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MICROSCOPY AND SPECTROSCOPY ANALYSES OF METHYLENE BLUE BIOSORPTION ON *Pennisetum clandestinum* WASTE

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Abstract: Dyes are common components of wastewater. It is estimated that there are more than 100,000 colorants available in the market ($7x10^5$ to $1x10^6$ tons per year). The methylene blue (MB) dye is one of the most used. The high concentration of MB causes health problems in humans and animals. On the other hand, the grass species *Pennisetum clandestinum* is an agro-industrial waste which is considered invasive of crops and agricultural areas. The aim of this work was to use a biosorbent obtained from *Pennisetum clandestinum* for removal of MB from aqueous solutions. This was evaluated by equilibrium and kinetic studies, as well as by infrared spectroscopy (FTIR) and chemical mapping by ESEM-EDS to elucidate biosorption mechanisms. The results showed 96% removal after 30 minutes. The mathematical model fitting reported the Freundlich isotherm and pseudo-second-order kinetics. The FTIR spectra showed the formation of new chemical bonds such as C-O, N-H. The elemental chemical mapping indicated the increase of S, C, and N, which evidenced the biosorption process. In conclusion, the pruning residue *Pennisetum clandestinum* showed to be a high-efficiency biosorbent for the removal of MB.
Keywords: Pruning waste; spectroscopy; electron microscopy; dyes; adsorption isotherms.

INTRODUCTION

There exist a huge variety of pollutants that are poured into different hydric bodies, such as heavy metals, dyes and organic matter. Industrial processes, such as those running for textile, chemical and other manufactures, generate effluents with high concentrations of pollutants, including a variety of organic compounds, dyes for example. As it is quoted by Ravikumar [1] it is estimated that there are more than 100,000 dyes available in the market with a production ranging from $7x10^5$ to $1x10^6$ tons per year. According to Anjaneyulu [2] more than ten thousand different types of pigments and synthetic dyes are used in industries such as the textile and paper one, which end up in the polluted effluents.

A dye is an organic substance that has a very stable chemical structure. Most of the dyes used in the industry have a synthetic origin with complex and varied molecular structures. Due to their chemical stability, they are slowly degraded by biological mechanisms. As a result of the high solubility in water, their high toxicity persists for a long period of time. Furthermore, dyes increase the organic charge, affecting the aquatic ecosystems and visually disturbing the hydric bodies.

The present research focused on the study of the methylene blue (MB) dye, which is used in the staining of cotton, wood, silk, paper and polyethene terephthalate. It is also used in certain proportions, in health services, among other uses [3-5]. One of the main problems with the handling of the MB is that at high concentrations MB may cause respiratory problems, nausea, headaches, confusion as well as the damage to the sea life [6].

Nowadays there are different methods used for the removal of this pollutants from wastewater, such as coagulation, flocculation, membrane filtration, adsorption, among others, although these methods are high-cost. Due to this, there is a necessity of an alternative process, cheap and easily accessible, such as biosorption. Biosorption is a process that uses biomass as raw material to remove different pollutants in a liquid o solid surface, through physicochemical mechanisms known as physisorption and chemisorption [7].

The use of biosorption is an effective alternative since the commonly adsorbent used is a waste material or an agro-industry tailing that requires a low procedure to turn into a biosorbent. In the present work,

the unused residues from the pruning of *Pennisetum clandestinum* were used as a biomaterial, this graminaceous species can be found in great amounts, even it is considered as a plague for the crops. In Mexico City this material is considered as an useless tailing, this means it cannot be reused or reincorporated into a productive process and does not represent an economic value [8]. In 2015, approximately 1503 tons of organic tailings were produced daily, of which about 153 tons were pruning waste [9]. The use of this tailing as a raw material can solve two different environmental difficulties, the first one is the cost of transportation and final disposal of the pruning tailing, and the second one is the pollution of effluents with MB. Given the above, this research focused on the study of the reused pruning tailings of *Pennisetum clandestinum* to determine how effective they are as a biosorbent of MB in aqueous solutions, as well as on the spectroscopic and microscopic analysis of this biomaterial to elucidate the biosorption mechanism.

MATERIAL AND METHODS

OBTAINING AND CONDITIONING OF THE BIOMATERIAL

The tailings of *Pennisetum clandestinum* came from the pruning of this grass, they were dried for 6 hours at 105 °C in an oven (Stable Temp, Cole-Parmer Instrument Company, USA), then they were immersed for 1 week in a concentrated methanol solution (Meyer, Germany) in order to extract the chlorophyll from the biomaterial [10]. Afterwards, the biomaterial was rinsed, filtered through cheesecloth and dried again; once dried, its activation began into a HCl 0.1M solution, in a glass flask, with magnetic stirring at 250 rpm at 25 °C for 30 minutes. Before the experiments, filtration and rinse procedures were again performed until neutral pH, the biomaterial was dried, grinded and sieved to obtained a size of 250 µm. The biomaterial was placed into polyethylene flasks for its subsequent use in the biosorption experiments [11].

INFLUENCE OF THE PH IN THE BIOSORPTION PROCESS

The influence of the pH on the capacity of the processed waste of *Pennisetum clandestinum* for biosorption in the aqueous solutions of MB was evaluated by using a concentration of 25 mg/L of MB in conical flasks of 125 mL at environmental temperature (25°C), using 0.4 g of the biomaterial, adjusting the pH with solutions of HNO_3 or NaOH in a range from 1 to 6.5 [12].

BIOSORPTION

For the determination of the amount of MB that was adsorbed to the surface of the biomaterial the following equation was used[13]:

$$q_e = \frac{V(C_i - C_e)}{1000m} \quad (1)$$

Where q_e is the amount of MB adsorbed by the biomass ($mg \cdot g^{-1}$), C_i is the initial concentration in the aqueous solution of MB ($mg \cdot L^{-1}$), C_e is the concentration ($mg \cdot L^{-1}$) of the adsorbate in the solution phase in balance with the biosorbent phase, V is the volume of the solution of MB (mL) and m is the mass (g) of the biomaterial used.

The percentage of removal was calculated with the next equation:

$$\%R = \frac{C_i - C_f}{C_i} x100 \quad (2)$$

Where %R is the percentage of removal of the MB, C_i is the initial concentration and C_f is the final concentration.

ADSORPTION ISOTHERMS

The adsorption isotherms were made by the addition of 0.4 g of the pruning tailings

of *Pennisetum clandestinum* in a conical flask of 125 mL, with 25 mL the solution of MB at different concentrations (5, 20, 40, 100 $mg{\cdot}L^{-1}$), each mixture was kept under stirring at 175 rpm for 24 hours at environmental temperature. Later, the blends were filtered through a 0.45 µm pore size cellulose nitrate membrane filter and the final solutions were measured using a spectrophotometer in order to know the concentration of MB (Zuzi 4210/20) at a wavelength of 665 nm. The results were adjusted to three different mathematic models, namely Langmuir, Freundlich and Sips, in order to estimate the maximum capacity of adsorption; additionally, once knowing the corresponding constants of the best-fitted physicochemical model of adsorption, it was possible to define the affinity that MB had with the active sites of the biomaterial[14].

The Langmuir model can be described by this equation:

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

The equation of the Freundlich model is shown as follows:

$$q_e = k_f (C_e)^{\frac{1}{n}} \quad (4)$$

Whereas the Sips model is described as:

$$q_e = \frac{(b * C_e)^{\frac{1}{n}}}{(1 + (b * C_e)^{\frac{1}{n}})} \quad (5)$$

The literals of equations 3, 4 and 5 represent the following parameters: q_e is the amount of retaining adsorbate per unit mass of adsorbate ($mg{\cdot}g^{-1}$), C_e is the balance concentration of the adsorbate in the liquid and biosorbent phases ($mg{\cdot}L^{-1}$), q_{max} and b are the Langmuir constants related with maximum capacity of adsorption for a complete monolayer ($mg{\cdot}g^{-1}$) and with the affinity between the adsorbent and adsorbate (g^{-1}), respectively. The term k_f is the dimensionless constant of Freundlich and it is related with the adsorption capacity of the biosorbent; n is a dimensionless constant related to the affinity between adsorbent and adsorbate.

BIOSORPTION KINETICS

In order to make the biosorption kinetics, 8 g samples of the biosorbent in 500 mL of MB dissolution at 100 $mg{\cdot}L^{-1}$ concentration were maintained under constant stirring at 300 rpm. Aliquots were taken at different time intervals for 24 hours, all of them at 25 ± 1°C. These aliquots were analyzed with a UV spectrophotometer (Zuzi 4210/20) at a wavelength of 665 nm. Two mathematical models were fitted to the results obtained, namely pseudo-first-order and pseudo-second-order, equations 6 and 7, respectively [5,14]:

$$q_t = q_e\,(1 - exp(-k_1 t)) \quad (6)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (7)$$

Where q_e ($mg{\cdot}g^{-1}$) and q_t ($mg{\cdot}g^{-1}$) respectively are the amount of dye adsorbed at equilibrium and at any time t (min), k_1 (min^{-1}) is the velocity constant of the pseudo-first-order model while k_2 ($g{\cdot}mg^{-1}{\cdot}min^{-1}$) is the velocity constant of the pseudo-second-order model.

MICROSCOPY AND SPECTROSCOPY TECHNIQUES

Microscopy techniques were performed to morphologically analyze the biomaterial in the different stages of the process (untreated, treated, and before and after the biosorption process) using an environmental scanning electron microscope (ESEM, JEOL 6360 LV). For the determination of the chemical elements present, an equipment that determines these constituents was coupled

using X-ray scattering, model INCAx-sight (OXFORD INSTRUMENTS)[5].

In order to identify functional groups present in the biomaterial, infrared spectra were obtained by using the Labra LabRAM HR 800 equipment with an FTIR module coupled with ATR. The determination was performed in a wavenumber range of 400 to 4000 cm^{-1} [15,16].

It should be important to say that the scans of the ESEM, as well as the FTIR scanners were performed in triplicate.

RESULTS

BIOSORPTION ISOTHERMS

Adsorption isotherms were fitted to three mathematical models which were the Langmuir, Freundlich, and Sips ones. As shown in Figure 1, the mathematical model that gave the higher goodness of fit was Freundlich's, with a coefficient of determination of R^2 = 0.9725, (R^2 values corresponding to the models of Langmuir and Sips were 0.5318±2.36 and 0.97±213, respectively). This result, of fitting to the Freundlich model, indicates that the surface of the adsorbent is heterogeneous. Commonly this model depicts isotherms that grow exponentially, as seen in Figure 1 that shows that as the concentration of MB increased the removal percentage progressively increased, starting with 69% at a concentration of 5 $mg{\cdot}L^{-1}$ and ending with a removal of 96% at a concentration of 100 $mg{\cdot}L^{-1}$. In contrast to this behavior, there are other biomaterials that have been used, for example the waste of *Morinda citrocifolia* among other agro-industrial waste, which has shown that the highest percentage of removal occurs at low concentrations, this is an inverse correlation between concentration and percentage of removal [5,17]. The Freundlich model also assumes that the positions available for sorption will be occupied depending on the affinity, allowing to form multilayers, dealing first with stronger sorbate-sorbant interactions; subsequently, the strength of interactions decreases by increasing the occupancy of the adsorption sites.

ADSORPTION KINETICS

Figure 2 shows the adsorption capacity of the biomaterial on the MB, as well as the mathematical adjustment to pseudo-second-order model, since this model was the best fitted to the kinetic behavior (R^2=0.8855), this result is consistent with the kinetic study reported by Rosas-Castor [5], in which the adsorption capacity increased with the initial concentration of the MB. However, this behavior occurs while the initial concentration does not reach very high concentrations, after which the adsorption capacity is lower since the surface of the adsorbent becomes saturated. In this study it was determined that the time in which equilibrium is achieved is 30 min, whereas K_2=0.122 and q_e=96.64 $mg{\cdot}g^{-1}$. The previous parameters indicate that the studied biosorbent has high potential for use in industrial processes because the time in which the adsorption process is achieved is sufficiently short for this purpose.

CHARACTERIZATION OF THE BIOMATERIAL BY SPECTROSCOPIC AND MICROSCOPIC METHOD

The characterization of the biomaterial was performed by spectroscopic and microscopic methods as shown in Figure 3. The scanning electron microscopy allows to observe the biomaterial untreated and treated before and after the biosorption process, as shown in Figures 3 a and c. The biomaterial untreated is not as porous as the treated biomaterial, which may indicate that the treatment allowed to increase the rate of removal of MB. In Figure 3e, it is shown the biomaterial after

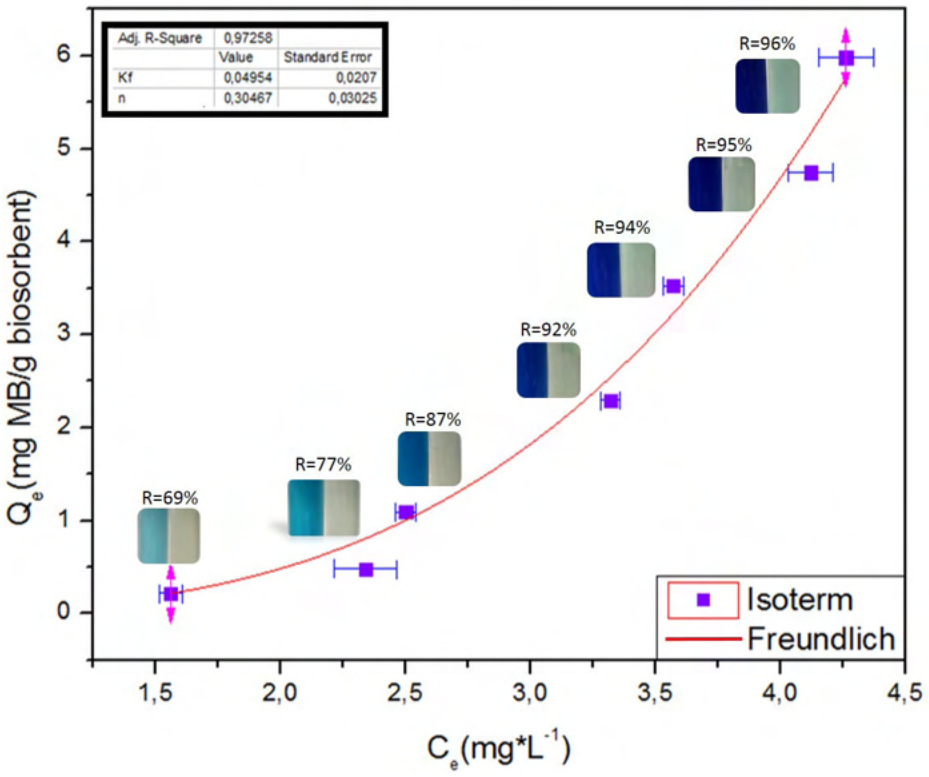

Figure 1. Adsorption isotherm for MB on the biomaterial *Pennisetum clandestinum*, adjusted to the Freundlich's mathematical model, as well as percentage of removal for a concentration range of 5 mg·L^{-1} to 100 mg·L^{-1}.

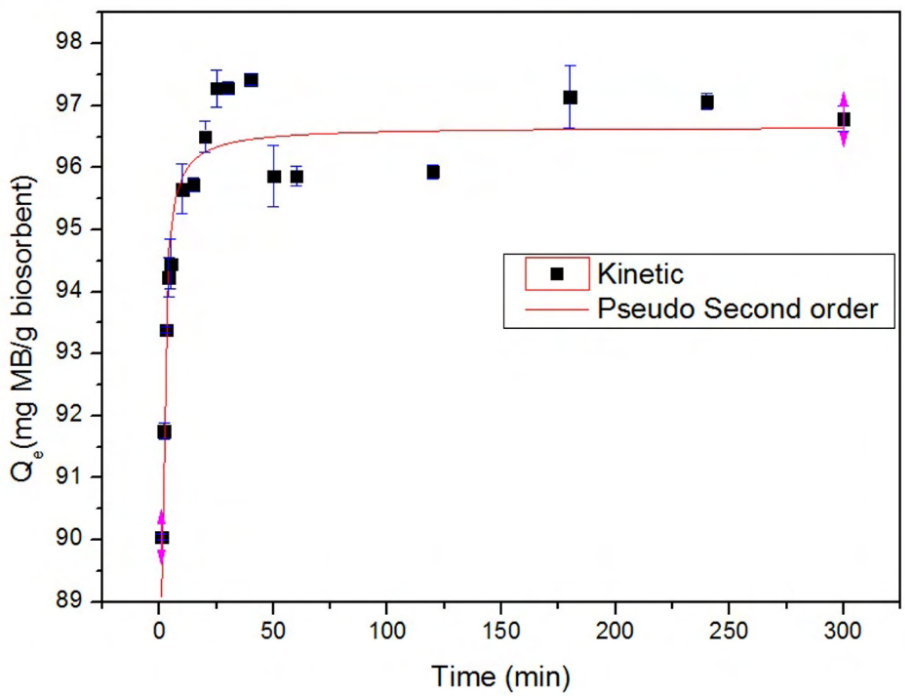

Figure 2. Adsorption kinetics for MB on the biomaterial *Pennisetum clandestinum* (100 mg·L^{-1}), adjusted to the mathematical model of pseudo-second-order.

the biosorption process. The EDS analysis was performed in order to know the main surface components of the biomaterial obtained from *Pennisetum clandestinum*. Figure 3b shows the biomaterial untreated, in which the following percentages (by-weight) were found: C, 29.41; N, 7.30; O, 45.68; Na, 0.24; Mg, 0.50; Al, 3.17; Si, 12.55; Cl, 0.35; and Ca, 0.79. After treatment with methanol and hydrochloric acid, as shown in Figure 3d, the biomaterial changed its composition as follows: C=41.25, O=48.38, Al=0.15, Si=10.02 and Cl=0.20; as it can be inferred, the treatment eliminates the Mg and N, these elements may correspond to the chlorophyll present in the biomaterial, also the Ca and Na disappears. The Figure 3f shows the result for the biomaterial treated after the biosorption process, N again is observed with a percentage (by-weight) of 12.73 indicating that the MB was adsorbed in the biomaterial, also Ca appears (0.12), Si (1.75) and O (44.06) decrease, and Al increases (0.22). These results may help to elucidate the mechanism of biosorption taking place in the biomaterial.

Correa [18], studied samples of *Pennisetum clandestinum* and reported the following composition (dry weight basis), crude protein (20.46%), ethereal extract (3.63%), ash (10.6%), neutral detergent fiber (58.6%), acid detergent fiber (30.29%) and non-structural carbohydrates (13.40%). As shown in this work, the highest percentage of the content of the biomaterial corresponds to neutral detergent fiber, specifically to the content of hemicellulose, cellulose, and lignin; as well as the fiber of acid detergent, which corresponds to the amount of cellulose and lignin, so that the biomaterial studied in the present work had an average percentage of 88.89% of hemicellulose, cellulose and lignin, responsible of the biosorption process.

Figure 4 shows the FTIR spectrum of the biosorbent before and after the biosorption of MB on *Pennisetum clandestinum*. As observed, there are different peaks that allow to identify functional groups. The peak in the frequency 3266.83 cm^{-1} is due to stretching and vibrations of several hydroxyl bonds C-OH, which indicate the presence of absorbed water, aliphatic primary and secondary alcohols found in molecules such as cellulose, hemicellulose and lignin. The signals in 2851.49 cm^{-1}, 2920.41 cm^{-1}, 2909 cm^{-1} 1020.65 cm^{-1} and 1368.24 cm^{-1} can be attributed to the stretch of methyl groups, $-CH_2$ and –CH, present especially in aliphatic cellulose fragments. The signals at 1642 cm^{-1} and 1612.93 cm^{-1} correspond to the vibration of C=C bonds present in lignin and C=O of carbonyl groups. In the case of 1694.94 cm^{-1} and 633.25 cm^{-1} they can be ascribed to the vibration by the presence of N-H bonds and C = S, respectively [19,20].

Each of these groups is involved in the processes of adsorption according to what is reported in literature. The signal displacement, the intensity decrease, as well as the disappearance and appearance of frequency peaks indicate that there are interactions between the biosorbent, the activating substance and dye, thus causing the attraction between components, which allows the removal of the contaminant studied in this work [21].

CONCLUSIONS

The residue of pruning of *Pennisetum clandestinum* proved to be an efficient biosorbent for the removal of MB, with 96 % of the total removal of dye. Adsorption isotherms were fitted to the Freundlich model, while kinetics to pseudo-second-order model, resulting in a short time to reach steady state, indicating that biomaterial has potential for use in industrial processes for removal of contaminants from wastewater. Microscopy and spectroscopy techniques depicted the biosorption mechanism, by the

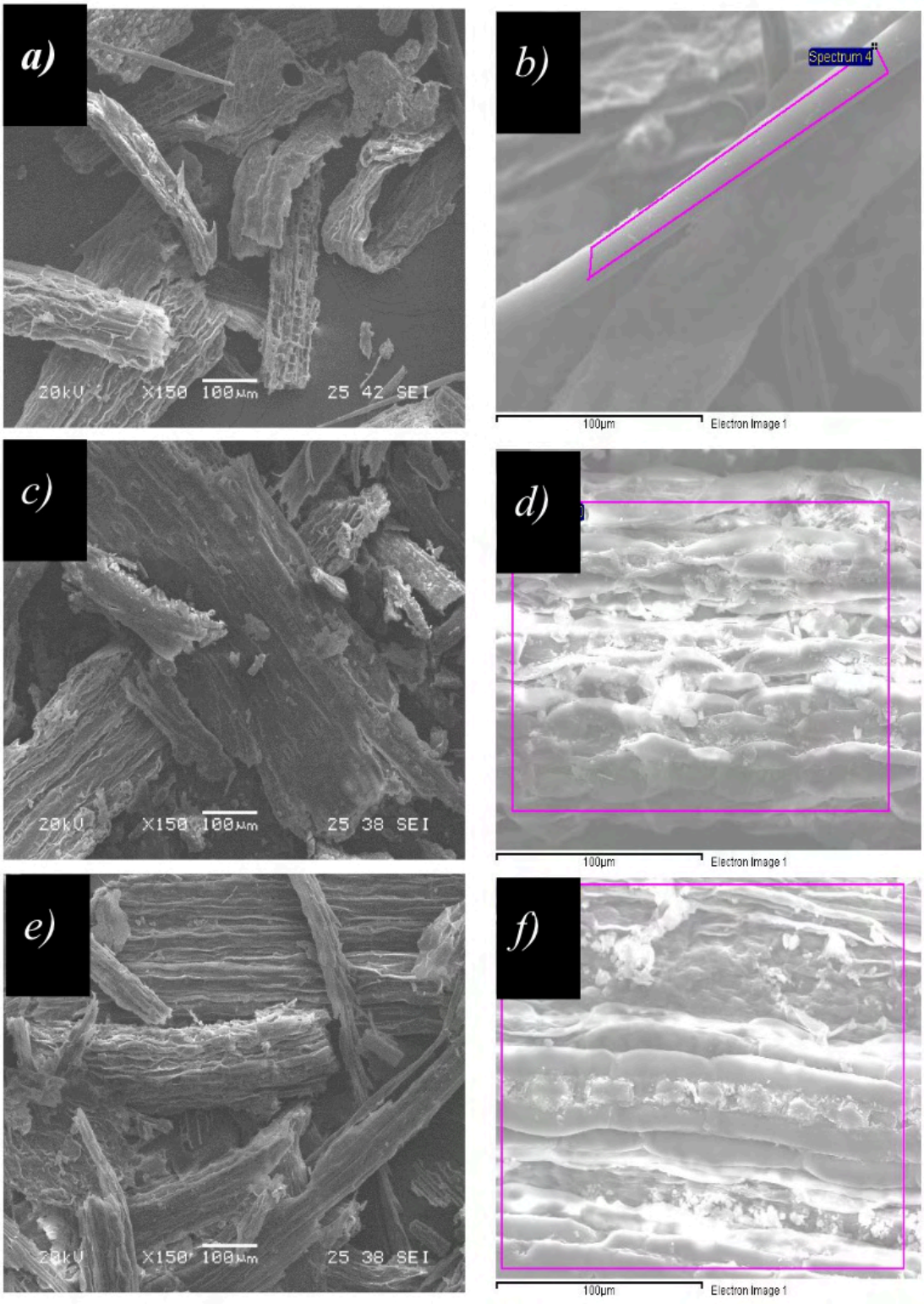

Figure 3. Scanning Electron Microscopy. a) and c) *Pennisetum clandestinum* untreated and treated before the biosorption process, respectively, e) *Pennisetum clandestinum* after the biosorption process with MB. EDS analysis b), d) *Pennisetum clandestinum* untreated and treated before the biosorption process, respectively and f) *Pennisetum clandestinum* after the biosorption process with MB.

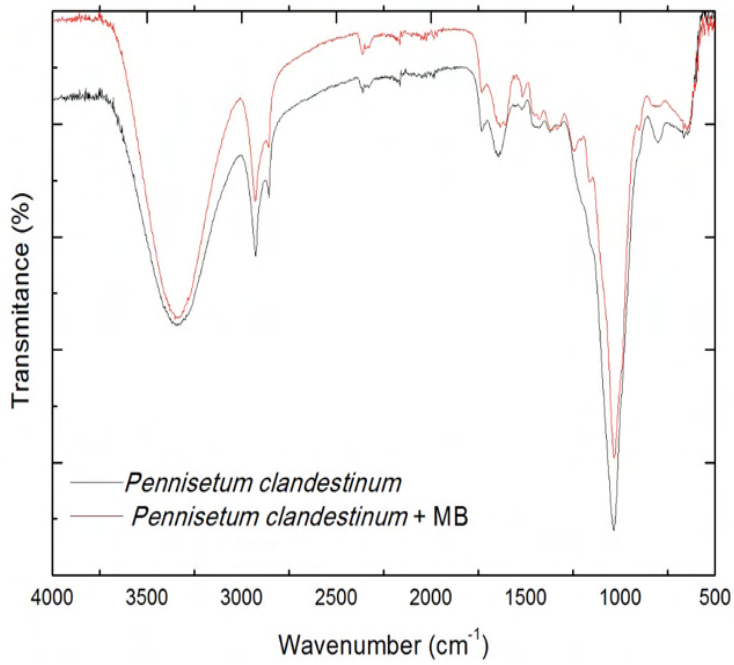

Figure 4. FTIR spectra of the biosorbent before and after the biosorption process of MB, on the biomaterial *Pennisetum clandestinum*.

presence of new chemical bonds after the biosorption process, which corresponded to the adsorbate, and this indicated the relationship that exists between the biosorbent and the constituents of the adsorbate such as hemicellulose, cellulose and lignin, which are responsible for the biosorption process.

This may lead to propose the pruning residue of *Pennisetum clandestinum* as a viable alternative for eliminating MB present in wastewater, which in turn would help to the decrease of pruning residues, not only from this species, since it is suggested that this work could be the beginning of broader studies covering other vegetable wastes.

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