



TANGERINE FRUIT SHELL (TFS) BIOSORBENT. PREPARATION, CHARACTERIZATION AND ITS USE FOR COPPER REMOVAL

B. M. A. Bortoluzzi¹; M. R. Cunha¹; N. F. G. Mendes¹; M. Peraça¹ F. A. Pavan¹

1-Departamento de Química – Universidade Federal do Pampa (Unipampa – Bagé)
Rua Travessa 45, 1650 – CEP: 96413-170 – Malaféia- RS – Brasil

Telephone: (53) 3247-2367 – Fax: (00) 0000-0000 – Email: flavio.pavan@unipampa.edu.br

ABSTRACT: The Tangerine fruit shell (TFS), an agro-residue was used effective biosorbent for removal copper ions from aqueous solution using the batch procedure at 25°C. The TFS was characterized by FT-IR, nitrogen adsorption-desorption isotherms (BET), elemental composition of carbon, hydrogen and oxygen and tritration analyses. Important parameters such as contact time, pH, dosage of biosorbent and initial metal ion concentration on the biosorption capacities were investigated. The adsorption kinetic is fast, the equilibrium was established within 30 min. The sorption occurred at pH 5.0 using 0.2 g of biosorbent. The equilibrium adsorption data were investigated using nonlinearized Langmuir, Freundlich and Redlich-Peterson adsorption isotherm at 25°C. The best fit equation for biosorption was obtained with Redlich-Peterson adsorption isotherm. The maximum biosorption capacity of TFS was 27.25 mg g⁻¹. Fourier transform infrared analysis confirms the existence of carboxyl, carbonyl and phenol sites on surface of biosorbent responsible to bind copper ion onto TFS.

Keywords: Tangerine fruit shell; Biosorption; Cu(II); aqueous solution; nonlinearized isotherm.

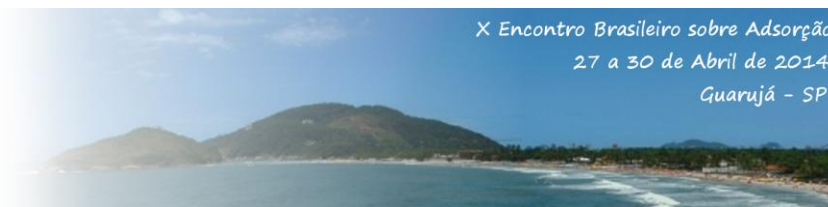
1. INTRODUCTION

The presence of toxic heavy metal ions in waters has generated considerable concern in recent years because these compounds has been responsible for several harmful effects to the health of animals, humans and plants (Aksu and Isoglu, 2005). Copper absorbed by man leads to gastrointestinal irritation, renal damage, depression and the other diseases (Gündogan et al., 2004). Heavy metals removal from aqueous solution can be accomplished by conventional techniques (Al-Rub, 2006; Satapathy and Natarajan, 2006; Kosasiha et al., 2010). The main disadvantages of these processes are high operational costs usually accompanied by the incomplete removal of the metal ion (Elangovan, et al., 2008).

Biosorption processes using low cost material have been developed into a promising alternative method in wastewater treatment, especially for the elimination of metal ions from

aqueous solutions (Volesky,1990). A remarkable number of papers have been published in this research field, showing the large potential of different agricultural and biological materials to remove metal ions from aqueous solution (Ho, 2003; Xuan et al., 2006; de Carvalho et al.,2001). Natural materials such as ponka peel (Pavan et al.,2006), yellow passion-fruit peel (Jacques et al, 2007), orange waste (Perez-Marin et al., 2007) crab carapace (Cochrane, Brazilian pine-fruit shell), coffee, and tea residues (Minamisawa et al., 2004) are promising raw materials used in wastewater treatment and have been successfully used as biosorbent to remove toxic metals from aqueous media due to their low cost and large availability.

Tangerine fruit shell is an important product in the food industry. It is consumed in nature or in different processed forms as juice, for instance (Fernandes et al., 2001). By-products such as tangerine shell create large environmental



problems and therefore represent a major disposal problem in the food industry. Using recycled by-products as shell material in other processes is of great interest and leads to cost reduction in all steps of the industrial process.

The aim of this investigation is to report the use of tangerine fruit shell (TFS-*Citrus reticulata* Blanco) as biosorbent for the removal of Cu(II) ions from aqueous solution using batch adsorption at room temperature. Characterizations of tangerine fruit shell were performed using FT-IR, scanning electron microscopy (SEM), nitrogen adsorption-desorption isotherms, elemental composition of carbon, hydrogen and nitrogen (CHN analysis) and titration analyses. Parameters such as pH, biosorbent dosage, contact time and initial metal ion concentration on the biosorption capacities were investigated. Biosorption capacities of TFS were evaluated using nonlinearized Langmuir, Freundlich and Redlich-Peterson isotherm models at 25°C.

2. MATERIALS AND METHODS

2.1 Metal solutions and analysis

A copper stock solution 1000.0 mg/l was prepared by dissolving copper sulfate (CuSO_4 , anhydrous 98% supplied by Acros Organic) in 1000.0 ml of de-ionized water. This stock solution was used to prepare solutions with appropriate concentrations. The pH of the sample solutions was adjusted with aliquots of 0.1 mol l⁻¹ of HCl or NaOH solutions utilizing a pH/mV hand-held meter provided with combined glass electrode. The concentration of the remaining metal in the solution after the biosorption was determined by flame atomic absorption (FAAS)

2.2 Preparation and characterizations of TFS biosorbent

TFS was purchased at the local market. After washing with bidistilled water for several times, the biomass was dried at 60°C in an air-supplied oven for 8 h. The dried biomass was ground in a disk-mill and sieved in order to reach a diameter of particle $\leq 400 \mu\text{m}$. The biosorbent was stored in desiccators and later used without any chemical or physical treatment.

The specific surface area of biosorbent was determined by the Brunauer, Emmett and Teller (BET) multipoint technique, obtained by the N₂

adsorption-desorption isotherm. The biosorbent was previously degassed at 100°C, in vacuum, for 1 h. The pore size distribution was made in the volumetric apparatus using nitrogen probe.

In order to identify the active sites of TFS capable of binding metal ions, the biomass was characterized by Fourier transform infrared (FT-IR) spectroscopy.

The surface functional groups on the TFS were investigated by Boehm titration (Boehm 1994). The amount of oxygen-containing groups (carboxyl, lactonic and phenol) on the TFS was determined by neutralization with 0.100 mol l⁻¹ NaHCO₃, 0.100 mol l⁻¹ Na₂CO₃, and 0.100 mol l⁻¹ NaOH solutions, respectively. The basic group contents of the activated carbons were determined with 0.100 mol l⁻¹ HCl. The acidic and basic sites were determined by adding 50.0 ml of 0.100 mol l⁻¹ titrating solution and 1.00 g of TFS to a 50.00 ml volumetric flask. The flask was left for 36 h at 30 °C. Afterwards, a sample of 10.00 ml was back-titrated with 0.100 mol l⁻¹ HCl or NaOH solution.

For the determination of point zero of charge (pH_{pzc}) of the biosorbent, the procedure similar to the one described was used (Utrilla et.al, 2001): 50.00 ml of 0.0100 mol l⁻¹ NaCl solution was placed in closed Erlenmeyer flasks. The pH of each solution was adjusted to values of 2.0, 4.0, 6.0 and 8.0 by adding 0.100 mol l⁻¹ HCl or NaOH solution. Then, 0.15 g of TFS sample was added to the system and the final pH measured after 48 h under agitation at room temperature. The pH_{pzc} is the point where the curve pH final versus pH initial crosses the line equal to pH final.

TFS was calcinated at 850 °C for 3 h in a furnace in the presence of air to obtain mineral ashes.

2.3 Batch biosorption studies:

The batch procedure allows determining the influence of parameters, such as contact time, pH, dosage biosorbent, and initial metal ion concentration on biosorption capacity of TFS. These parameters have significant practical importance, mainly in industrial scale, as auxiliary data for the construction of more efficient and economic small reactors.

All the experiments were carried out at 25 °C. The biosorption capacity of TFS for Cu(II) ion was investigate using the batch procedure biosorption. For this study a fixed amount of biosorbent (0.100-1.00g) was placed in a 125.0 ml



Erlenmeyer flask containing 50.00 ml of metal solution (5.00-1000.0 mg.l⁻¹) at pH values ranging from 2.0 to 8.0 and the contact time ranging (5.00-120.0 min). Afterwards, the mixture was placed horizontally in a shaker for 60 min at 150 rpm, the biosorbent was removed by filtration and the filtrate analyze by flame atomic absorption spectrophotometer (FAAS).

The amount of compound adsorbed by the biosorbent is given by the equation 1.

$$q = \frac{(C_o - C_f)V}{m} \quad (1)$$

where q is the amount of metal ion adsorbed by the biosorbent (mg g⁻¹); C_o is the initial metal ion concentration (mg l⁻¹); C_f is the metal ion concentration (mg l⁻¹) after the batch biosorption procedure; V is the volume of the metal ion solution (l) put in contact with the biosorbent and m is the mass (g) of biosorbent.

3. Results and Discussion

3.1 Characterization of TFS biosorbent

The textural properties of TFS biosorbent obtained by nitrogen adsorption-desorption isotherm were: specific surface area (SBET) 52.11 m²/g; average pore diameter (BJH) 4.85 nm and average pore volume (BET) 0.110 cm³/g of native TFS biosorbent. The physical and chemical characteristics of TFS biosorbent are summarized.

Several authors have demonstrated that functional groups such as hydroxyl and mainly carboxylic groups are responsible for the metal uptake from aqueous solution (Minamisawa et al., 2004; Menon et.al., Kosasiha et.al., 2010). The amount of acid and basic sites on the surface of TFS determined by Boehm titration method found were: 2.01 mmol g⁻¹ for carboxylic groups, 0.98 mmol g⁻¹ for carbonyl group and 0.18 mmol g⁻¹ for phenolic group (Table 1). The results obtained shown that carboxyl and hydroxyl groups were present in abundance on TFS biosorbent. The FT-IR spectrum of TFS confirm the presence these functional groups on chemical composition of TFS biosorbent.

The presence of functional groups on TFS surface potentially able to bind copper ions were investigated by infrared spectroscopy technique. FT-IR spectra were obtained before and after copper ions biosorption. Based on Figure 1, it is

possible to detect several functional groups that might be responsible for the uptake of copper ions.

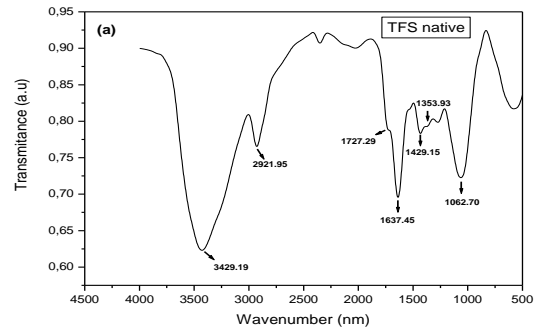


Figura 1. FT-IR spectra of native tangerine fruit shell

The strong band observed from 3000 cm⁻¹ to 3600 cm⁻¹, are assigned to O-H bonds (stretch) of macromolecular association with alcohols, phenols and carboxylic acid, present in lignin, cellulose and pectin of the TFS (Minamisawa et al., 2004).

The band at 2929.6 cm⁻¹ corresponding the asymmetric C-H vibration of aliphatic group (Gottipati and Mishara, 2010). The peak observed at 1730.0 cm⁻¹ is attributed to the stretching vibration of the C=O bond of carboxylic acids and esters (-COOH and -COOCH₃). The peaks at 1641 cm⁻¹ and 1433.cm⁻¹ corresponding the vibration of deprotonated carboxylic groups (-COO). The peak at 1375.0 cm⁻¹ may be assigned the vibration of C-O-O groups of lignin-cellulosic materials. The peaks observed at 1072.3 cm⁻¹ can be assigned to the stretching vibration of C-O groups of alcohols, carboxylic acid, ester and phenols. In Figura 2, the TFS biosorbent was loaded with Cu(II) ions, and it is possible to observe slight changes in the band wavenumbers of hydroxyl and carboxyl groups.

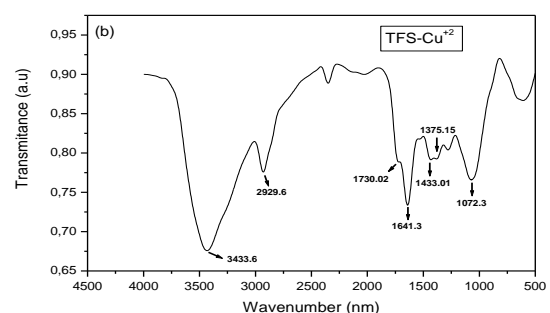


Figura 2. FT-IR spectra after biosorption of copper

3.2 Effect of pH biosorption

One of the most important factors on biosorption studies is the effect of the acidity of the medium. Figure 1 shows the effect of pH on the biosorption capacity of copper ions from aqueous solution onto TFS. Based in Figure 3 is possible to observe a gradual increasing on biosorption capacity of TFS with increasing solution pH from 2.0 to 4.0 (the percentage of removal increased from 38.7% to 77.8%).

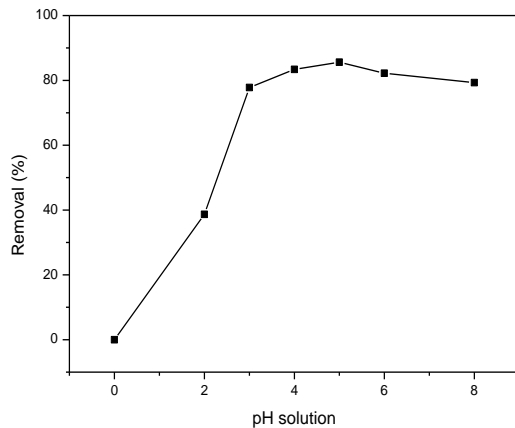


Figura 3. Effect of pH biosorption

The highest biosorption occurs rapidly when initial pH solution was increased from 4.0 to 5.0, attaining 85.6% adsorbate removal. Above pH 6.0, the precipitation of copper ions can occur resulting in a decrease in the biosorption capacity. These data can be explained considering the point of zero charge, pH_{pzc} of TFS biosorbent. At pH values lower than pH_{pzc} ($pH < 4.20$), the surface TFS as positively charged, hindering the electrostatic attraction between a copper decrease on adsorption is observed. However, at pH values higher than 4.2 the TFS adsorption is facilitated because the surface of adsorbent is negatively charge consequently an increase on adsorption occur.

3.3 Effect of biosorbent dosage

The influence of the biosorbent dosage on copper ions biosorption is showed in Figure 4.

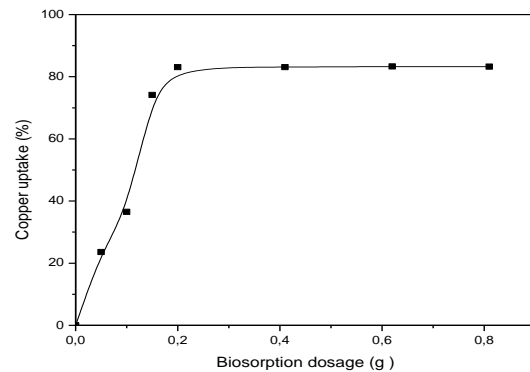


Figura 4. Effect of biosorption dosage

Increasing the concentration of biosorbent up to 0.2 g results in a rapid increase in the percentage of Cu(II) uptake (0 to 83%). If the amount of biosorbent increases, the number of active sites increases and, consequently, a higher biosorption may occur. For adsorbent masses ranging from 0.2 to 1.0 g, the percentage of Cu(II) removal was kept constant. The increase in adsorbent mass at fixed Cu(II) concentration and volume will lead to unsaturation of adsorption sites through the adsorption process. Similar trends have been observed with Cu(II) adsorption onto palm kernel fiber (Ho and Ofomaja 2006c). In further experiments the biosorbent dosage used was 0.2 g.

3.4 Effect of shaking time e initial metal concentration

The effect of the contact time between the metallic ions and the biosorbent in the range of 5 to 120 min was carried-out at pH 5.0, at 25 °C using a biosorbent dosage of 0.2 g. Figure 3 shows a plot of the amount of metal ion uptake q_t versus contact time at different initial metal ion concentration for 5.0, 10.0 e 20.0 $mg.l^{-1}$. As can be observed in Figure 5, that the amount of metal ion uptake increases. The equilibrium was established within 30 min for all initial adsorbate concentrations. The fast kinetic biosorption of Cu(II) is attributed to a higher number of vacant active sites available on TFS surface at the initial stage. As the TFS active site are being occupied, few active sites are left for being filled, after 30 min, the equilibrium is attained. In further experiments the contact time between the biosorbent and biosorbate was fixed at 30 min.

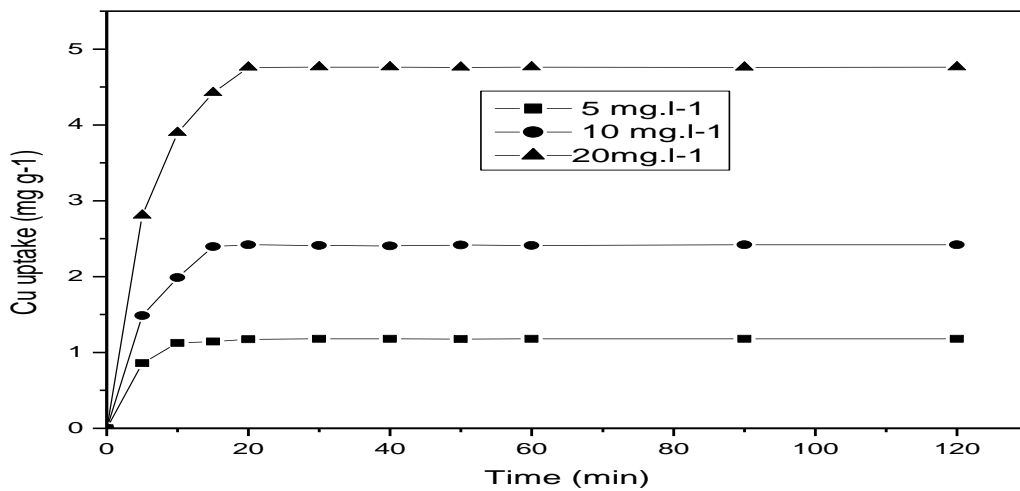


Figura 5. Effect of shaking time e initial metal concentration

3.5 Equilibrium biosorption data

In order to investigate the equilibrium biosorption capacity of TFS three isotherm models were employed, the Langmuir (Langmuir 1906), the Freundlich (Freundlich 1906) and Redlich-Peterson (Redlich and Peterson, 1959) model. The Langmuir isotherm model assumes that biosorption occurs on a homogenous biosorbent surface of identical sites that are equally available and energetically equivalent with each site carrying equal numbers of biosorbed species. The Langmuir model isotherm is expressed follow:

$$q = \frac{Q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

Where, C_e is the supernatant concentration after the equilibrium of the system (mg l^{-1}), K_L the Langmuir affinity constant (l mg^{-1}), and Q_{\max} is the maximum capacity of the material (mg g^{-1}) assuming a monolayer of biosorbate taken up by the biosorbent.

Freundlich isotherm which is valid for multilayer biosorption on the surface of biosorbent. The Freundlich model isotherm is expressed follow:

$$q = K_F \cdot C_e^{1/n} \quad (3)$$

Where K_F is the Freundlich constant related to biosorption capacity [$\text{mg.g}^{-1} \cdot (\text{mg.l}^{-1})^{-1/n}$]

and n is the Freundlich exponent (dimensionless).

The Redlich-Peterson isotherm proposed an empirical equation to represent equilibrium data:

$$q_e = \frac{K_{RP} \cdot C_e}{1 + a_{RP} \cdot C_e^\beta} \quad (4)$$

where kR (l/g), aR (l/mmol) and β are Redlich-Peterson isotherm constants. This equation reduces to a linear isotherm in the case of low surface coverage and to a Langmuir isotherm when $\beta = 1$.

The ability of different biosorption isotherm to correlate with experimental data, the theoretical plots from each isotherm model have been shown with experimental data for biosorption of copper onto TFS at the temperature of 25°C in Figure 6.

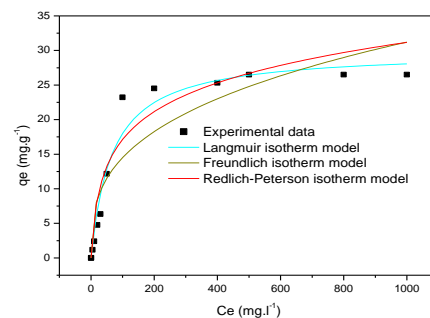


Figura 6: Isotherms of copper biosorption by TFS: Simulation with Langmuir, Freundlich and Redlich-Peterson isotherm models.



Figure 6 plots copper adsorbed per unit mass of TFS (q_e) vs copper ions remaining in solution, C_e . In the Table 1 are summarized the determination coefficient (R^2) and Chi-square test (χ^2) for the three biosorption isotherm models.

Table 1. Isotherm parameters for copper ions biosorption, using TFS as biosorbent.

Langmuir	Copper
Q_{max} ($mg.g^{-1}$)	29.7105
K_L ($L.mg^{-1}$)	0.01893
R^2	0.969
χ^2	0.290
Freundlich	
K_F ($mg.g^{-1}.(mg.L^{-1})^{-1/n_F}$)	3.4315
n_F	3.05402
R^2	0.86924
χ^2	1.346
Redlich –Peterson	
K_{R-P}	0.50756
a_{R-P}	0.01028
β	0.99807
R^2	0.987
χ^2	0.268

It can be seen from Table 1 that the Redlich-Peterson isotherm best fitted to the experimental data since it had the highest values for the determination coefficient, R^2 (0.977) and also the low values for Chi-square, χ^2 (0.26). The Freundlich isotherm appears greatest deviation from the experimental data and the least values of determination coefficient, R^2 (0.8692) and highest values for Chi-square, χ^2 (1.3460). The Freundlich equation is considered not suitable to describe the biosorption process for Copper-TFS system. The Langmuir isotherms also had good degree of fitness to the experimental data with relatively high values of determination coefficient, R^2 (0.969) and relatively low values for Chi-square, χ^2 (0.290). The Redlich-Petersen isotherms appear best degree of fitness to the experimental data with good values of coefficient R^2 (0.987) and β ($0 < \beta < 1$) and lowers value for Chi-square, χ^2 (0.268) when compared to Langmuir and Freundlich isotherm models. Considering these results obtained is possible to conclude that the Redlich-Peterson isotherm is the most suitable of the three isotherm models applied to the biosorption

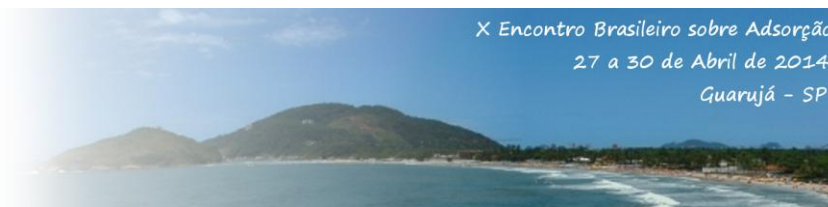
Copper-TFS system. Based on nonlinear Redlich-Peterson model isotherm the equilibrium biosorption capacity of TFS for biosorption of Copper ions from aqueous solution was $27.25 mg g^{-1}$.

4. CONCLUSION

TFS is a locally available and low cost material that can be used as new alternative biosorbent for the removal of copper ion from aqueous solutions. The optimum pH for the biosorption of Copper was between 4.5-5.0 and the shaking contact time necessary for the equilibrium was 30 min. The pseudo- second-order equation was chosen for to represent the Copper-TFS biosorption system. The equilibrium data fitted well to the Redlich-Peterson isotherm. The equilibrium biosorption capacity of TFS for biosorption of Copper ion found to be $27.25 mg g^{-1}$ based on nonlinear Redlich-Peterson model isotherm at the temperature $25^\circ C$. FT-IR analysis confirm the participation of hydroxyl and carboxyl groups on the copper uptake.

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