efficiency of methylene blue dye was further studied for evaluating the adsorption capacity of the fir wood sawdust.*

Keywords: *fir wood sawdust; methylene blue; micrometric properties; chromaticity diagram.*

1. INTRODUCTION

Methylene blue is also known as tetramethyl thionine chloride, and has the appearance of dark green crystals with bronze-like lustre [1]. Methylene blue is widely used as chemical indicator, and also for the production of dyes and biological dyes. As result, it leads to the obtaining of large amounts of residual water that contain highly coloured species and organic compounds from pharmaceutical, dyeing, textile or printing industries [2-4]. The coloured wastewater affects the appearance of water by reducing the light penetration, and negatively influences the photosynthesis activity of aquatic organisms due to the high content of metals, chlorides, nitrate and other dangerous compounds [5]. Generally, dyes are carcinogenic and mutagenic, having a great impact on the activities of plants and aquatic organisms in the marine environment [6]. The chemical structure of methylene blue is shown in Fig. 1a.

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[1] National Institute for Research and Development in Chemistry and Petrochemistry – ICECHIM, 060021 Bucharest, Romania.
**Corresponding author*: carla.paduretu@icechim.ro.
[2] Valahia University of Targoviste, Doctoral School of Materials Engineering, 130004 Targoviste, Romania.

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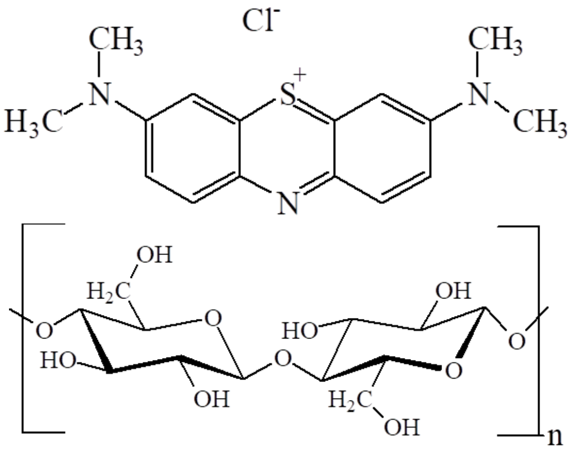

(a) (b)

Figure 1. Chemical structure of: (a) methylene blue [7] and (b) cellulose [8].

In this regard, several techniques for removing contaminants have been developed, such as flocculation, flotation, ion exchange, coagulation, etc. [9]. Among all of these methods, adsorption is a very effective, inexpensive and feasible separation technique in terms of initial cost and proved to be versatile concerning the use of materials in different removal processes [3, 10]. Activated carbon is widely used as adsorbent material to remove the organic and inorganic pollutants in water phase [2], and also showed good efficiency for removing dyes and pigments, but the main drawback of this material is the high price [11]. The goal is to replace the activated carbons with equally efficient, non conventional and low-cost adsorbent materials such as hull ash, sawdust, pine needle, sugarcane bagasse, eucalyptus bark and mango seed kernel powder [3, 12]. Moreover, new activated carbon adsorbents from lignocellulosic wastes of vegetable origin such as coffee grounds, melon seeds or orange peels were recently developed [13].

On the other hand, sawdust is one of the most attractive materials for removing pollutants from wastewater [14]. Large amounts of sawdust and wood residues are produced every year, generally from fir wood which is used for furniture and building materials [15]. Being a by-product of wood resulting from cutating, grinding, drilling, sanding and slicing wood with a saw or other tools, in many parts of the world the sawdust waste is subjected to dumping or burning [16]. Sawdust is a biodegradable material [17] that could be obtained from different sources, among lemon trees; palm and eucalyptus were previously reported [18].

Sawdust contains lignin, cellulose (Fig. 1b), hemicellulose and functional groups such as hydroxyl, carboxyl, amide and phenolic groups, which positively influence the adsorption process [17, 19].

Previously in other studies [11, 20], the hydrolysed oak sawdust calcium alginate composite, the cedar sawdust, pine sawdust, wheat straw and Provence cane showed high efficiency as adsorbent materials for removal of methylene blue dye from aqueous solutions.

The main purpose of this study is to evaluate the adsorption efficiency of the fir wood sawdust cellulosic waste which proved to be valuable as adsorbent material when using methylene blue as potential polluant agent. In the adsorption experiments, the retention efficiency of the methylene blue dye on the sawdust obtained from fir wood was followed. The adsorption experiments were carried out in order to analyze the effects of some experimental parameters (adsorbent support dose, concentration, temperature, contact time, volume and stirring rate) that have an important influence on the reduction of water pollution.

2. MATERIALS AND METHODS

2.1. MATERIALS

Methylene blue from Fluka Chemie AG (standard for microscopy analysis) was used in this study. The absorbance of methylene blue was measured at 640 nm fixed wavelength using a visible spectrophotometer from JKI (Shanghai Jingke Scientific Instrument Co., Ltd.), JK-VS-721N model, 010102 number. The infrared spectra were obtained using an instrument from Perkin Elmer Spectrum GX. The spectra were registered by ATR technique, with 32 scans at 4 cm^{-1} spectral resolution, in the range of 4000–600 cm^{-1}.

Colorimetric analysis was performed using an instrument from Konica Minolta, CR-410 model, under illuminant C and 2 degree standard observer conditions. The color analysis was processed with ColorCalculator software (v 7.77) by Osram Sylvania, Inc. (71 Cherry Hill Drive, Beverly, MA).

Fir wood sawdust was obtained from a local timber market and was minced by grinding operation. The sawdust was used in the experimental study without any treatments. The size of fir wood sawdust fibers was measured at 10x magnification using a Novex Microscope B-range from Euromex Microscopen BV. The instrument was equipped with a digital camera attached (Euromex – Holland, model CMEX DC.1300), and the microscope software (ImageFocus Professional, v. 2.0.0.0) allowed real-time image acquisition.

2.2. METHODS

The removal efficiency (R, %) of methylene blue dye was calculated with the following equation:

$$R(\%) = \frac{C_i - C_e}{C_i} \cdot 100 \qquad (1)$$

where: C_i = initial concentration (mg/L); C_e = equilibrium concentration (mg/L).

The micrometric properties (bulk density, tapped density) were measured in order to evaluate the flow properties of the fir wood sawdust powder before and after each adsorption treatment. Interparticulate interactions are less significant in free-flowing powders, and the bulk and tapped densities have close values. Poorer flowing materials usually exhibit greater interparticle interactions, as the existing bridges between particles often results in lower bulk density and a greater difference between the bulk and tapped densities [21]. The material was passed through a 12 mm sieve, and the obtained powder was further used for the measurements. A modified method of Walke et al. [22] was used. A centrifuge tube was placed on the top of a cylinder, and when the powder reached a specified mark of 1 cm^3, the mass of powder was measured as bulk density. The tapped density was evaluated by gently tapping the powder up to the specified mark until the powder was settled. The obtained values were inserted in the equations presented in Walke et al. [22] for calculation of compressibility index (Carr's index) and Hausner ratio, in order to evaluate the flowing properties of powders.

3. RESULTS AND DISCUSSION

3.1. INFLUENCE OF WORKING PARAMETERS ON THE DYE ADSORPTION PROCESS

3.1.1. Influence of the amount of adsorbent material

The adsorption process of methylene blue is easily influenced by the amount of adsorbent mass. In this study, a constant volume of 100 mL methylene blue solution of 100 mg/L concentration and different amounts of sawdust in the range of 0.4-2 g were used to evaluate the efficiency of the adsorption process. The obtained solutions were stirred for 30 minutes, filtered, and their absorbances were measured using the UV-Vis spectrophotometer at 640 nm wavelength. Fig. 2 shows that the removal efficiency has increased with the increase of the amount of fir wood sawdust, from 97 % (0.4 g sawdust) up to 99 % (2.0 g sawdust).

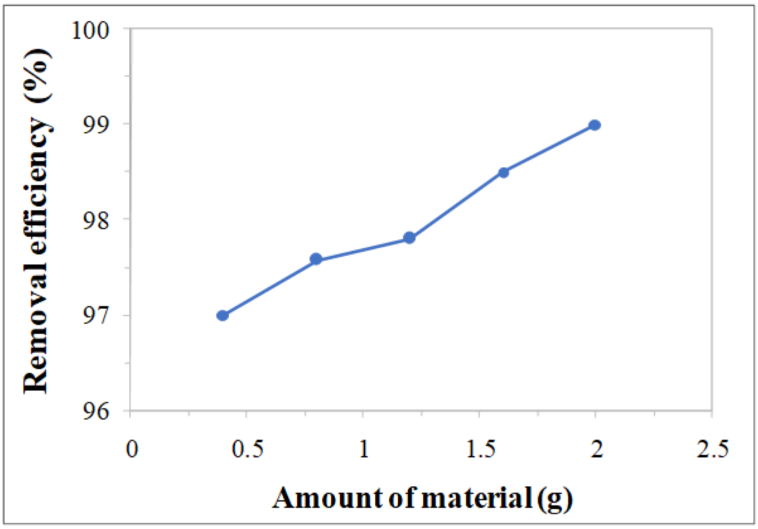

Figure 2. Removal efficiency of methylene blue dye removal on fir wood sawdust.

3.1.2. Influence of contact time

The effect of contact time on the removal of methylene blue dye when using fir wood sawdust as adsorbent material is given in Fig. 3 which shows the potential of the adsorbent material in the process of retaining the methylene blue dye due to the presence of lignocellulosic components (cellulose, hemicellulose and lignin) in the sawdust structure that are mainly responsible for the adsorption process [23]. The adsorption is achieved through the interaction of dyes and functional groups – mainly hydroxyl and carboxyl groups – of these polymers [23]. Usually, wood sawdust contains about 40-45 % cellulose, 20 % hemicellulose and 30 % lignin [24, 25]. For the first 30 minute the adsorption process is fast and the efficiency is almost 98.0 % for 0.4 g sawdust. A proportional increase of the contact time and the adsorption process was observed. The maximum time used (150 minutes) showed a retention about 99.5% of the dye.

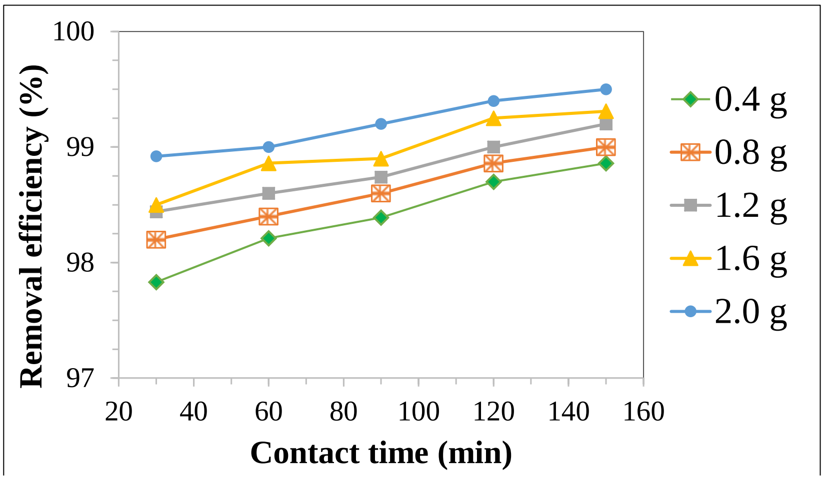

Figure 3. Methylene blue dye removal efficiency on fir wood sawdust by variation of the contact time.

3.1.3. Influence of dye concentration

When using a constant volume (100 mL) and different concentrations (20-100 mg/L) of methylene blue, the dye removal efficiency at different amounts of sawdust (0.4-2.0 g) decreases with the increase of the concentration. As seen in Fig. 4, the maximum retention value is 99.5 % and the minimum removal efficiency is 94.0 %. A reduction of the adsorption capacity per unit mass of adsorbent was observed with the increase of methylene blue concentration because all effective adsorption sites from the structure of wood sawdust became less available for adsorption as the concentration increased [2].

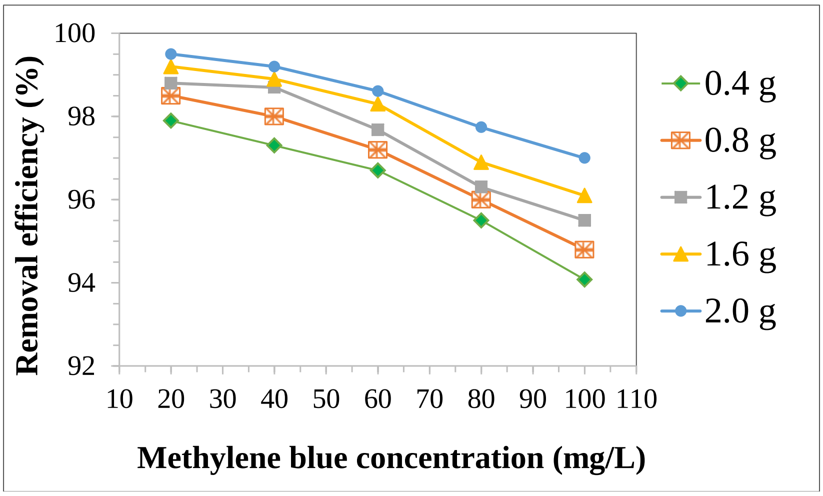

Figure 4. Methylene blue dye removal efficiency on fir wood sawdust using different concentrations of methylene blue.

3.1.4. Influence of temperature

The effect of temperature on the removal process of methylene blue dye from wastewater was evaluated. A constant concentration of 100 mg/L methylene blue solution and a constant volume of 100 mL dye on different adsorbent masses of sawdust (0.4-2 g) were used. The prepared solutions were stirred for 30 minutes on a stirring plate, at 300 rpm and at temperatures between 30-60°C.

After filtering the samples, the absorbances were measured on the UV-Vis single-beam spectrophotometer at $\lambda = 640$ nm.

Fig. 5 shows that the percentage of elimination decreases with increasing temperature. Temperature is an important physical-chemical parameter in the adsorption process of dyes. As the temperature increases, the adsorption capacity of the adsorbent material (fir wood sawdust) is subjected to changes [26].

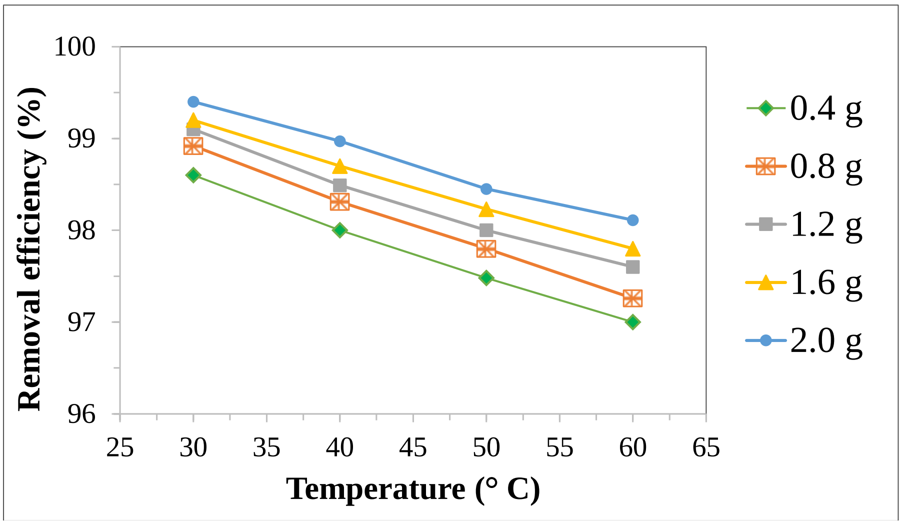

Figure 5. Methylene blue dye removal efficiency on fir wood sawdust by variation of temperature.

3.1.5. Influence of stirring speed

The stirring rate is an important parameter in the adsorption process of dyes. To determine the effect of the stirring speed on the sawdust retention efficiency, different quantitites of fir wood sawdust (0.4-2.0 g) were used, and 100 mL of dye solution. The samples were stirred for 30 minutes, in the range of 300 up to 600 rot/min. After filtering the samples, the absorbances were read on UV-Vis single-beam spectrophotometer. It has been observed that the retention efficiency increases with increasing the stirring rate due to better homogenization of the solution (Fig. 6).

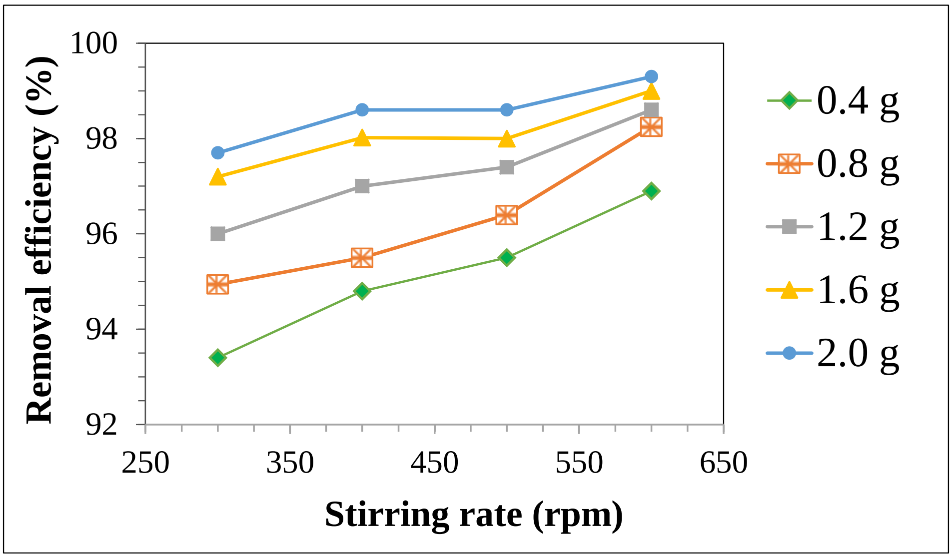

Figure 6. Methylene blue dye removal efficiency on fir wood sawdust by variation of the stirring rate.

3.2. MICROMETRIC PROPERTIES

The results obtained for the evaluation of micrometric properties are presented in Table 1, as Hausner ratio and Carr index, which establish the flow properties of powders. If the Hausner ratio is smaller than 1.25, the powder is free flowing, while a larger value than 1.25 indicates poor flow ability [22]. As seen in Table 1, the untreated fir wood sawdust and sample 1 indicate that the powders are free flowing. The retention capacity increases with the methylene blue concentration and forms aggregates into the powder. As result, the samples 2 up to 5 present higher values than 1.25 for the Hausner ratio, therefore low flow capacities are exhibited. Samples from 1 to 5 consisted of constant 100 mL solution of 100 mg/L methylene blue concentration, but different masses of fir wood sawdust were used: 0.4 g; 0.8 g; 1.2 g; 1.6 g and 2.0 g.

Table 1. Micrometric properties of powders for sawdust and methylene blue adsorbed on sawdust.

Sample	**Carr index (%)**	**Hausner ratio**
Fir wood sawdust	**14.90 ± 5.23**	**1.18 ± 0.07**
Sample 1	**12.60 ± 6.47**	**1.15 ± 0.09**
Sample 2	26.50 ± 5.12	1.36 ± 0.09
Sample 3	23.65 ± 3.26	1.31 ± 0.06
Sample 4	27.98 ± 1.40	1.39 ± 0.03
Sample 5	31.84 ± 3.62	1.47 ± 0.08

The compressibility index, known as the Carr index, with values between 5 and 15% is an indicator of powders with excellent flow properties, between 12 and 16% the flow properties are good, from 18 to 21% are fair, while values higher than 23% indicate poor flow capacity of powders [21, 22]. The sample 2 up to sample 5 indicate poor flow ability, while the untreated fir wood sawdust and the sample 1 indicate excellent flow ability. This is an important parameter to be determined for a further reuse of the material by desorption process.

3.3. INFRARED SPECTROSCOPY

The most representative transmission bands were identified in the wavenumber region of 960-630 cm^{-1}, and the obtained spectra are shown in Fig. 7.

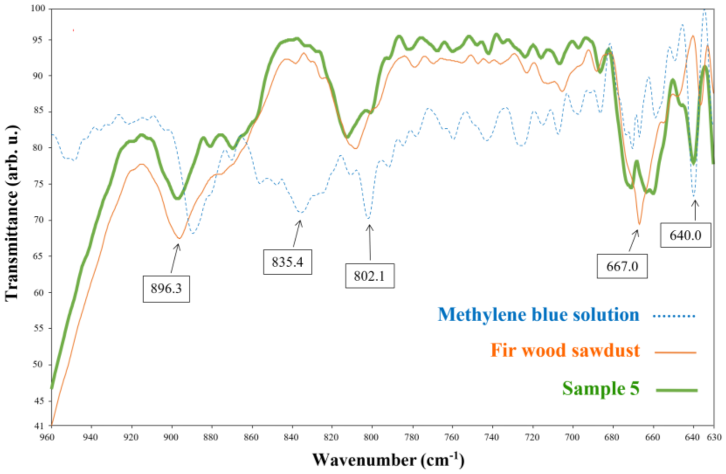

Figure 7. Infrared spectra of methylene blue solution, untreated sawdust and sawdust after adsorption of methylene blue.

Specific bands characteristic to the functional groups of aromatics in cellulose [27], and bonded C-C groups in sawdust were identified at 897 cm^{-1} and 896 cm^{-1} [28]. The transmission bands under 720 cm^{-1} are assigned to C-H groups in cellulose [29]. The sawdust spectrum showed at 667 cm^{-1} a specific band for C-H groups [29]; for sample 5 this band is splitted into two bands (671 and 660 cm^{-1}) that are found at the same wavenumbers in the methylene blue solution spectrum, and are specific for the skeleton vibration mode of C–S–C [30]. This shows an interaction between sawdust and the methylene blue dye by adsorption process.

3.4. OPTICAL MICROSCOPY

Optical microscopy analysis was used to study the surface morphology of the adsorbent material before and after the adsorption process. The Figs. 8a-d show the particle size distribution at 10x magnification. The measured sawdust fibers presented approximate widths between 100 μm and 1200 μm. Cellulose from fir wood sawdust presents a linear arrangement of macromolecules that forms fibrils with highly ordered crystalline and less ordered amorphous regions [31].

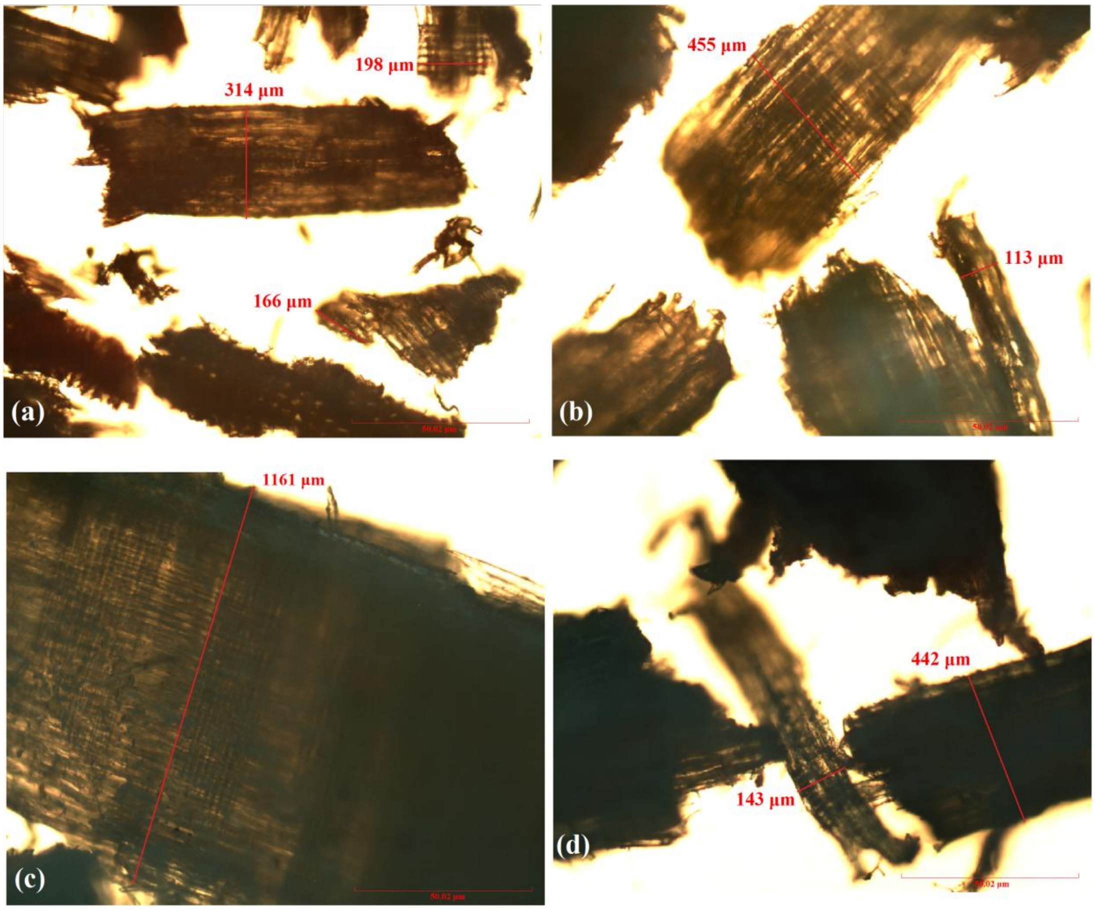

Figure 8. Microscopic evaluation at 10x magnification of methylene blue adsorbed on different masses of sawdust: (a) untreated fir wood sawdust, (b) sample 1, (c) sample 3, and (d) sample 5.

3.5. *COLORIMETRIC ANALYSIS*

The colorimetric analysis was performed for dried fir wood sawdust samples and the obtained results are presented in Table 2. Defined as a three-dimensional color space system, CIE L*a*b* separates the color information into lightness-darkness (L*), red-green (a*) and yellow-blue axes (b*) [32]. The visual appereance of fir wood sawdust showed a yellow tint, which is in agreement with the result obtained for the untreated sawdust. As the mass of sawdust increases, the yellowness index decreases. Negative values of yellowness index does not estimate yellowness, as the yellowness index presents positive values to yellowish objects, and negative values to bluish objects [33]. Moreover, the hue values in Table 2 show a shift toward green-blue as the sawdust mass increase. The yellowness index was calculated using the formula presented in Hirschler [34] and ASTM E313-05 [35], under illuminant C and 2° standard color observer conditions (CIE 1931).

Table 2. Colorimetric parameters of the obtained sawdust samples.

Sample	L*	a*	b*	C*	h	Yellowness index [%]
Sawdust	79.49 ± 0.25	5.12 ± 0.15	17.20 ± 0.84	17.94 ± 0.85	73.43 ± 0.33	40.01 ± 1.77
Sample 1	79.00 ± 0.08	-2.60 ± 0.03	8.62 ± 0.06	9.01 ± 0.06	106.78 ± 0.08	16.38 ± 0.09
Sample 2	77.71 ± 0.34	-5.35 ± 0.08	7.72 ± 0.14	9.39 ± 0.17	124.73 ± 0.05	12.20 ± 0.26
Sample 3	79.52 ± 0.47	-4.87 ± 0.21	2.48 ± 0.14	5.46 ± 0.24	152.98 ± 0.33	1.19 ± 0.12
Sample 4	79.87 ± 0.12	-4.72 ± 0.06	0.93 ± 0.01	4.82 ± 0.06	163.63 ± 0.04	-2.14 ± 0.01
Sample 5	70.46 ± 0.07	-12.29 ± 0.04	-3.61 ± 0.02	12.81 ± 0.04	168.84 ± 0.04	-3.10 ± 0.01

In Fig. 9 the samples before and after the adsorption process are shown. The untreated sawdust is yellow and slightly red, while the samples with methylene blue are slightly green and blue, according to the results obtained for the yellowness indices.

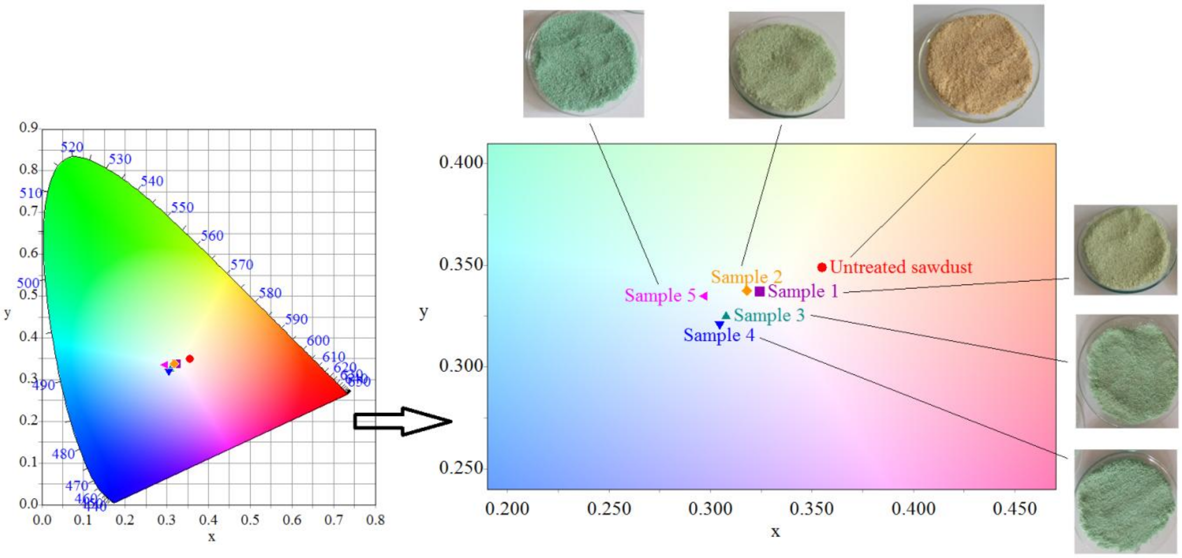

Figure 9. Chromaticity diagram of methylene blue adsorbed by fir wood sawdust with respect to the sawdust mass.

The obtained results were plotted in the chromaticity diagram CIE 1931 2° (Fig. 9). With the increase of sawdust mass, a shift from yellow-red to green-blue was noticed. This information is valuable because the chromaticity diagram shows a global vizualization for a further potential desorption process (i.e., decoloration of materials) or for the recovery of materials.

4. CONCLUSIONS

The fir wood sawdust, which was used as cellulosic waste, showed good adsorption properties of methylene blue dye. This study focused on some specific parameters influencing the adsorption process: the adsorbent support dose, concentration, temperature, contact time, volume and stirring rate. The adsorption experiments presented good retention capacities in most of the experimental stages. A proportional relation was noticed between the adsorption capacity and the adsorbent mass: with the increase of the adsorbent mass, the retention capacity of methylene blue dye, also increased from 94 % up to almost 100 %.

The infrared spectroscopy allowed to identify the specific transmission bands of methylene blue solution and the untreated sawdust, and also the interaction between these materials. Optical microscopy showed particle sizes between approximately 100 and 1200 μm, with sawdust fibers having a paralell arrangement. As the mass of adsorbent dose increases, the colorimetric analysis showed a more intense color adsorbed on the surface of sawdust. The calculated yellowness indices were found in agreement with the macroscopic observations of all samples. Moreover, the images aquired on the optical microscope indicated that all effective adsorption sites from the structure of wood sawdust became less available for adsorption as the mass of sawdust increased; as the mass increased, darker areas were observed suggesting an uniformity of the adsorption process.

In this experimental study, it was shown that methylene blue dye can be succesfully adsorbed on the surface of untreated fir wood sawdust with high efficiency for removing the dye dispersed in aqueous solution.

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