A BIOSORBENT MATERIAL FROM *BRAHEA EDULIS* PALM LEAVES – APPLICATION TO AMOXICILLIN ADSORPTION

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Received January 31, 2023

In this study, fibers from the leaves of *Brahea edulis* palm (BEF) have been successfully used as a cheap, sustainable and eco-friendly biosorbent to remove the antibiotic Amoxicillin (AMX) from an aqueous solution using a batch process. This pharmaceutical product is present in domestic and industrial waste water. The characterization of BEF was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transform infrared spectroscopy (FTIR). The results of XRD showed that BEF has a semicrystalline structure. SEM images revealed its morphology, surface structure and porous nature. FTIR results showed the presence of different functional groups (hydroxyls, carboxyls, amines, *etc.*). Several physicochemical parameters, such as porosity, ash content, moisture content, and isoelectronic point (pHpzc), were analyzed. The batch biosorption process of Amoxicillin by BEF was monitored with a UV-visible spectrophotometer at λ = 228 nm. Different operating parameters, such as contact time, biosorbent mass, pH, temperature and adsorbate concentration, were evaluated to find the maximum level of biosorption. The contact time of 90 minutes, 50 mg/L initial Amoxicillin concentration, 1.5 g biosorbent mass and 313 K temperature were found to be the optimum conditions that led to a percentage removal of AMX of 58% at pH 6.5. The maximum adsorption at high temperature indicates that this biosorption process is spontaneous and endothermic.

Keywords: characterization, biosorbent, adsorption, natural fibers, *Brahea edulis*, Amoxicillin

INTRODUCTION

The contamination of water by complex pollutants of various origins is a current problem. In the pharmaceutical industry, in particular, waste water is one of the most important sources of pollution of both water and aquatic ecosystems. There are two main pathways by which pharmaceutical products enter the water cycle: the industrial and the domestic one. Such products may be fully degraded or remain intact in the effluents of discharged waters, and this makes them a threat to the environment.

Several studies have established that pharmaceutical compounds and their metabolites are generally identified in wastewater, sewage, surface water, groundwater and even in drinking water, within a concentration range from nano-grams per liter (ng/L) to micrograms per liter (mg/L).[1] As a new form of trace organic pollutant, Amoxicillin (AMX), the most frequently used antibiotic, is difficult to decompose and it persists as an active compound in urine and feces.[2] The structure of amoxicillin exhibits amphoteric characteristics due to three important functional groups: -NH2, -COOH, and -OH. It has been demonstrated that after 2 hours, more than 80% of amoxicillin is eliminated from the human body via urine and that the presence of amoxicillin in surface waters can cause serious environmental problems.[3] Hence, before antibiotic-contaminated effluents are discharged into the environment, they must be treated.

Antibiotics can be removed from wastewater using many different methods, to name just a few: advanced oxidation process,[4,5] photocatalysis,[6,7] membrane filtration,[8,9] and adsorption.[10,11] Among these methods, adsorption is generally considered to be the simplest and the least expensive. This

physicochemical treatment method has been demonstrated to be successful in eliminating a variety of contaminants from aqueous solutions. The objective of our research has been to discover a low-cost and environmentally friendly biosorbent that can effectively remove pharmaceutical contaminants from discharged wastewater.

Inexpensive adsorbents made from plant wastes have been investigated instead of expensive techniques for removing complex contaminants from wastewater. Many cellulosic waste products that are widely available have been examined for their use as inexpensive adsorbents.[12] The leaves of *Brahea edulis* could be used to develop one such adsorbent. This palm is plentiful and cheap, being quite common in the Mediterranean countries.

In this study, an eco-friendly biosorbent was prepared from the leaves of *Brahea edulis* palm, and was characterized. To prepare the biosorbent, *Brahea edulis* leaves were subjected to a number of treatments designed to eliminate impurities and non-cellulosic elements.[13,14,15] Then, the obtained biosorbent was applied for the removal of amoxicillin from an aqueous environment. The impact of key parameters, such as pH, adsorbate concentration, contact time and biosorbent dose, on the sorption efficiency was investigated.

EXPERIMENTAL

Preparation of *Brahea edulis* fiber biosorbent (BEF)

BEF were obtained from large leaves of *Brahea edulis* palm grown in Chlef, Algeria. The fibers were repeatedly washed with distilled water and boiled for 15 min to remove dirt particles, dried at 80 °C for 24 h. After drying, the fibers were treated with a 12% sodium hydroxide (NaOH) solution for 45 minutes at ambient temperature several times. This treatment was followed by bleaching with 12° sodium hypochlorite (NaCLO) solution for 3 hours and then by washing with distilled water, and finally drying at 105 °C.[16] The material was then pulverized and sieved to achieve particle sizes with an average diameter of 60 µm. The biosorbent powder was kept in an airtight container until usage.

Determination of pH point of zero charge (pHpzc)

The point of zero charge (pH_{pzc}) of BEF was evaluated by the solids addition method using a NaCl solution (0.01 M). The experiments were carried out in 100 mL Erlenmeyer flasks with a stopper containing 50 mL of NaCl solution. The initial pH ($pH_{initial}$) in each flask was adjusted between 2 and 12 by adding solutions of NaOH or HCl (0.1 M). Then, 0.5 g of BEF was added to each flask, which was kept for 24 h under intermittent shaking to reach equilibrium.[17] The pH_{pzc} is the point where the curve of pH_{final} *versus* $pH_{initial}$ intersects the straight line corresponding to $pH_{initial} = pH_{final}$; at this pH, the net surface charge of the biosorbent is zero.

Characterization of biosorbent BEF

The biosorbent BEF was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

Physico-chemical analysis of biosorbent BEF

Prior to conducting the adsorption study, it was important to analyze the physico-chemical properties of the biosorbent, specifically for particles with an average diameter of 60 µm.

Moisture content

The moisture content is expressed as a percentage ratio and is determined by drying the adsorbent in an oven at 105 °C until its weight remains constant. It was calculated by the following formula (1):

$$H(\%) = \frac{(M0-M1)}{M0} \times 100 \quad (1)$$

where M_0: initial mass of the material before drying, M_1: the mass of the material after drying.

Ash content

The ash content reveals the amount of mineral matter in the material. One gram of dry adsorbent was weighed and introduced into a calcination crucible, which was placed into an oven at 600 °C for 4 hours. After cooling, the crucible was weighed again. The ash content is expressed by the equation:

$$C\ (\%) = \frac{W_2}{W_1} \times 100 \quad (2)$$

where W_1 is the weight of the adsorbent placed in the crucible, and W_2 is the weight of the ashes in the crucible.

Real density

The real density is defined by placing the adsorbent in an oven to be dehydrated. A specific quantity of the substance to be analysed (m_0) was placed into a weighed pycnometer, which was filled with methanol and then weighed. Knowing the tare weight and the methanol density ρ_m (0.792 g/cm^3) allows determining the real density, using the following equation:

$$\rho s = \frac{m0 \times \rho m}{(m1-m2)} \quad (3)$$

where m_1: mass of methanol to add to m_0 to fill the pycnometer (in g), m_2: mass of methanol filling the pycnometer (in g).

Porosity

Porosity is defined as the ratio of the volume of voids to the total volume of the material. To determine

the porosity (ε), a 10 mL test tube was filled with the substance being examined until it reached a volume (V2), which corresponded to mass m_1, then methanol was added until the volume reached V_T corresponding to mass m_2. The porosity was calculated as follows:

$$\varepsilon = \frac{V1}{VT} = \frac{\frac{m2-m1}{\rho m} - V2}{VT} \times 100 \quad (4)$$

where V_1: void volume in cm^3; V_2: volume of the solid in cm^3; V_T: total volume in cm^3; ρ_m: density of methanol in g/cm^3.

Biosorption of amoxicillin by BEF

In order to study the retention of amoxicillin (AMX) onto BEF through adsorption, the influence of specific physico-chemical parameters, such as contact time, initial AMX concentration, BEF mass, and pH, was investigated by varying a single parameter at a time, while keeping the others constant.

Various solutions were prepared for the tests from the stock solution. These solutions were obtained by mixing a mass (m) of amoxicillin in a 0.1 M phosphate buffer solution at pH 6.5. A dilution to different proportions of the stock solution for a volume of the buffer solution was made to obtain concentrations of AMX ranging from 5 to 50 mg/L. The resulting solutions were checked periodically using a UV-Visible spectrophotometer and a pH meter.

Biosorption was performed in 500 mL conical Pyrex flasks at constant stirring speed of 350 rpm. The experiments were conducted by varying several parameters as follows: contact time (10–160 min), biosorbent dose (0.5–2 g/250 mL), concentration of AMX (5–50 mg/L), pH (2–12), and temperature (298, 303 and 313 K). Following each biosorption test, the sample was filtered. The residual AMX concentration was analyzed using a UV–Vis spectrophotometer (UV Schimadzu 18000) at λ_{max} 228 nm.

The quantity of amoxicillin adsorbed over time was estimated using the following equations:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (5)$$

$$Removal\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (6)$$

where q_e (mg/g) is the adsorption capacity of the biosorbent for the adsorbate at equilibrium, C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of amoxicillin in solution, m (g) the mass of the biosorbent and V (L) is the volume of the solution used.

RESULTS AND DISCUSSION

Characterization of biosorbent

X-ray diffraction

The X-ray diffraction pattern presented in Figure 1 exhibit two peaks in the studied domain (0-90°), one of which is 2θ= 22.3° representing the maximum intensity attributed to cellulose (crystalline and non-crystalline phases) and the other at 2θ= 17.6°, representing the minimum intensity and is attributed to the amorphous phase.[18] This indicates that the fiber is semicrystalline.

The crystallinity index (CI) was calculated using Equation (7):[19]

$$CI = \frac{I_{22.3} - I_{17.6}}{I_{22.3}} \quad (7)$$

The crystallinity index of BEF was evaluated to be 57.84%.

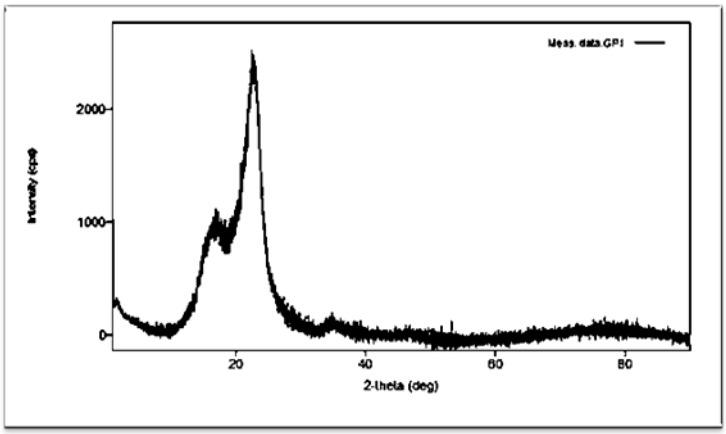

Figure 1: X-ray pattern of BEF (showing peaks at 2θ of 17.6° and 22.3°)

SEM analysis

Figure 2 (a-f) depicts the morphology and surface structure of BEF. Indeed, the images (a), (b), and (c) provide a clear view of the rough surface of the fibers, due to their chemical treatment, which dissolved the non-cellulosic components, including lignin and hemicelluloses. This has led to increased porosity of the

biomaterial, which is explained by the low value of the BEF density. Moreover, it may be noted in image (d) that each fibre is composed of an assembly of fibrils, with the core region of each fibril, known as the lumen, being porous.[20] Finally, images (e) and (f) exhibit a cross-section of a punctate fiber, revealing the biomaterial's internal porosity.

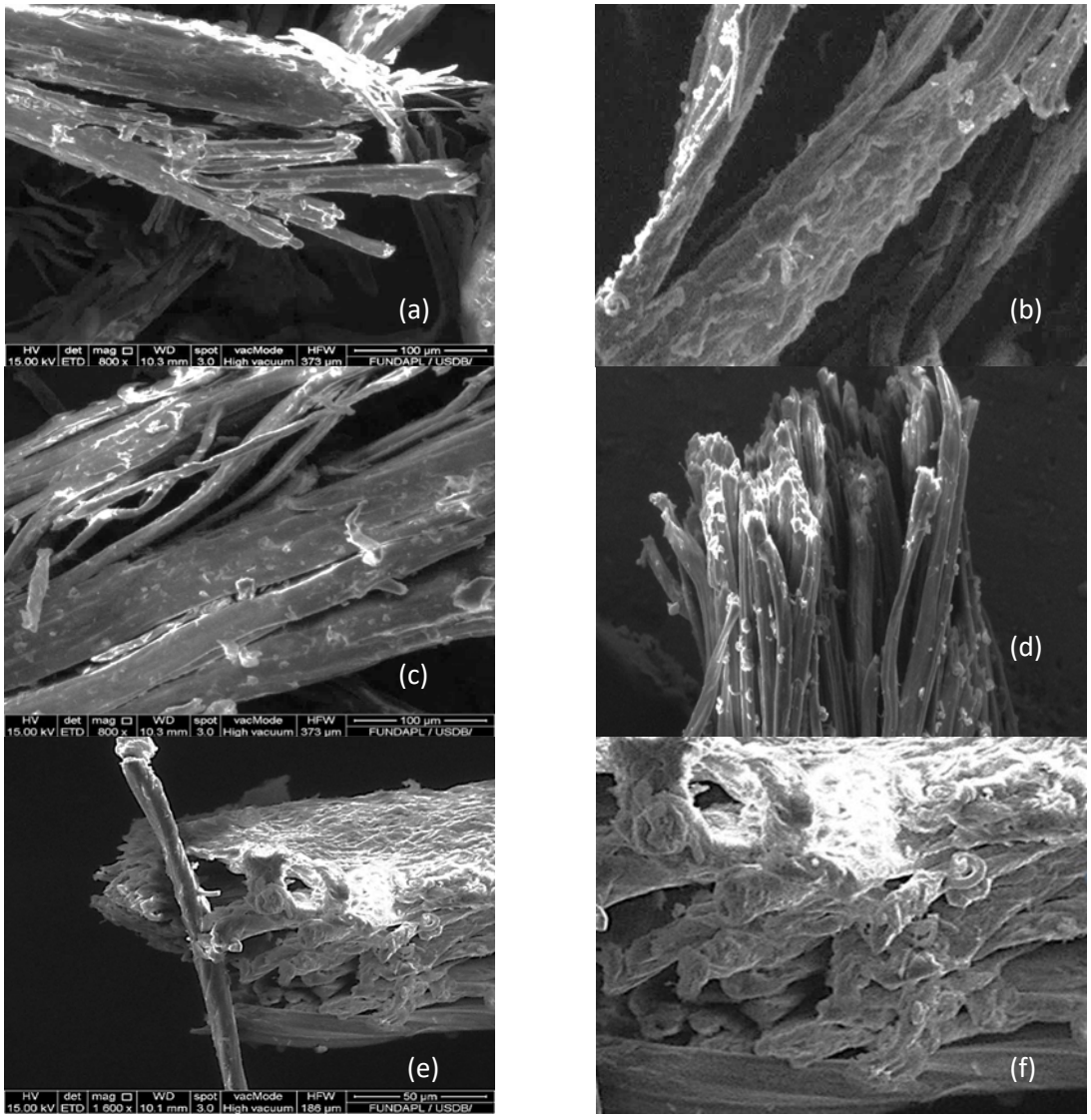

Figure 2: SEM images of *Brahea edulis* fibers at different magnification

FTIR spectroscopy

The infrared spectrum of BEF displayed in Figure 3 shows the presence of specific functional groups, confirming the chemical structure of the material. The first absorption peak is found at 3417 cm^{-1} due to cellulose and lignin denoted by O-H stretching (intermolecular H-bonds), N-H stretching (primary and secondary amines), and N-H of pyrrole and imide groups. Then, another peak observed at 2919 cm^{-1} is attributed to C-H stretching (-CH_2- or -CH_3), that at 1641 cm^{-1} is due to C=O stretching in uronic ester and acetyl groups in hemicelluloses. The peaks located at 1383 and 1309 cm^{-1} are related to the aromatic ring vibrations, symmetric CH_3 deformation, and O-H bending of phenols, confirming the presence of cellulose, lignin, and hemicelluloses. The peak at 1030 cm^{-1} is due to the stretching vibration of COO groups. The peak at 616 cm^{-1} is due to the torsional vibration of the pyranose ring present in glucose. Thus, the obtained spectrum confirmed the presence of cellulose, lignin, and hemicelluloses in the adsorbent material.[21]

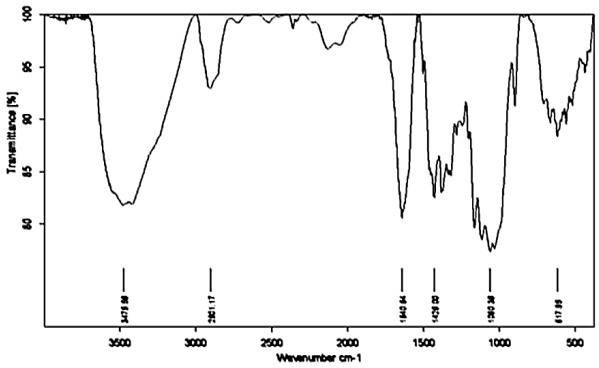

Figure 3: FTIR spectrum of *Brahea edulis* fiber

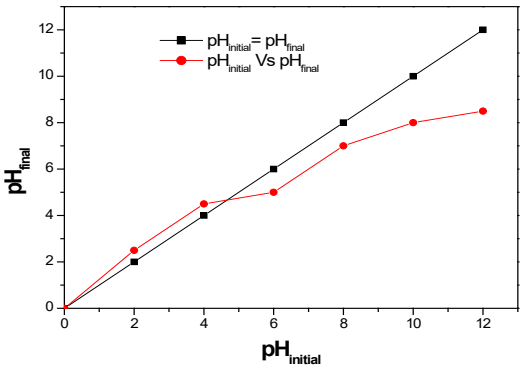

Figure 4: Determination of pH point of zero charge for BEF

Table 1
Physico-chemical characteristics of BEF

Characteristic	BEF
Moisture content (%)	4.71
Dry matter (%)	95.29
Ash rate (%)	3.77
Volatile matter (%)	96.23
Real density (g/cm^3)	1.41
Porosity (%)	46

Determination of pH point of zero charge (pH_{pzc})

According to Figure 4, the pH_{pzc} value is 4.8, leading to a positively charged adsorbent, when the pH is below 4.8, because the hydroxyl, carboxylic, and amine groups become protonated. Above pH 4.8, the surface of the biomaterial is negatively charged, and the adsorption may be favored. It is important to note that the pH_{pzc} is acidic, suggesting the dominancy of acidic groups over basic groups, at the surface of the biomaterial.[22]

Physico-chemical analysis of BEF

Table 1 illustrates the analysis results conducted on the physico-chemical properties of BEF. The low content of mineral matter – within the standard range (<10%) – in the biomaterial indicates a good adsorbent. While having low ash content, according to the data, the BEF material has a high amount of volatile matter. This can be explained by the plant's composition, which is low in lignin and high in cellulose and hemicelluloses (producing high volatile organic compounds), as *Brahea edulis* is not a woody plant. The moisture content of BEF is low (within recommended limits <5%), showing some residual moisture within the material. Its higher porosity percentage tends to increase the adsorption surface of the adsorbents, hence it is beneficial for the adsorption capacity of such materials. This effect is more evident for adsorbents with high carbon content, such as BEF, with 46% porosity.

Biosorption study of amoxicillin (AMX) onto BEF

Effect of biosorbent dose

Determining the minimum quantity of adsorbent material necessary to remove a given pollutant is an essential step in an adsorption study.[23] Figure 5 reveals an increase in AMX adsorption as a function of the BEF dose. For this antibiotic, the optimal dose of the biomaterial is 1.5 g in the solution of 5 mg/L AMX. As the biosorbent dose increases, the rate of amoxicillin removal also increases, which is due to the availability of a larger surface area with many easily accessible active sites.

Effect of contact time

The kinetic study of adsorption showed that the adsorbed amount increased linearly with increasing the adsorption time and rapidly at the beginning of the adsorption mechanism (Fig. 6). Once saturation is reached, the amount adsorbed

reaches a plateau, remaining constant for a period of time, and then decreases. It was established that the biosorption of amoxicillin onto BEF reached equilibrium after 90 minutes of adsorption.

Effect of pH on the adsorption capacity

The pH of the aqueous solution is an essential parameter that controls the adsorption process, as it significantly affects the amount of pollutant adsorbed. It can also change the surface charge of the adsorbent, the degree of ionization of the adsorbate, and the degree of dissociation of the functional groups from the active sites of the adsorbent. To determine the impact of this parameter, we conducted experiments at pH levels ranging from 2 to 12. According to the findings presented in Figure 7, the adsorption capacity is low in acidic medium (pH between 2 and 4), probably because of the high concentration of H^+ species, which favors the protonation of adsorption sites (carboxyl and amine groups).

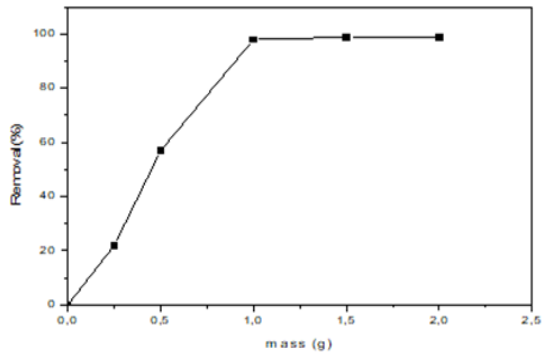

Figure 5: Effect of BEF dose on biosorption efficiency of AMX (d_p = 60 µm, T = 298 K; C_0 = 50 mg/L; pH 6.5 and V = 250 mL)

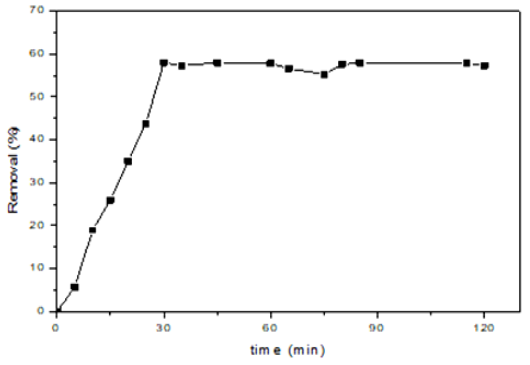

Figure 6: Effect of contact time on biosorption efficiency of AMX onto BEF (d_p = 60 µm, T = 298 K; C_0 = 5 mg/L, m = 1.5 g; pH 6.5 and V = 250 mL)

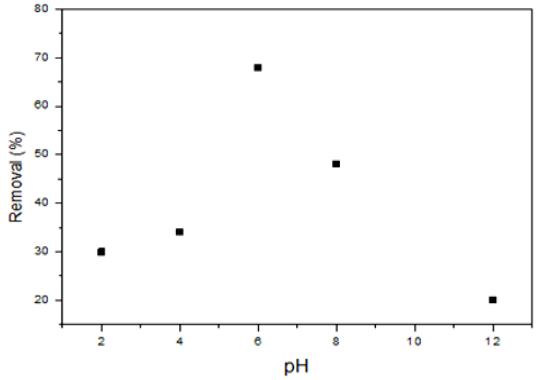

Figure 7: Effect of pH on biosorption efficiency of AMX onto BEF (d_p = 60 µm, T = 298 K; C_0 = 50 mg/L, m = 1.5 g; pH 6.5 and V = 250 mL)

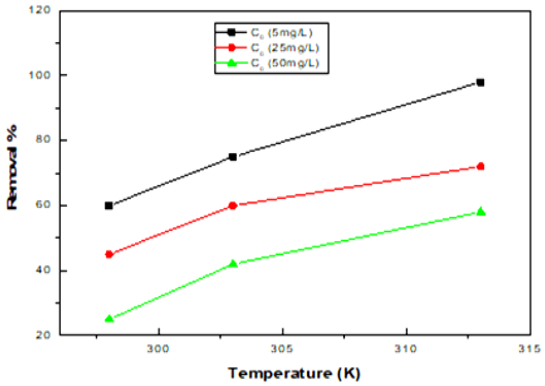

Figure 8: Effect of temperature on biosorption efficiency of AMX onto BEF (d_p = 60 µm; C_0 = 50 mg/L, m = 1.5 g; pH 6.5 and V = 250 mL)

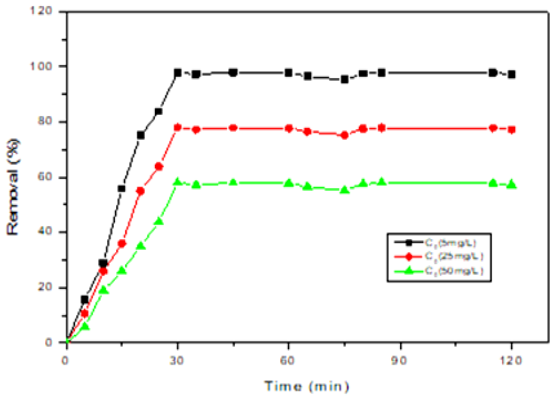

Figure 9: Effect of initial concentration of AMX on biosorption efficiency of AMX onto BEF (d_p = 60 µm, T = 298 K; m = 1.5 g; pH 6.5 and V = 250 mL)

On the other hand, when the pH reaches 6, the BEF material has a greater ability to adsorb amoxicillin.

This can be explained by the fact that the material's surface charge becomes negative, as indicated by the pH_{pzc} value of 4.8. At this pH, the adsorption of amoxicillin can be considered to be governed by the electrostatic interactions between the functional groups of this molecule (sulfonic group) and the adsorption sites of BEF, which can be reinforced by the polarity of AMX.

Effect of temperature

To study the effect of temperature on the adsorption of amoxicillin by BEF, the experiments were carried out in a thermostated bath at different temperatures: 298, 303, and 313 K. The other operating conditions were as follows: initial concentration of the pollutant – 50 mg/L, mass of biosorbent – 1.5 g, pH 6.5, and stirring speed of 350 rpm. The results obtained are illustrated in Figure 8. As may be noted, temperature has a considerable effect on the adsorption rate. This is because an increase in temperature encourages the diffusion of molecules through the outer boundary layer and the inner pores of the adsorbent particles, which is a significant factor in the adsorption process.[24] At temperatures between 298 to 313 K, we find that the adsorption is favored by increasing temperature. It should be noted that the increase in the rate of adsorption with temperature finds its origin on the thermodynamic level. The fixation of amoxicillin onto the adsorption sites of BEF is an endothermic phenomenon, as the increase in temperature implies an increase in the quantity adsorbed.

Effect of initial concentration of AMX

The interaction between the aqueous solution of amoxicillin and the BEF biosorbent leads to increasing amount of AMX adsorbed onto BEF over time. The adsorption study was conducted at different concentrations of AMX (5, 25 and 50 mg/L) to see the effect of initial concentration of the pollutant on the adsorption kinetics. The adsorption curves shown in Figure 9 indicate that the adsorption rate is fast at the beginning of the process, and then slows down until it reaches equilibrium. The adsorption equilibrium for all three concentrations of AMX is reached in approx. 90 min. The adsorption rate was found to increase with decreasing initial concentration of AMX. This can be explained by the fact that, at low concentrations of amoxicillin, the ratio between the adsorption sites available on the biosorbent's surface and the dissolved molecules is high, which favors the elimination of the antibiotic. Conversely, high amoxicillin concentrations led to a lower rate of adsorption because of faster saturation of the adsorption sites.[25]

CONCLUSION

The results of this research have shown that *Brahea edulis* fibers (BEF) can be efficiently employed to remove the complex pollutant AMX, with an elimination rate of 58%. The characterization of the biosorbent by FTIR, XRD and SEM revealed that BEF has functional groups (hydroxyls, carboxyl, amines, *etc*.) characteristic of cellulose, and a semi-crystalline structure ($2\theta = 22.3°$ – maximum intensity attributed to cellulose, and $2\theta = 17.6°$ – minimum intensity attributed to the amorphous phase). SEM images indicated that the chemical treatment of BEF improved the porosity of the material, by dissolving a part of the non-cellulosic components. The results of the physico-chemical analyses of BEF (moisture content, mineral matter, ash content, porosity and real density) also suggested that this material could be used as a biosorbent.

The influence of contact time, initial adsorbate concentration, biosorbent dosage, pH and temperature on the adsorption efficiency of amoxicillin onto BEF was examined, and the optimum conditions favouring the biosorption were determined. The best experimental results were obtained at the contact time of 90 min, amoxicillin concentration of 50 mg/L, biosorbent dose of 1.5 g, pH 6, and the temperature of 313 K. The high biosorption capacity at high temperature suggests that this biosorption process is based on a physical adsorption mechanism, and has a spontaneous and endothermic nature.

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