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Determination of the Biosorption of Cd(Ⅱ) by Coconut Fiber

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Abstract: The coconut fiber is produced in large quantities in Brazil, even though very small quantities are being used by some industries, mainly cordage mats and handicrafts. An alternative usage would be the use of these fibers in biosorption of heavy metals from aqueous solutions. This present study aimed to evaluate the potentiality of cadmium biosorption by coconut fiber. The coconut fibers were used at kinetic analysis, influence of pH and adsorption isotherms were also carried out. It can be concluded that there is great potential for the use of coconut fiber, and the optimum pH for adsorption was around 5.0. The adsorption kinetics is fast and equilibrium occurs within 120 min. The Langmuir isotherm was considered the most suitable to describe the experimental data.

Key words: Coconut fiber, biosorption, cadmium.

1. Introduction

The presence of industrial effluents is undesirable by the urban and rural population since such residues contain dangerous chemical compounds [1].

Processes for surface treatment of metal and electroplating generate significant quantities of effluents containing heavy metals (e.g., cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver and titanium) for a variety of applications. Nowadays, large amounts of industrial wastewater containing these heavy metals are released to the aquatic environment as rivers, seas, urban and rural environment [2, 3].

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Thus, these metals can be absorbed by living organisms and, once they enter the food chain, large concentrations can accumulate in the human body [3-7]. Amongst heavy metals, cadmium is of particular concern due to its serious health and environmental impact [8].

The treatment of industrial effluents containing heavy metals, often involves processes for reduction of toxicity to meet the standards procedures, based on technologies, such as adsorption on new adsorbents, membrane filtration, electrodialysis and photocatalysis. The coconut fiber seems to be a viable alternative for cadmium removal from aqueous solutions, because it has great availability in Brazilian coastal areas [1-3].

The plant *Cocos nucifera* L. is known as coconut and is introduced by the Portuguese in Brazil, reaching a height of 20 m. The fruit known as coconut has three basic structures: the endocarp (inner region with water chestnut), mesocarp (region with coconut fiber) and epicarp (outer region) [1-3, 8].

The edible coconut "flesh" and water are used as sources of food and production of oil in many applications. The fiber can be used in industries such as cordage industries or crafts. However, a considerable percentage of these fibers are discarded, thus generating large amounts of waste in coastal regions [1-3, 8, 9].

The coconut fiber is rich in lignin (35%-45%) and cellulose (23%-43%), characteristics providing greater application potential in the treatment of aqueous solutions for the removal of heavy metals. In the basic composition of coconut fiber, it is possible to observe the presence of N, P, K, Ca, Mg, Fe, Cu, Zn, Mn and Al [1-3, 8, 9].

This present study aimed to determine the ability of coconut fiber on the removal of Cd(II) from aqueous solutions.

2. Materials and Methods

2.1 Coconut Fibers

The coconut fiber was washed with deionized water, dried and crushed (40 mesh).

2.2 Biosorption Experiments

The experiments on the biosorption of Cd(II) were carried out in three stages:

(1) Kinetic analysis was performed with 0.04 L of cadmium solution (90 mg/L) and 0.1 g of crushed coconut fiber. The pH was adjusted to 5.0 with NaOH or H_2SO_4, and was stirred at 150 rpm by 24 h.

(2) Analysis of the influence of pH was studied with a similar system as above. The pH was adjusted to 2.0, 5.0 and 8.0 with NaOH or H_2SO_4, and was stirred at 150 rpm by 24 h.

(3) Similarly, the analysis of the equilibrium adsorption was otherwise studied for an initial concentration range of Cd(II) solution of 10-140 mg/L.

Eq. (1) was used for the determination of the amount of metal (mg) adsorbed per gram of biosorbent [8, 10-14].

$$q_e = \frac{C_0 - C_e}{M} V \tag{1}$$

where q_e is metal concentration in the biosorbent (mg/g), C_0 and C_e are initial and final concentrations of the metal in solution (mg/L), respectively, and M is the mass of the biosorbent (g). To determine the percentage rate of removal of cadmium, R_e (%), from solution, Eq. (2) was employed [8, 10-14]:

$$R_e\% = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

2.3 Characterization of the Adsorbent Mass

To characterize the coconut fiber, X-ray diffraction (XRD) Rigaku, Model Miniflex II was used. The operating conditions were 30 kV and 15 mA, the anode was a copper $K\alpha$ = 0.1542 nm and Ni filter. Analysis occurred in the range between 5° and 80° (2θ) and the step was 0.02°. The phases were analyzed using the software X software-Philips High Score.

The chemical nature of coconut fiber was also analyzed by Fourier transform infrared spectroscopy (FTIR) using the attenuated total reflectance (ATR) mode directly on the powder (NEXUS-470-FTIR, 04 resolution, 32 scans).

The morphology and structure of coconut fiber was examined by scanning electron microscopy (SEM) with accelerating voltage of 20-30 kV and magnifications of 75× and 30.000×. Energy dispersive X-ray (EDS) analysis was performed with the equipment TM3000 (15 kV).

3. Results and Discussion

3.1 Characterization of Coconut Fiber

3.1.1 XRD Analysis

The diffractogram of coconut fiber is shown in Fig. 1. The following peaks were observed: 14.91°, 22.22° and 37.77°.

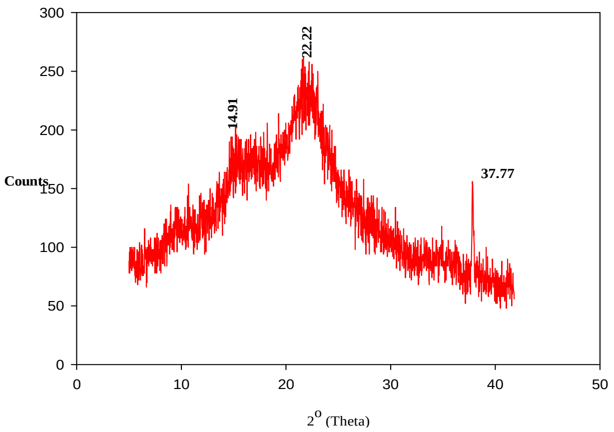


Fig. 1 X-ray diffractogram of coconut fiber.

Through these diffraction peaks, it could be determined that higher peak intensity (22.22°) represents the diffraction of the crystallographic structure of cellulose [1, 9, 15, 16]. Relative to the structure of coconut fiber, this peak as well as the other peaks (14.91° and 33.77°) represent the peaks of Mg_2Si, C, SiO_2, Al_2O_3 and MgO, characteristic of the composition of hemicelluloses, cellulose and lignin that stand out in coconut fiber due to its high percentage composition [15, 16].

3.1.2 FTIR Analysis

The FTIR spectrum of coconut fiber (Fig. 2) shows the characteristic peaks of cellulose structure. The large, broad peak in the range of 3,329 cm^{-1} corresponds to the vibration of hydroxyl groups (OH). The amine groups (NH) corresponds to the intense peak at 1,024 cm^{-1}, while the peak 2,928 cm^{-1} refers to the CH_2 group. The other peaks and headings correspond to the following peaks: 1,606 (COO-), 1,245 (CO) per cm [17, 18].

3.1.3 Characterization by SEM/EDS

In the SEM analysis of the coconut fiber (Fig. 3), it is possible to observe the presence of oil, wax and lignin on the untreated fiber [9].

According to Carvalho et al. [9], the difference for a surface treated fiber would be the observation of contiguous globular protrusions called tyloses, which are concealed by the material surface waxes, oils and extracts lignin.

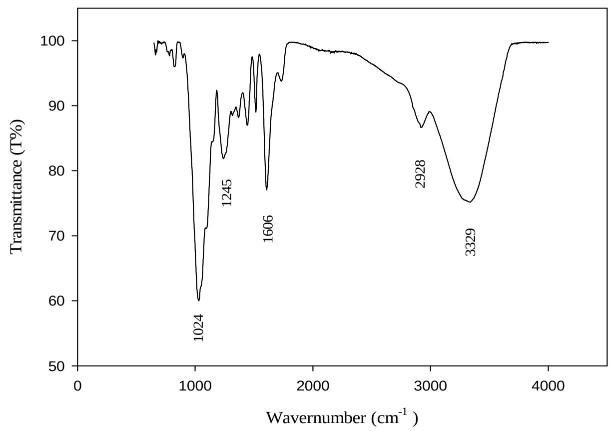


Fig. 2 FTIR analysis of coconut fiber.

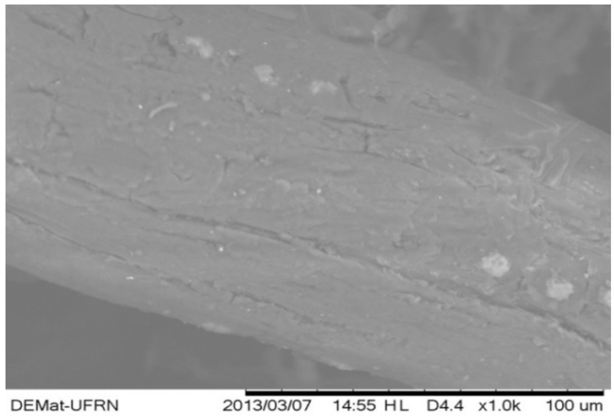


Fig. 3 Micrographs of coconut fiber surface (untreated).

Similar to that observed in this study, demonstrates much of the surface masked by natural fiber materials (waxes, extracts and lignin).

In the analysis performed by EDS area mapping, it was possible to verify the coconut fiber for occurrence of bands representing the chemicals naturally present incoir (Cl, K and Al) as well as the representation of its organic composition (cellulose and lignin) through the presence of C and O (Fig. 4).

This characterization is similar to that carried out by Sarki et al. [15], indicating that the elements Cl, K and Al may influence the adsorption of heavy metals in the ion exchange process.

3.2 Analysis of Adsorption

3.2.1 Kinetic Analysis

Kinetic studies indicated that the adsorption process of Cd(II) on the coconut fiber is fast, reaching equilibrium in less than 120 min (Fig. 5).

Different masses of adsorbents showed similar results regarding the rapid equilibrium in the kinetic system of the Cd adsorption. Kumar et al. [14] found the maximum removal was less than 90 min on the removal of cadmium by rice husk. Similar result was observed by Semerjian [10] where they used sawdust in the removal of cadmium and the equilibrium was reached closer to 20 min.

3.2.2 Influence of pH

The effect of pH on the adsorption of Cd(II) is shown in Fig. 6. The pH of the aqueous solution is an important operating parameter in the adsorption process as it affects the solubility of metal ions, the concentration of the counterions to the functional groups of the adsorbent and the degree of ionization of the adsorbate during the reaction [8, 11, 13].

Based on the results, it was possible to determine that, at low pH there is low uptake of Cd(II) but the adsorption capacity increases with pH, reaching a plateau in the range of 5.0-8.0. The results were justified because, at low pH, the active sites of the adsorbent mass are closely associated with the hydronium ions (H_3O^+) and the repulsion of cations of cadmium is significant.

Besides, at low pH the dissociation of carbonyl groups and hydroxide are affected by reducing the sorption capacity of the biomass [8, 11, 13, 19]. When pH was higher than 8.0, the Cd(II) begins to precipitate in the form of $Cd(OH)_2$. Thus, in most of the experiments the use of pH 5.0 is justified. Pino et al. [8] observed similar results with a percentage increase in adsorption capacity.

However, other studies involving cadmium adsorption show that above pH 7.0 the metal adsorption capacity starts declining. Kumar et al. [14] observed that at pH 5.0, the metal adsorption was above 80% using seeds of *Strychnos potatorum*. Gupta and Rastogi [12] used seaweed (*Oedogonium* sp.) with the same pH range and considered ideal. On the other hand, Perez-Marin et al. [13] showed that

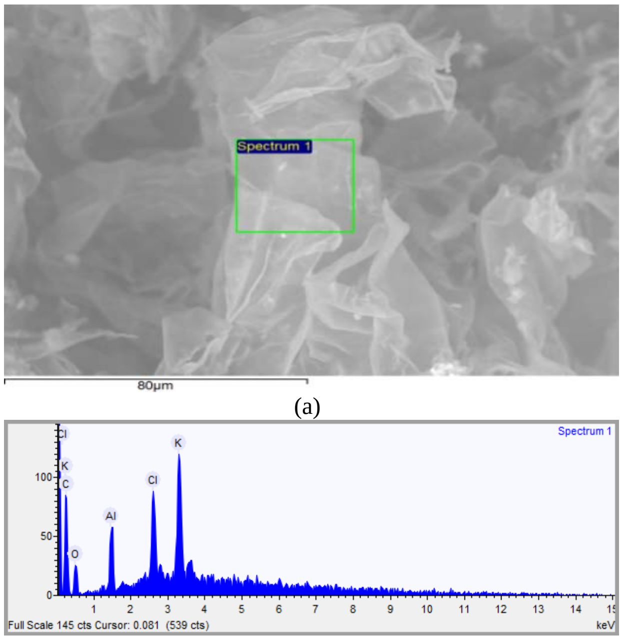


Fig. 4 Analysis of SEM/EDS—fresh coconut fiber.

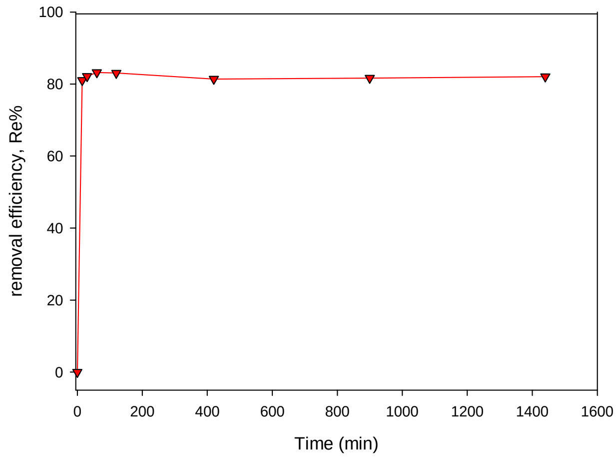


Fig. 5 Effect of contact time on the removal efficiency (R_e) of Cd(II) by the adsorbent.

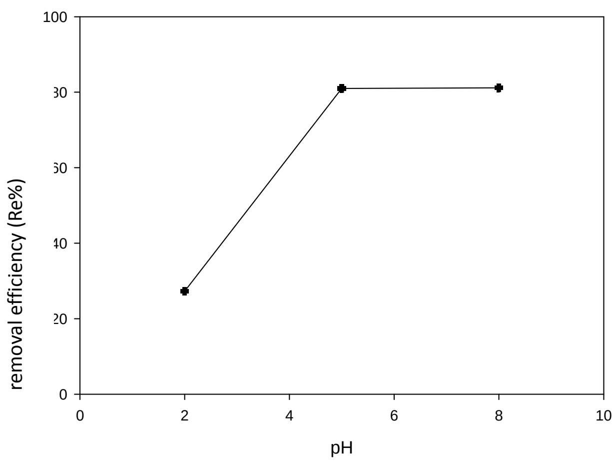


Fig. 6 Effect of pH on the R_e of Cd(II) by the adsorbent.

deprotonation of the carboxylic groups occur in the pH range of 5.0-6.0, thus generating negative charges, which favors better metal adsorption. Azouaoua et al. [19] observed a reduction in the adsorption of Cd(II) by a material derived from coffee above pH 7.0, suggesting that this might be due to the lower polarity of the metal in this range of pH.

3.2.3 Analysis of the Adsorption Equilibrium

Fig. 7 illustrates the amount of Cd(II) adsorbed q_e on the basis of the equilibrium concentration (C_e) by varying the initial concentration of the metal (10-140 mg/L). This is because the initial concentration of cadmium provides the driving force required to overcome the resistance of the metal mass transfer between the liquid and the solid phase. Moreover, the increase in the concentration favors greater interaction between the metal ion in solution and the active sites of coconut fiber [14].

However, in terms of percentage removal (Fig. 7), there is a decrease from 98% for an initial concentration of 10 mg/L to 55.9% at a concentration of 140 mg/L.

Similar values have been reported in the literature. Kumar et al. [14] observed a decrease of 98.9% to 68.6%, whit concentrations ranging from 20-100 mg/L, of adsorption of cadmium by rice husk. Semerjian [10] used wood sawdust, in which a decrease was observed between 100% and 85% with initial concentrations between 1 mg/L and 50 mg/L.

3.2.4 Adsorption Isotherm

The study of isotherms helps in describing the adsorption mechanisms of Cd, where these are characterized by specific constants which express the surface properties of affinity of coconut fiber by metal ion in solution [8, 10-14]. Both Langmuir and Freundlich models were adopted in the present study, both plotted in Fig. 8.

(1) Langmuir isotherm

The Langmuir equation has been used in several studies to describe the phenomena of adsorption isotherm with the Eq. (3) [8, 10-14]:

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{3}$$

where, q_e is the metal quantity adsorbed at equilibrium (mg/g), q_m is the maximum binding capacity (mg/g), C_e is the equilibrium concentration of the metal in solution (mg/L), and K is an apparent equilibrium constant (L/mg).

The Langmuir isotherm constant was plotted in a non-linear curve according to Eq. (3). The Langmuir constant, q_m, which is a measure of the monolayer adsorption capacity of coconut fiber was calculated as 31.12 mg/g, and the constant K was equal to 0.621 L/mg. Indeed, Fig. 8 shows good agreement between experimental values and the fitting of the isotherm model (R^2 = 0.988), confirming the monolayer

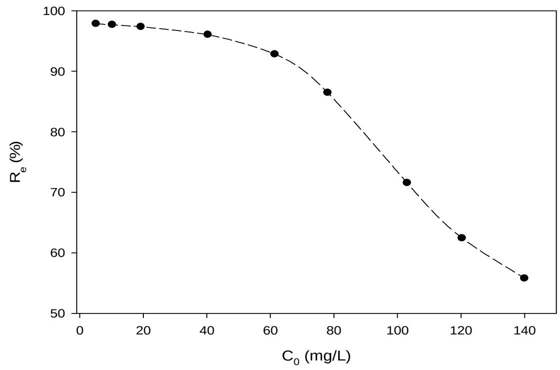


Fig. 7 Effect of initial ion concentration on the R_e of Cd(II) by the adsorbents.

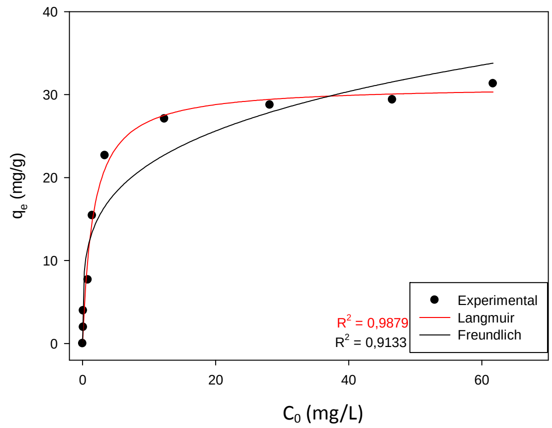


Fig. 8 Langmuir and Freundlich isotherm models for Cd adsorption by coconut fiber.

adsorption of Cd by coconut fiber.

Based on the result obtained from this analysis, a study was conducted to determine whether the process of Cd(II) adsorption is favorable or not, through the equilibrium constant K, which is used to calculate the R factor [8, 10-14]:

$$R = \frac{1}{1 + KC_0} \quad (4)$$

If the value of R is greater than 1, it indicates that the isotherm is unfavorable, while values between 0 and 1 are indicative of favorable isotherm. The values calculated for the adsorption of Cd(II) were in the range of 0.244-0.0114, when C_0 varied from 10 to 140 mg/L. Thus, the process of adsorption is favorable.

(2) Freundlich isotherm

The Freundlich model, Eq. (5), was used in this analysis [8, 10-14]:

$$q_e = K_f C_e^{\,n} \quad (5)$$

where, q_e is the amount of cadmium adsorbed (mg/g), C_e the equilibrium concentration of Cd(II) in solution (mg/L), K_f (mg/g) the measurement of the adsorption capacity and n is the intensity of the adsorption.

The Freundlich equilibrium constants were also determined from the non-linear fitting to q_e versus C_e, represented in Fig. 8, based on Eq. (5). The values of K_f and n obtained were 12.26 and 0.246, respectively. The correlation coefficient between the experimental values and the adsorption isotherm was considered low (R^2 = 0.913). Therefore, the experimental behavior is best explained by the Langmuir isotherm.

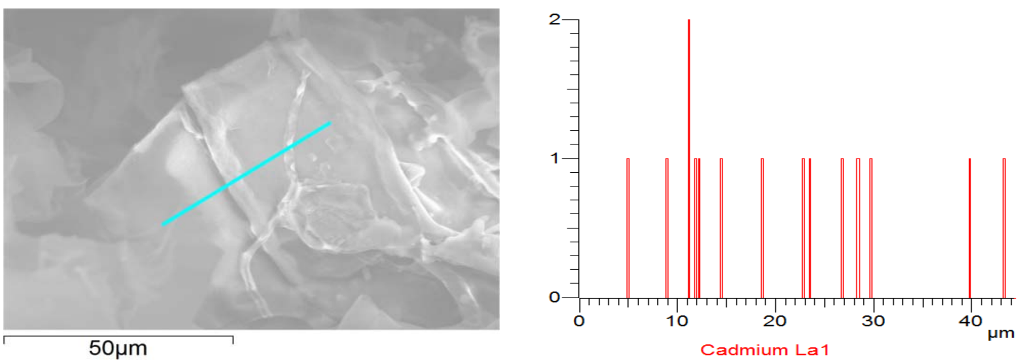
The adsorption capacity of Cd(II) by fresh coconut fiber was compared to other adsorbents described in the literature in Table 1. Monolayer adsorption of Cd by the coconut fiber is predominant in most of the cases. In this study, the maximum adsorption capacity, q_m, under the experimental conditions tested was superior than in most published studies.

(3) SEM/EDS analysis of mass biosorbent

Based on the results from electron microscope analysis, EDS analysis was extended to determine the presence of cadmium on the fiber surface exposed to metal solution. The results are shown in Fig. 9, where the presence of Cd on the fiber surface is confirmed.

Table 1 Isotherm constants for different adsorbents, for Langmuir and Freundlich models.

Adsorbent	Langmuir isotherm			Freundlich isotherm			Reference
	q_m (mg/g)	K (L/mg)	R^2	n	K_f	R^2	
Coconut fiber	31.12	0.621	0.99	0.246	12.26	0.913	This study
Sawdust	7.35	0.782	0.94	4.194	2.213	0.960	Ref. [10]
Coffee grounds	12.19	0.055	0.98	0.370	1.692	0.919	Ref. [19]
Terminalia catappa	35.84	0.03	0.99	2.79	4.33	0.98	Ref. [20]
Chestnut	4.07	0.278	0.95	2.70	1.077	0.993	Ref. [21]
Bamboo charcoal	12.08	0.485	0.99	4.6	5.32	0.989	Ref. [22]
Wood	175.4	0.320	0.99	2.053	3.410	0.968	Ref. [23]



(a) (b)

Fig. 9 Analysis by (a) SEM and (b) EDS of coconut fiber surface after adsorption tests.

4. Conclusions

The experimental results obtained in this study indicated that the coconut fiber has good performance as biosorbent in the removal of Cd(II) from aqueous solutions.

The tests revealed that as the pH increases from 2 to 5, the adsorption of Cd(II) increases from 27% to 81%, for an aqueous solution containing 90 mg/L of Cd. The adsorption kinetics is fast and the equilibrium can be achieved within 120 min.

On the study about the influence of the initial concentration of Cd(II), it was observed that there is an increase in the sorbate uptake and a reduction in the percentage adsorption, when the initial concentration is increased. In addition, it was observed that Langmuir adsorption isotherm was able to describe the equilibrium data. The maximum adsorption capacity of Cd on the coconut fiber is 31.12 mg/g.

The occurrence of Cd(II) adsorption on the fiber surface was confirmed by SEM/EDS analysis.

In summary, based on the experimental data, it was determined that the coconut fiber reveals high efficiency in the removal of cadmium from aqueous solutions, with the advantage of having high availability and low cost.

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