ORIGINAL PAPER

MODELLING OF METHYLENE BLUE DYE ADSORPTION ON BEECH AND FIR WOOD SAWDUST AS ADSORBENT SUPPORT MATERIALS

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Abstract. *The purpose of this study is to find new alternative methods for removing dyes (methylene blue dye) regularly present in wastewater by using adsorbent materials obtained from vegetable waste (beech and fir wood sawdust) due to their low-cost adsorbent properties. The used dye used as model was methylene blue and the effect of the initial concentration (30 - 50 mg/L), the adsorbent dose of the support material (2-10 g) and the effect of the initial pH of the solution (3, 5, 7, 9, and 11) were investigated. The optimization of the volume and flow rate was investigated, too. The maximum efficiency of removal of methylene blue dye present in aqueous environments it was 97%. The mathematical modelling of the Langmuir, Freundlich and Temkin adsorption isotherms using the experimental results, was used and properly discussed, demonstrating that Langmuir model is the most suitable for the experimental results.*

Keywords: *wood sawdust, dyes, adsorption isotherms.*

1. INTRODUCTION

Nowadays, the reduction of environmental pollution has drawn attention due to the growing of industrialization processes [1]. Without the correct treatment, industrial processes generate significant quantities of wastewater containing different pollutants [2], such as: benzene, toluene [3], phenol [4], pesticides [5] and textile dyes [6], accumulating in various species while their discharges are increasing in the environment [7]. The discharges pose great concern due to their toxicity [8]. It is very difficult to remove dyes that are present in effluents since they do not biodegrade easily [9].

Waste waters contain many potentially noxious elements and compounds, such as: suspended solids, organic matter and heavy metals. The presence of unfixed dyes is considered to be one of the major environmental problems we face nowadays. Therefore, the colouring agents in dyes need to be removed before evacuation [10].

Dyes are usually used in the industry sector due to their synthetic origin and aromatic functional groups which make them more stable in environmental conditions and more difficult to biodegrade. The problem of water and wastewater decontamination has increased with the rapid industrialization such as: dyestuff, textiles, leather, paper, plastic, carpet and wool industry [11, 12]. The unloading of dyes in the environment [13] has a mutagenic,

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teratogenic and carcinogenic effect on the health of both human life and aquatic species, having a great impact on flora and fauna ecosystem [14].

Approximately a 1000000 tones of dyes are produced every year [15]. The textile industry uses important quantities of dyes in the industrial process, a majority of these are represented by direct, reactive, acid and basic dyes [16]. Due to the low biodegradability of dyes, a conventional biological treatment operation is not very effective in wastewater treating [17]. The removal of dyes and the presence of the volatile suspensions has become a current issue.

For removing dyes from the industrial effluents many techniques are regularly used such as: flotation [18], coagulation [19], membrane separation [20], ion exchange [21], oxidation [22], biosorption [23], precipitation [1]. The whole batch of methods is quite expensive and no very efficient. Compared with other methods, adsorption on sawdust is considered an attractive option in treating the industrial outflow [24], due to its simplicity and efficiency for removing pollutants [25, 26]. Adsorption technology using suitable adsorbents plays an important role in the removal process of synthetic dyes [27]. Several adsorbents are known to be capable of removing dyes from industrial effluents [28].

In accordance to literature studies, there are many types of natural adsorbent support materials that are regularly used in adsorption experiments for removal of polluting species, such as: activated bituminous coal [16], clay [29] leaf powder [30], garlic peel [31], hazelnut, peanut, rice husk [22], coconut husk [32], bagasse pith [33], sawdust [2], fly ash, lignite [34]; these have been found to be highly effective, cheap and eco-friendly. In the adsorption process, activated carbon is most widely used due to its surface area, particle size and micro-porous structure [35]. Among them, sawdust is one of the main sources of biomass for the production of solid fuels for generating warmth in both centralized systems, in cogeneration installations and in a decentralized system for residential use, and also in classic kettle for thermal energy generation [36].

The lignin cellulosic biomass behaves as a good effective adsorbent [37], knowing that cellulose was used in wood fiber as an energy source for constructed materials [38]. Due to the presence of cellulose and lignin in the sawdust structure, this material has a high adsorption capacity. Cellulose is the most abundant natural organic polymer and its structure is crystalline and simple. Adsorbents containing high levels of cellulose can irreversibly adsorb basic dyes through Coulombic attraction since a negative surface charge is acquired by cellulose on contact with water [39].

The aim of this studies was focuses to investigate the potential of wood sawdust, as a viable substitute for treatment and removal of methylene blue dye from aqueous solutions by adsorption mechanism [40]. This study deals with the removal efficacy of untreated fir and beech wood sawdust at various concentrations of dyes and mathematical models of Langmuir, Freundlich and Temkin have been used in order to evaluate the adsorption and mechanism responsible for these processes.

2. MATERIALS AND METHODS

2.1. MATERIALS

Methylene blue dye (with a molecular weight of 319.85 g/mol) supplied by Fluka Chemie AG, CH-9470 Buchs was used in this study (Fig. 1). The solutions at the desired concentrations were prepared with distilled water [41]. The minimum concentration used in the study was 30 mg/L, and the maximum was 150 mg/L.

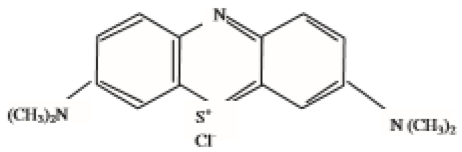

Figure 1. Chemical structure of methylene blue dye.

For preparing a stock solution of 1000 mg/L, a fixed quantity of methylene blue dye was weighed, dissolved in a volumetric flask and diluted up to the mark with distilled water.

A series of standard solutions was prepared with the initial concentrations of MB dye of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L for making the calibration curve and we observed that the correlation coefficient has the value R^2 = 0.9996 (Fig. 2). The absorbance was measured using a UV-Vis spectrophotometer at the wavelength of 590 nm.

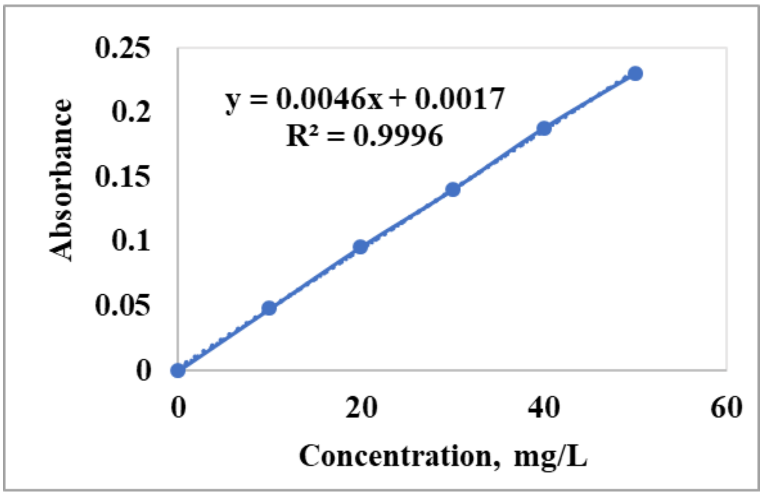

Figure 2. Calibration curve of methylene blue dye.

The sawdust was obtained by a grinding operation. The particle size depends on the type of wood sawdust and the size of the blade [48]. Sawdust is a waste product of the timber industry [49]. It can be used as a low-cost material due to its lignocellulosic composition, stability in environmental conditions and its difficulty to biodegrade [50-52]. It was discovered that sawdust has a high potential for the removal of organic and inorganic dyes.

In order to carry out the assessment of the adsorption process, the untreated fir and beech wood sawdust was used. The adsorbent materials are reduced to small particles by a grinding operation and then used in the experimental studies.

A column study was used for carrying out the adsorption experiments. The sawdust was inserted into a column and distilled water was passed through to the column in order to eliminate all the volatile stuff that can be found in the wood substrate. For the treatment of the adsorbent material, glass wool was firstly ushered into a column that functions as a support for the material. The experiments were carried out at room temperature.

2.2. METHODS

The adsorption experiments were carried out in a column in order to analyze the effects of some experimental parameters that are necessary for the reduction of pollution. The adsorption method relies on the amount of adsorbent (2-10 g), the effect of the flow rate (5-25 mL/min), the optimization of the maximum volume necessary for saturation of sawdust, the initial dye concentration and the influence of the pH solution on the removal of methylene blue. The pH was adjusted with HCl and NaOH solutions. The volume of dye solution which was passed through the column was 100 mL with a flow rate of 10 mL/min. The experimental study was maintained at ambient temperature.

In order to carry out the experimental part, firstly, an initial dye concentration of 150 mg/L was prepared in a volumetric flask of 100 mL. The dye solution was passed through to the column, and five fractions were collected, the volume of each fraction was 15 mL with a flow rate of 10 mL/min.

The absorbance was measured and the removal efficiency (*%R*) and adsorption capacity (q_e) of methylene blue dye was calculated with the following equations:

$$\%R = C_o - C_e : C_o \times 100 \quad (1)$$

$$q_e = (C_o - C_e) \times (V : W) \quad (2)$$

where:

C_o is the initial concentration of methylene blue dye;
C_e is the equilibrium concentration of methylene blue dye;
V is the volume in L;
W is the mass of adsorbent in g.

3. RESULTS AND DISCUSSION

This study was carried out in order to find new alternative methods for removing dyes used in the industry sector, and to study the consequences of their discharge in water and wastewater. The results demonstrated that the efficiency of removal increased from the 65 % to 97 %. The use of a raw conventional material was found to be effective for the adsorption mechanism. For the removal of organic dyes, it is necessary to use a low concentration. The particle size of the sawdust plays an important role in the experiments that were carried out.

The effect of the flow rate on the removal of methylene blue dye

Methylene blue (MB), also known as tetramethylthionine chloride is a cationic dye, one of the most widely used pigments in the textile industry for dyeing leather, silk and paper [42]. The toxic effects of methylene blue include permanent breathing difficulties, gastritis, vomiting, mental confusion, etcetera [43, 44]. Methylene blue is also used in microbiology, surgery, diagnostics [45, 46] and as a sensitizer in the photo-oxidation of organic pollutants [47]. In this step, the removal efficiency of methylene blue dye decreased with increasing the flow rate. 10 grams of untreated fir and beech wood sawdust are introduced in the adsorption column, with an initial concentration of 150 mg/L, and the flow rate is between 5 to 25 mL/min. Thus, molecules of methylene blue dye interact with the sawdust composition through the adsorption mechanism. Fig. 3 shows that the maximum capacity of removal efficiency of the sawdust is nearly 98 %. The small particles of the sawdust are necessary to absorbs dye molecules by retention of the polluting species. When the flow rate was 5 mL/min the dye solution interacts with the active surface of the adsorbent support material. 10 g of sawdust was selected to be the maximum natural vegetable waste quantity necessary to carry out the adsorption experiments.

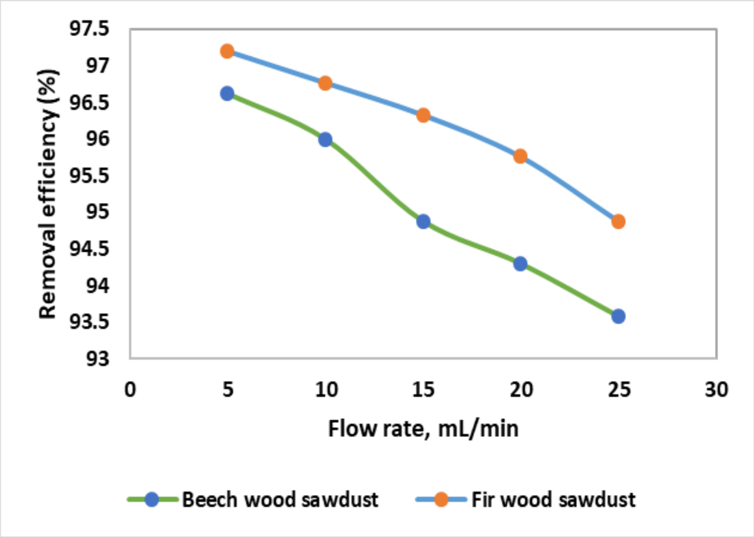

Figure 3. Effect of flow rate on the removal of methylene blue dye by adsorption.

Optimization of the volume for the removal of methylene blue dye

In order to find the optimum conditions for achieving the adsorption process a volume of 300 mL of methylene blue dye was inserted into the adsorption column to study the retention capacity of sawdust. The column was filled up with 10 grams of sawdust (untreated fir and beech wood sawdust). It was observed that sawdust was saturated after adding 200 mL. The volume saturation occurred once there were no more sites to absorb the dye molecules.

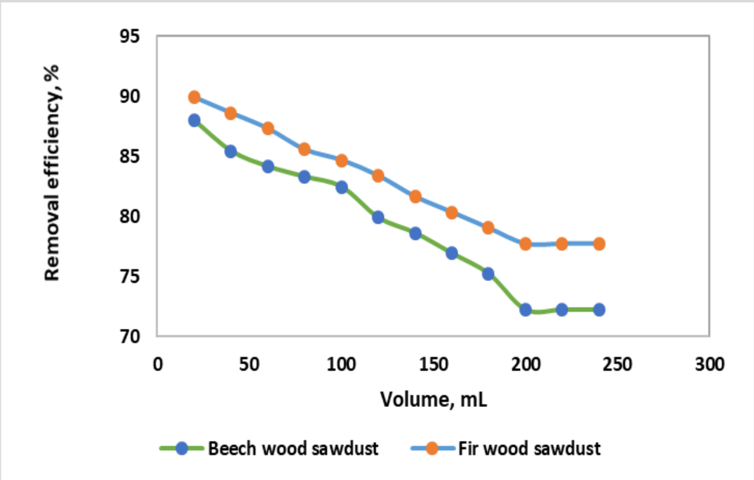

Figure 4. Optimization of the volume of methylene blue dye by adsorption.

The adsorption of untreated sawdust was considered completed when the saturated volume of pollutant species reaches the maximum threshold of 200 mL.The volume of each fraction was 20 mL, with a flow rate of 10 mL/min and the initial dye concentration was 150 mg/L. Fig. 4 points out that the removal efficiency decreased with the increasing of the volume. The removal percentage decreased from almost 90 % to 72 %.

The effect of the solution pH on the removal of methylene blue dye by adsorption

The dye removal capacity present in the aqueous middle also depends on the pH of the solution. The pH of methylene blue dye solution was modified with acidic and basic solutions. Fig. 5 shows the removal efficiency of methylene blue dye by using two different species of sawdust. A series of solutions of methylene blue dye were prepared at different pH values (3, 5, 7, 9, and 11). The pH was modified with HCl and NaOH solutions 0.1 n. The volume of dye, the initial concentration and the flow rate were maintained at constant values. The mass of adsorbent varied of the 2 grams to 10 grams. A significant increase of the pH of the solution will lead to increased removal efficiency; the value of the pH depends on the substrate nature of the support material. It was observed that the removal efficiency increased due to the modification of the pH value. For pH of 11, the removal capacity was 94.45 %. The maximum removal efficiency has been reached at the maximum pH value.

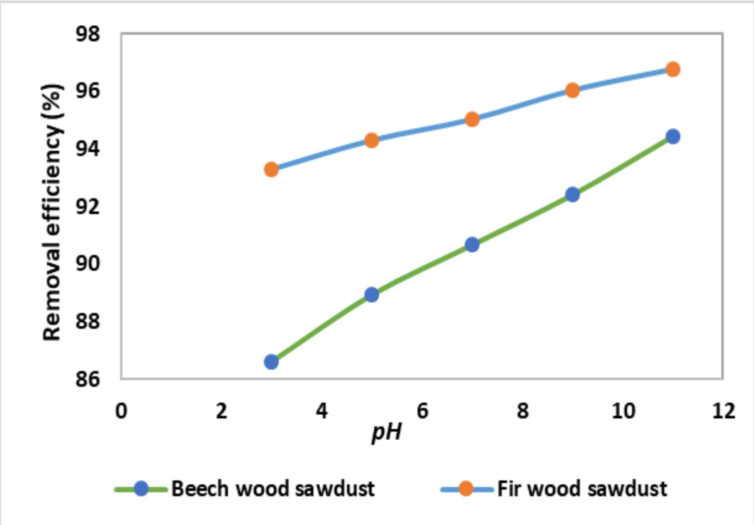

Figure 5. Effect of the pH solution on the removal of methylene blue dye.

The effect of the adsorbent amount

The effect of the amount of adsorbent for the removal of methylene blue dye was studied by placing different quantities of wood sawdust in an adsorption column. Fig. 6 shows that the removal percentage increased by increasing the amount of adsorbent. The percent of removed dye present in aqueous solution increased up to 87 % when the adsorbent dose is 2 g and up to 96 % when the amount of adsorbent is 10 g. The continued increase of the material's quantity does not completely retain the dye because concentration is directly proportional with the amount of adsorbent. The initial dye concentration was maintained constant at 150 mg/L and the volume of dye solution which passed through the column was 100 mL. Five fractions were collected, with a flow rate of 10 mL/min, and the volume of each fraction was 15 mL.

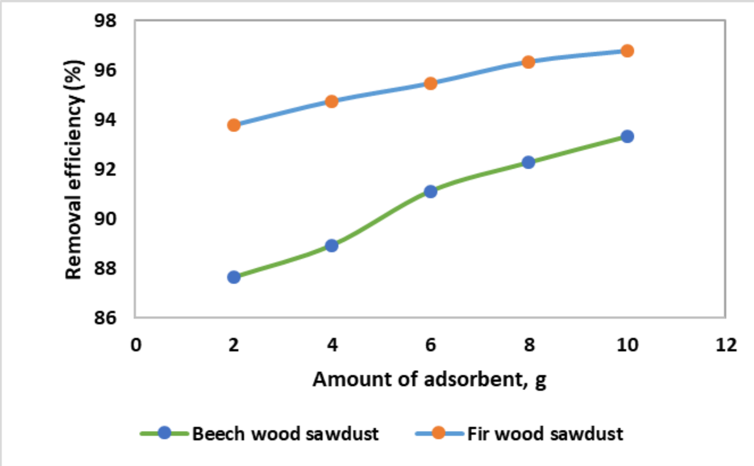

Figure 6. Effect of the amount of adsorbent on the removal of methylene blue dye.

THE EFFECT OF THE INITIAL DYE CONCENTRATION ON THE REMOVAL OF METHYLENE BLUE DYE.

Removal efficiency depends of the initial concentration of the dye solution. The polluting species interacts with the adsorbent due to the contact of methylene blue dye with the adsorbent's surface. The initial dye concentration varied from 30 mg/L to 50 mg/L, with a constant mass of wood sawdust of 2 g. It was observed that the removal efficiency decreased with the increase of the initial concentration of the solution, Fig. 7. As it has been observed, a high concentration present in the solution is not adequate to complete the removal process. An initial concentration of 30 mg/L is necessary to remove 80 % of dye adsorbed on the adsorbent substrates.

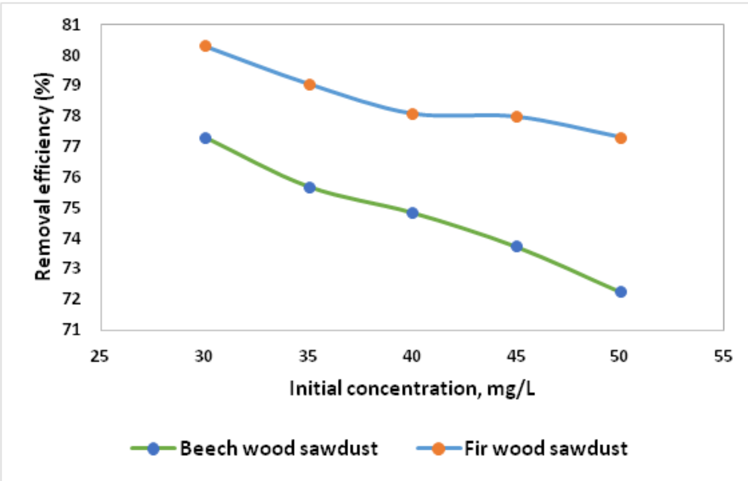

Figure 7. The effects of initial concentration on the removal of methylene blue dye.

3.2. ADSORPTION ISOTHERMS

Adsorption isotherms are important in order to describe how solute interacts with the adsorbent, and critical in optimizing the adsorbent. For modeling the adsorption process we use the Langmuir [53], Freundlich [54] and Temkin [55] isotherms. The three linearized forms of the Langmuir model were used with success in the adsorption mechanism.

The Langmuir model shows that adsorption can happen on homogenous adsorbent surfaces. The saturation occurs when the dye molecules appear in the place of adsorption.

The three linearized forms of the Langmuir model are represented by the following equations [56]:

Form 1:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_a l} + \frac{C_e}{q_{max}} \quad (3)$$

Form 2:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_a l\, q_{max} C_e} \quad (4)$$

Form 3:

$$q_e = -\frac{q_e}{K_a l\, C_e} + q_{max} \quad (5)$$

The Freundlich isotherm assumes that the adsorption of the dye molecule occurs layer by layer over the surface of adsorbent. Freundlich isotherm is expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Temkin and Pyzhev studied adsorption heat and adsorbent-adsorbed interactions with adsorption isotherms, where they assumed that the energy of molecule adsorption has a linear growth trend with coverage [57].

The linearized form of Temkin [55] adsorption isotherm follows the equation:

$$q_e = B \ln A + B \ln C_e \quad (7)$$

$$B = RT/b \quad (8)$$

where:

- q_{max} (mg/L) and K_a (L/mg) are the Langmuir constants of adsorption capacity, and consequently, the adsorption energy. The constants q_{max} and K_a can be calculated to the plot to C_e / q_e versus C_e (eq. 4);
- C_e (mg/L) and q_e (mg/g) are equilibrium concentration and dye quantity at adsorption equilibrium;
- B is the Temkin constant plot to adsorption energy (J/mol);
- A is the Temkin constant (L/g);
- K_F is the Freundlich constant related to the adsorption capacity of adsorbents (mg/g) and n is the Freundlich constant related to the adsorption intensity of adsorbents;
- R is the universal constant of gas (8.314 J/mol K);
- T is the absolute temperature in (K);

– *b* is the constant of Temkin isotherm.

The adsorption process was evaluated from the experimental data of methylene blue dye on sawdust, by using three linearized forms of Langmuir, Freundlich and Temkin adsorption isotherms at different initial concentrations of dye (Figs. 8-13).

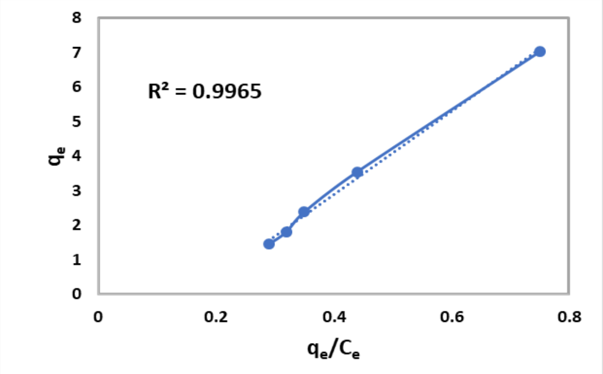

Figure 8. Langmuir adsorption isotherm for methylene blue dye adsorption on untreated fir wood sawdust.

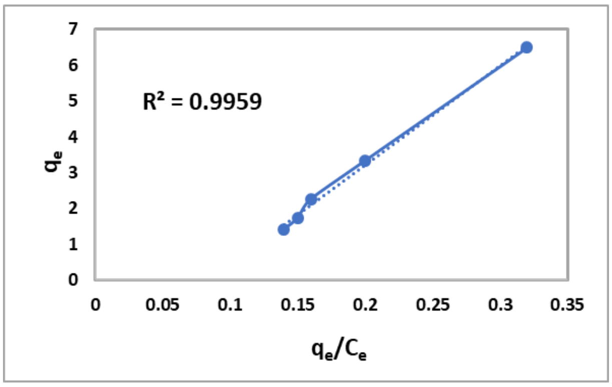

Figure 9. Langmuir adsorption isotherm for methylene blue dye adsorption on untreated beech wood sawdust.

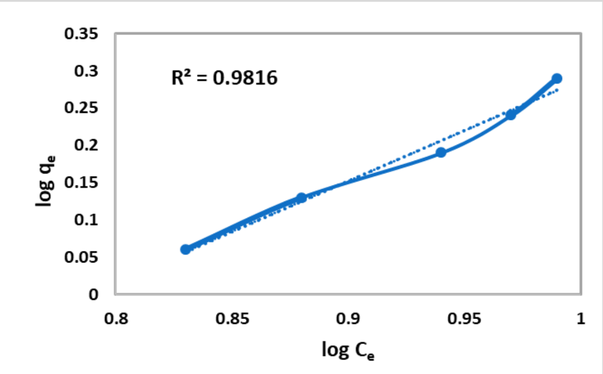

Figure 10. Freundlich adsorption isotherm for methylene blue dye adsorption on untreated fir wood sawdust.

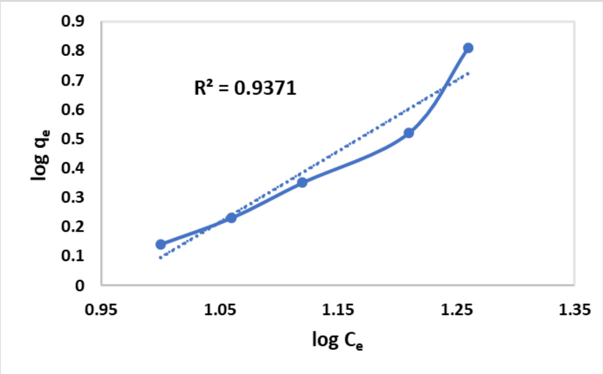

Figure 11. Freundlich adsorption isotherm for methylene blue dye adsorption on untreated beech wood sawdust.

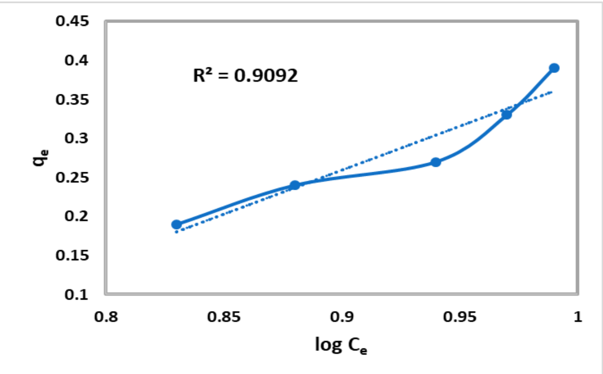

Figure 12. Temkin adsorption isotherm for methylene blue dye adsorption on untreated fir wood sawdust.

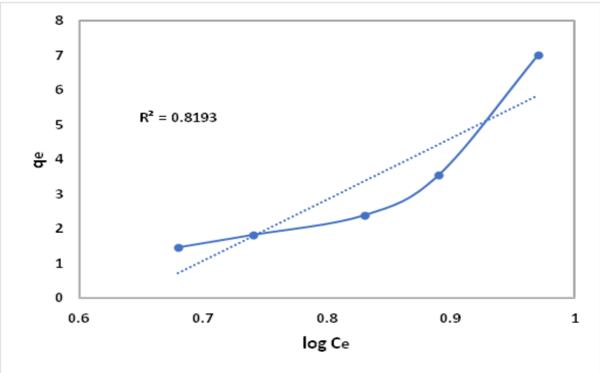

Figure 13. Temkin adsorption isotherm for methylene blue dye adsorption on untreated beech wood sawdust.

The results' analysis of the Langmuir model showed that the biosorption is more suitably correlated with the experimental results, compared to Freundlich and Temkin isotherms. The results point out that the Langmuir model has a correlation coefficient value R^2 (0.9965) comparative with the rate of correlation coefficient R^2 (0.9959) for beech wood sawdust. The isotherms were used to explain the adsorption of natural materials by using a cellulosic waste for the removal of methylene blue dye [53, 58, 59]. A comparison established between the linearized forms of the adsorption isotherms allows us to conclude that the model is correctly used to describe the properties of the adsorption mechanism. The sawdust adsorption area is evenly distributed for the whole surface of adsorbent.

4. CONCLUSIONS

The experimental study was carried out by using cellulosic wastes for the removal of pollutants present in aqueous environments. The application of cellulosic waste in the reduction process of environmental pollution has an economic justification, due to the fact that essential cellulosic wastes can be easily available and that they can be used in various areas, with significantly reduced costs.

The experimental studies were concerned with the use of cellulosic wastes (the untreated fir and beech wood sawdust) for the adsorption removal of an organic coloring agent (methylene blue) from an aqueous solution. From the experimental results could be concluded:

- there are some preliminary parameters which influence the adsorption of methylene blue dye;
- the use of different concentrations for different amounts of adsorbent and volume which passed through the column depend on the pH of the solution; the removal efficiency increased due to the modification of the *pH* value. For *pH* of 11, the removal capacity was 94.45 %. The maximum removal efficiency has been reached at the maximum *pH* value.
- the adsorption depends on the effect of flow rate which varied from 5 to 25 mL/min;
- the removal efficiency of methylene blue dye decreased with increasing the flow rate;
- The removal percentage increased by increasing the amount of adsorbent. The removal efficiency decreased with the increase of the initial concentration of the solution and a high concentration present in the solution is not adequate to complete the removal process. An initial concentration of 30 mg/L is necessary to remove 80 % of dye adsorbed on the adsorbent substrates.
- The adsorption process follows the Langmuir with a high value of R^2 (0.9965) of untreated fir sawdust and R^2 (0.9959) for beech sawdust as compared to Freundlich (0,9816 and 0.9371) and Temkin (0.9092 and 0.8193) adsorption isotherms. The experimental data shows that the Langmuir adsorption isotherm was more suitably correlated with the experimental results. The results show that the percentage of methylene blue dye removal increased from 72.3 % up to 97 %. The increasing of the removal percentage depends on the experimental parameters.

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