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ADSORÇÃO DE MICROCISTIN-LR POR CARVÃO ATIVADO GRANULAR PRODUZIDO A PARTIR DE CASCA DE COCO DE DENDÊ

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ADSORPTION OF MICROCYSTIN-LR BY GRANULAR ACTIVATED CARBON PRODUCED FROM PALM (DENDÊ) COCONUT SHELLS

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Abstract

The effects of initial concentration of microcystin-LR (14.56 and 29.26 µg.L-1), pH of influent solution (6.4 and 8.3) and adsorbate / adsorbent contact time (60 and 90 s) on the adsorption of cyanotoxin by granular activated carbon (GAC) was studied. GAC produced from palm (coconut shells) was highly efficient (between 88 - 92%) in removing microcystin-LR from aqueous solution, and concentrations of cyanotoxin in treated effluents were below the maximum level (1 µg.L-1) permitted By Brazilian legislation. The variables initial concentration of toxin and contact time exerted strong effects on adsorption, while the influence of pH was much weaker.

Keywords: water treatment; cyanotoxins; *M. Aeruginosa*; adsorption; granular activated carbon.

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Revista AIDIS de Ingeniería y Ciencias Ambientales:
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6 de diciembre de 2018

Resumo

Os efeitos da concentração inicial de microcistina-LR (14.56 e 29.26 µg.L-1), pH da solução afluente (6.4 e 8.3) e tempo de contato adsorvato/ adsorvente (60 e 90 s) na adsorção de cianotoxina por carvão ativado granular (GAC) foram avaliados. O GAC produzido a partir de cascas de dendê de coco foi altamente eficiente (entre 88-92%) na remoção da microcistina-LR da solução aquosa e as concentrações da cianotoxina em efluentes tratados foram inferiores ao nível máximo permitido (1 µg.L-1) Pela legislação brasileira. As variáveis concentração inicial de toxina e tempo de contato exerceram fortes efeitos na adsorção, enquanto a influência do pH foi muito mais fraca.

Palavras chave: tratamento de água; cianotoxinas; *M. Aeruginosa*; adsorção; carvão ativado granular.

Introduction

The occurrence of cyanobacterial blooms in reservoirs serving as sources for the public water supply represents a serious health issue because of the likely presence of harmful toxins (Rodríguez et al., 2006; Chorus and Bartram, 1999). The microcystins comprise a family of more than 80 cyclic heptapeptides that differ in respect of two variable amino acid residues, and some members of this group are among the most toxic of metabolites generated by the cyanobacteria (Rouhiainen et al., 2004). The microcystin variants LR (containing L-leucine and L-arginine), RR (L-arginine and L-arginine), YA (L-tyrosine and L-alanine) and YR (L-tyrosine and L-arginine) have received considerable research attention, particularly the LR variant since it is most commonly encountered in the environment (Rouhiainen et al., 2004; Carmichael, 1992).

Microcystins inhibit protein phosphatases type 1 and type 2A in the cytoplasm of liver cells, leading to the accumulation of phosphorylated proteins and, ultimately, to hepatotoxicity, necrosis of hepatic cells and the formation of tumors (Calijuri et al., 2006; Humpage and Falconer, 2003). Values of the median lethal dose (LD_{50}) of microcystins determined in experimental animals are reported to vary between 50 and 1200 $\mu g.kg^{-1}$ body weight when administered by intraperitoneal injection, and between 5000 and 10900 $\mu g.kg^{-1}$ body weight when administered orally (Chorus and Bartram, 1999). Following the recommendations of the World Health Organization, the Brazilian Ministry of Health issued guidelines for the control and surveillance of water quality in which the maximum concentration of microcystin-LR in water destined for human consumption was established at 1 $\mu g.L^{-1}$ (Brasil, 2011).

The removal of microcystins from drinking water by conventional treatments involving solid-liquid separation is effective for intracellular toxins, but it is not satisfactory when the cyanotoxins are present in extracellular or dissolved forms (Brasil, 2011; Chow et al., 1999). The main difficulty in removing dissolved microcystins by separatory techniques is associated with the resistance of the compounds to hydrolysis and oxidation, which impedes the action of the coagulants used for the precipitation of solids. This problem, together with the increased frequency of occurrence of cyanobacterial blooms in water reservoirs, has intensified the search for new operationally and

Revista AIDIS de Ingeniería y Ciencias Ambientales:
Investigación, desarrollo y práctica. ISSN 0718-378X
Vol. 11, No.3, 319–331
6 de diciembre de 2018

economically viable methods by which to enhance the quality of distributed water in full compliance with existing legislation (Hoeger et al., 2005; Di Bernardo et al., 2010).

Filters containing activated carbon (AC) are used extensively to remove taste, odor and organic contaminants from domestic water supplies. The carbonaceous material, which is normally produced from wood products, coconut shells or peat, is extremely porous with a very large surface area that can adsorb a wide range of organic compounds, including pesticides and cyanobacterial metabolites such as 2-methylisoborneol, geosmin and cyanotoxins. Although there are many special types of AC, the pulverized or granular forms are most commonly employed in the treatment of domestic and public water supplies. Powdered AC is added directly to processing units (i.e. mixing tanks) to form a suspension that is subsequently filtered, while the granular form (GAC) is used in adsorption columns, cartridges and filters. The key advantages offered by GAC are the reduced volume of sludge produced by the process and the possibility of reutilizing the adsorbent after appropriate treatment. The removal of dissolved cyanotoxins, including microcystins, using GAC alone or in combination with other conventional techniques has been reported previously (Himberg et al., 1989; Ho et al., 2011; Pendleton et al., 2001).

The efficiency of adsorption depends on the characteristics of the carbonaceous material (i.e. particle and pore size, surface area, surface chemistry, density, hardness, etc) and on the hydrophobicity of the adsorbate and its attraction to the carbon surface. Additionally, the adsorptive capacity of GAC is reduced over time owing to saturation of the active sites by the adsorbate and reduction of the active surface area. After contaminant breakthrough has occurred, the partially treated water is no longer considered potable according to the norms issued by the regulatory agencies. For this reason, it is important to estimate the performance of GAC towards mycrocystin-LR at the laboratory and pilot scales by analyzing the physicochemical factors that influence the adsorption of this contaminant (Brady, 1997; Bansal and Goyal, 2005). The objective of the present study was, therefore, to analyze the influence of the variables initial concentration of mycrocystin-LR, pH of the influent solution and contact time between adsorbate and adsorbent on the adsorption of the contaminant by columns filled with GAC produced from shells of the palm (dendê) coconut (*Cocos nucifera*).

Method (Experimental)

Cultivation of cyanobacteria and preparation of toxin solutions.

Cultures of *M. aeruginosa* (World Data Center for Microorganisms 835) were provided by the Department of Botany of the Universidade Federal de São Carlos (São Carlos, SP, Brazil). Cell cultivation was performed at the Estação Experimental de Tratamento Biológico de Esgoto Sanitário (EXTRABES), which is a company associated with the Universidade Estadual da Paraíba and Companhia de Água e Esgoto da Paraíba (Campina Grande, PB, Brazil). *M. aeruginosa* cells were incubated in test tubes (10 mL) or conical flasks (250 mL) containing ASM-1 medium (pH

Revista AIDIS de Ingeniería y Ciencias Ambientales:
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Vol. 11, No.3, 319–331
6 de diciembre de 2018

8.0) (Gorham et al., 1964) maintained at 24°C under a 12 h photoperiod (with light intensity of approximately 1200 lux supplied by 40 W fluorescent tubes) and with daily agitation. *M. aeruginosa* culture growth was monitored by cell counting with the aid of an inverted microscope using the method described by Uthermöhl [(Uthermöhl et al., 1958). In finish of stationary phase, which occurred between 15 and 18 days, the cell density was 106 cells.mL^{-1}, the cultures were transferred to a freezer at 20°C and maintained in the dark at until required for further experimentation.

Cell-free extracts containing microcystin-LR were obtained by repeated (at least four times) freeze/thawing of *M. aeruginosa* cells in order to release intracellular toxins into the medium, and filtration of the lysates through 1 µm Whatman® glass microfiber filters (grade GF) and subsequently through 0.45µm Millipore™ membrane filters. The cell-free extracts were combined, homogenized, divided into aliquots and stored in the freezer. The concentration of microcystin-LR in the cell-free extracts was determined by enzyme-linked immunosorbent assay (ELISA) using a commercial kit (Beacon Analytical Systems Inc, Saco, ME, USA) and a Thermoplate (São Paulo, SP, Brazil) TP-reader. The detection limit of the microcystin-LR was 0.16 µg.L^{-1}. All glassware and tools used in the manipulations were previously sterilized under ultraviolet light. Prior to the assays, microcystin-LR solutions of different concentrations and pH (influents I to IV; Table 1) were prepared from the bulked cell-free extracts by dilution with deionized water, and 4 L aliquots of each influent were transferred to separate 5 L plastic containers. The pH was adjusted by add of H_2SO_4 0.1M or NaOH 0.1M. The microcystin-LR concentrations and pH of the influent were adjusted according to Table 1. These values were chosen according with highest values found in raw water in the semi-arid region of the State of Paraíba, Brazil.

Table 1. Characterization of the influents fed to columns comprising granular active carbon produced from palm (dendê) coconut shells.

Influent	Concentration of microcystin-LR (µg.L^{-1})	pH
I	14.56	6.4
II	14.56	8.3
III	29.26	6.4
IV	29.26	8.3

Preparation of GAC columns.

The adsorption columns employed in the experiment were filled with GAC produced from palm (dendê) coconut shells and marketed by company Carbonmar (Comércio e Indústria de Carvão Ativado Ltda), located in Simões Filho City, Bahia, Brasil. The characteristics of the GAC are shown in Table 2.

Revista AIDIS de Ingeniería y Ciencias Ambientales:
Investigación, desarrollo y práctica. ISSN 0718-378X
Vol. 11, No.3, 319–331
6 de diciembre de 2018

Table 2. Characteristics of the Granular Activated Carbon produced from palm (Dendê) coconut shells.

Parameter	Value
Iodine number	Min. 900 $mg.g^{-1}$
Specific Mass	Min. 0.45 - 0.55 ± 0.05 $g.cm^{-3}$
Hardness	Min. 95%
Abrasion	Min. 85%
Ash	Max. 10%
Grain size	12x40 mesh (0.42-1.40mm)
Humidity when packing	Max. 3%

Prior to use, the GAC was washed several times with distilled water, dried in the oven at 110°C, transferred to a 500 mL conical flask containing distilled water and boiled for 10 min to remove volatile impurities. The resulting suspension was submitted to vacuum suction for 15 min, in order to remove trapped air and allow complete penetration of water into the interstitial spaces, and finally packed into 21 or 30 cm lengths of polyvinyl chloride to form columns of GAC with configurations A and B, respectively, as outlined in Table 3. Spectroscopic characterization of the GAC packing was carried out by Fourier transform infrared spectroscopic (FTIR) analysis according to the method described by Lopes and Fascio (2004).

Table 3. Configuration of developed columns with granular active carbon produced from palm (dendê) coconut shells.

Parameter	Configuration	
	A	B
Volume (mL)	38	57
Mass (g)	20	30
Height (cm)	11	17
Void volume (mL)	17	25
Theoretical contact time (s)	60	90

Experimental design and collection of data.

The experiment was of full factorial design and involved three factors each at two levels (2^3), namely, initial concentration of microcystin-LR [14.56 (-) and 29.26 (+) $\mu g.L^{-1}$], pH of influent [6.4 (-) and 8.3 (+)] and time of contact between adsorbate and adsorbent [60 (-) and 90 (+) s according to length of column employed. The eight treatments were each replicated three times requiring 24 columns in the experimental stage. The treatments were termed T1 to T8 and the configuration of each treatment was developed according to Table 4.

Revista AIDIS de Ingeniería y Ciencias Ambientales:
Investigación, desarrollo y práctica. ISSN 0718-378X
Vol. 11, No.3, 319–331
6 de diciembre de 2018

Table 4. Full factorial design (2^3) experiment indicating the level of each factor: (+) high level and (-) low level

Parameter	Treatment							
	T1	T2	T3	T4	T5	T6	T7	T8
Concentration of M-LR in the influent	-	-	+	+	-	-	+	+
Contact time in the adsorption	-	+	-	+	-	+	-	+
pH of the influent	-	-	-	-	+	+	+	+

The assay was performed by connecting one container of influent solution to two columns (one of configuration A and one of B) via two peristaltic pumps, each operating at a flow rate of 1 $L.h^{-1}$. The container was agitated manually every 30 min, fresh influent was supplied every 90 min, and the columns were operated continuously for 15 h. The concentrations of microcystin-LR in the effluents collected from the columns were determined with the aid of enzyme linked immunosorbent assay (ELISA) kits (Beacon Analytical Systems Inc, Saco, ME 04072, USA) providing a limit of detection of 0.16 $\mu g.L^{-1}$. Two assays (each with two columns) comprising four treatments were performed each day such that the whole experiment was completed within six days.

Adsorption capacity and carbon usage rate of the GAC.

The amount of microcystin-LR adsorbed per unit mass of GAC (q_e, $\mu g.g^{-1}$) were calculated from:

$$q_e=[(C_i-C_f) / m].Q.T \qquad \text{Equation 1}$$

In which C_i is the initial concentration of adsorbate ($\mu g.L^{-1}$), C_f is the final or equilibrium concentration of adsorbate ($\mu g.L^{-1}$), m is the mass of adsorbent (g), Q is the flow rate ($L.h^{-1}$) and t is the time corresponding to microcystin breakthrough (> acceptable concentration).

Statistical analysis.

The experiment aimed to test the hypothesis that the amount of microcystin-LR adsorbed by GAC produced from shells of the palm (dendê) coconut varied significantly according to the initial concentration of toxin, the pH of the influent solution and the contact time between adsorbate and adsorbent. In order to test this hypothesis, data were submitted to analysis of variance (ANOVA) with the confidence interval set at 95% ($P < 0.05$). The standardized effects of the studied parameters on the response variable (adsorption of microcystin-LR) were examined using Pareto charts. From these charts, the parameters or interactions between parameters that most influenced the adsorption of the toxin under the applied experimental conditions could be identified. Statistical analyses were performed using Minitab 16 (Minitab Inc., State College, PA, USA) software.

Revista AIDIS de Ingeniería y Ciencias Ambientales:
Investigación, desarrollo y práctica. ISSN 0718-378X
Vol. 11, No.3, 319–331
6 de diciembre de 2018

Results and discussion

Characteristics of the GAC.

The characteristics of the GAC used to make the columns are presented in Table 5.

Table 5. Characterization of granular activated carbon (GAC) produced from palm (dendê) coconut.

Parameter	Value
Particle size (12 x 40 mesh)	0.42 - 1.40 (mm)
pH_{pzc}	9.58
Specific surface area*	374.036 ($m^2.g^{-1}$)
Micropore volume	0.209 ($cm^3.g^{-1}$)
Micropore area	587.930 ($m^2.g^{-1}$)
Mean micropore size	14.202 (Å)
Total pore volume	0.225 ($cm^3.g^{-1}$)
Maximum pore diameter	754.0 (Å)
Mean pore diameter	18.22 (Å)

*Note: * (BET[24] method).*

The small size (0.42 - 1.40 mm) of the GAC particles favored adsorption since particle size determines the time required for transport within the pores, where effective adsorption occurs, whereby smaller particles exhibit greater adsorption (Snoeyink, 2000; Di Bernardo and Dantas, 2005). The specific surface area of the GAC particles, as determined by the BET method, (Brunauer et al., 1938) was lower than the minimum value (650 $m^2.g^{-1}$) recommended for the treatment of drinking water (Brady, 1997). However, the correlation between specific surface area of GAC and the adsorption of microcystin-LR is weak, suggesting that this parameter is not a useful indicator of adsorption capability (Donati et al., 1993). The total pore volume of the GAC (0.225 $cm^3.g^{-1}$) was comparable with those of ACs commonly employed for water treatment, which vary between 0.20 and 0.60 $cm^3.g^{-1}$ (Bansal and Goyal, 2005). However, micropores represented 92.88% of the total pore volume in the GAC employed, a finding that is relevant since many researchers have reported that microcystin-LR exhibits a greater affinity for mesopores than for micropores (Pendleton et al., 2001; Donati et al., 1993; Newcombe and Nicholson, 2004; Huang et al., 2007). Nevertheless, adsorption of microcystin-LR by the micropores of GAC may be verified by consideration of the maximum and minimum lengths of the molecule (2.94 and 1.4 nm, respectively) at all possible angles (Sathishkumar et al., 2010).

The pH at the point of zero charge (pH_{pzc}) of the GAC employed was 9.0, a value that was higher than the pHs of the influent solutions (6.4 and 8.3). The surfaces of ACs with high pH_{pzc} values are typically positively charged or neutral, conditions that would favor the adsorption of the negatively charged microcystin-LR (Bansal and Goyal, 2005; Huang, et al., 2007; Moreno-Castilla, 2004).

Revista AIDIS de Ingeniería y Ciencias Ambientales:
Investigación, desarrollo y práctica. ISSN 0718-378X
Vol. 11, No.3, 319–331
6 de diciembre de 2018

Spectroscopic analysis of the GAC.

The FTIR spectrum of GAC It is shown in Figure 1. The analysis as shown in Figure 1 revealed bands at 3546 and 1098 cm^{-1} associated, respectively, with the stretching vibrations of phenolic–OH and C-OH groups, bands at 1633 and 1612 cm^{-1} that are characteristic of CH_2 vibrations in the R-NH_2 plane, and a band at 615 cm^{-1} corresponding to N-CH_2 out of plane stretching.

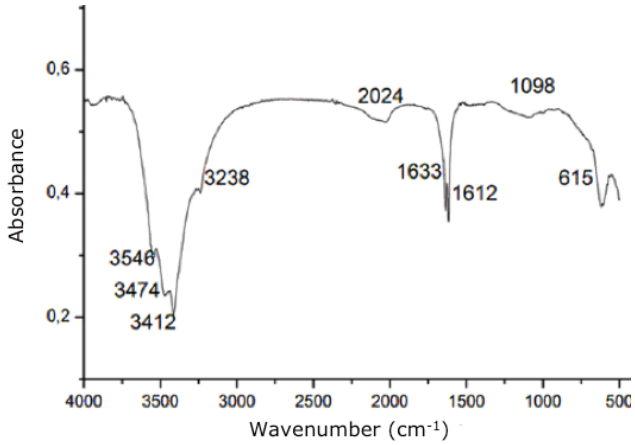

Figure 1. Fourier transform infrared spectroscopy spectrum of granular active carbon produced from palm (dendê) coconut shells.

Moreover, the band at 3238 cm^{-1} is typical of the stretching vibration of ≡C-H, while that at 2024 cm^{-1} can be attributed to the vibration of a terminal alkyne. Weak bands were also observed in the region 3500-3400 cm^{-1}, and these may be attributed to the stretching vibration of a free primary amide.

Effects of treatment conditions on the adsorption of microcystin-LR.

In all of the applied treatments, more than 88% of the initial concentration of microcystin-LR was adsorbed by GAC after 15 h of process, thereby demonstrating that the method was efficient for the removal of the toxin from aqueous solutions. Plots of concentration of microcystin-LR in the effluent as a function of process time for the treatments are shown in Figure 2. The treatments T3 and T7 were the least efficient with average values for the removal of toxin over the 15 h period of 92.4 and 88.8%, respectively, while the most efficient treatment T2 and T4 presented an average removal efficiency of 98%.

The excellent efficiencies of the GAC columns may be explained in part by the absence of competition for adsorption sites by other natural organic compounds and/or byproducts of water chlorination in the experimental solutions **(**Wang at al., 2007; Donati et al., 1993; Huang *et al*., 2007; Kuroda *et al*., 2005). In this context, the adsorption efficiency was reduced when the

Revista AIDIS de Ingeniería y Ciencias Ambientales:
Investigación, desarrollo y práctica. ISSN 0718-378X
Vol. 11, No.3, 319–331
6 de diciembre de 2018

influent contained high concentrations of microcystin-LR (treatments T3, T4, T7 and T8) in comparison with treatments in which the concentration of toxin was low (treatments T1, T2, T5 and T6). Thus, when the influent contained 29.26 µg.L^{-1} of microcystin-LR the average removal after 15 h was 94.5%, but when the concentration was 14.56 µg.L^{-1} the average removal increased to 96.8%. The contour plot displayed in Figure 3 confirms that the efficiency of removal of microcystin-LR by GAC was inversely proportional to the initial concentration of toxin but directly proportional to the time of contact with the adsorbent. Adsorption of microcystin-LR by GAC was slightly favored by an acidic influent (96.35% average removal efficiency at pH 6.4) in comparison with an alkaline influent (94.97% average removal efficiency at pH 8.3).

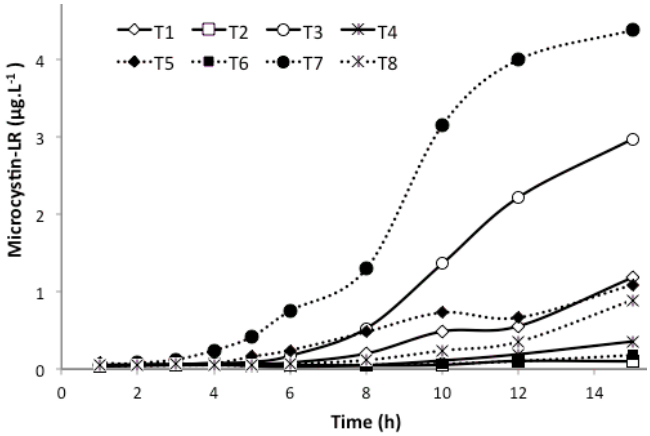

Figure 2. Concentration of microcystin-LR in the effluent from columns containing granular active carbon produced from palm (dendê) coconut shells during 15 h of treatment.

Six of the eight treatments produced effluents containing concentrations of microcystin-LR that complied with the Brazilian legislation (< 1 µg.L^{-1}) after 15 h monitoring. However, effluents from treatments T3 and T7 contained microcystin-LR at levels that were higher than the permitted value, although it is important to emphasize that in both treatments the influent contained toxin at an initial concentration of 29.26 µg.L^{-1} and the time of contact with the adsorbent was 60 s. The occurrence of breakthrough of microcystin-LR in the column effluent enabled the adsorption capacity (q_e) of the GAC to be estimated at 21.2 µg.g^{-1}, a value that is comparable with those of other adsorbents.

Pareto charts were constructed in order to determine the standardized effects of the studied variables (initial concentration of microcystin-LR, pH of the influent and contact time between adsorbate and adsorbent) on the response variable (adsorption of microcystin-LR) during the 15 h process periods. In all treatments, the levels of toxin in the effluents monitored during the first 3 h of process were below the limit of detection (0.16 µg.L^{-1}) of ELISA, indicating the uniform

Revista AIDIS de Ingeniería y Ciencias Ambientales:
Investigación, desarrollo y práctica. ISSN 0718-378X
Vol. 11, No.3, 319–331
6 de diciembre de 2018

behavior of the systems during the initial stages. Consequently, none of the variables exerted a statistically significant influence on adsorption within this period, a result that can be explained by the availability of adsorption sites and the facile diffusion of adsorbate molecules through the GAC pores. However, from 6 h onwards, the situation changed and the influence of the individual variables and their interactions could be observed.

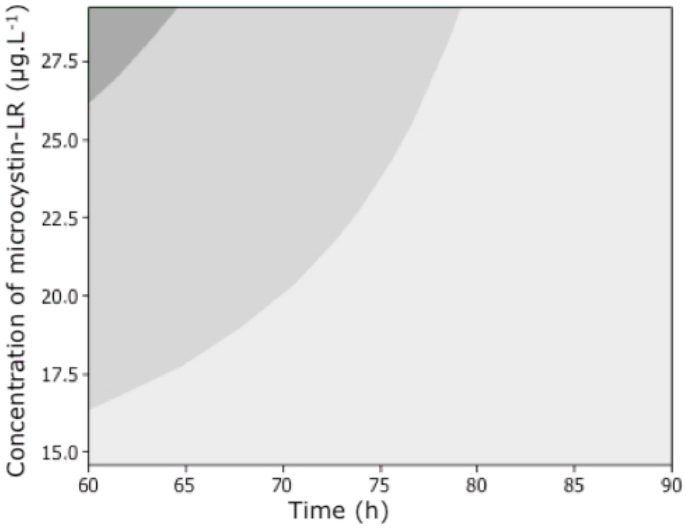

Figure 3. Contour plot of the final concentration of microcystin-LR according to the initial concentration of toxin and the time of contact with granular active carbon produced from palm (dendê) coconut shells. Note: ■ (>0.8 µg.L^{-1}); ■ (0.2-0.6 µg.L^{-1}); ■ (<0.2 µg.L^{-1}).

The Pareto charts shown in Figures 4 reveal the magnitude of the effects (represented by the bars) and the statistical significance (corresponding to the line transversal to the bars) of each variable and their interactions at 6, 10 and 15 h of process. The time of contact between adsorbate and adsorbent exerted the greatest influence on the adsorption of microcystin-LR, and this effect, which was observable during the initial stages of treatment, became statistically significant at 6 h and remained so until the end of the process. The initial concentration of microcystin-LR in the influent solution also exerted a statistically significant effect at 6, 10 and 15 h of process. The progressive reduction in the number of active sites on the GAC over time would account for the increased influence of these two parameters on the adsorption of toxin.

Revista AIDIS de Ingeniería y Ciencias Ambientales:
Investigación, desarrollo y práctica. ISSN 0718-378X
Vol. 11, No.3, 319–331
6 de diciembre de 2018

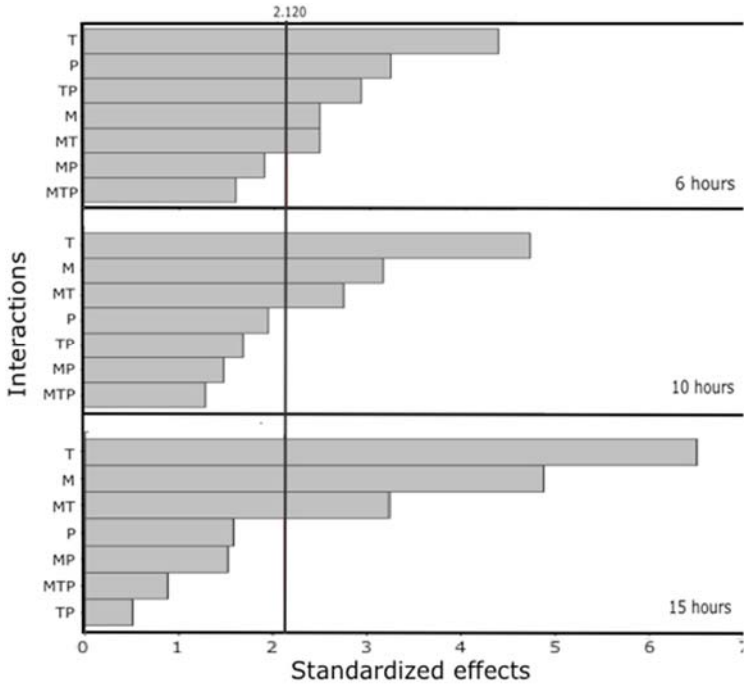

Figure 4. Effects of variables and their interactions on the adsorption of microcystin-LR by columns made of granular active carbon produced from palm (dendê) coconut shells at 6, 10 and 15 h process time. Note: M – concentration of microcystin-LR in the influent; T – contact time between adsorbate and adsorbent; P – pH of the influent solution. The bars represent the magnitude of the effects; statistical significance is indicated by the line transversal to the bars.

The pH of the influent solution exerted a statistically significant influence on the adsorption of microcystin-LR at 6 h of process, but the effect was not significant at 10 and 15 h. The limited effect of pH established in the present study differs from literature indications that pH is a key factor in the adsorption of organic electrolytes and polyelectrolytes. Since pH determines the charge on the surface of the GAC and the dissociated/protonated status of electrolytes, it regulates electrostatic interactions and, consequently, has a direct influence on adsorption (Moreno-Castilla, 2004). According to previous reports, the adsorption of microcystin-LR by GAC is improved at acidic pH values because the electrostatic repulsion between neighboring adsorption sites carrying negative charges provokes a reduction in the stretching of the toxin molecule (Sathishkumar et al., 2010; Huang et al., 2007). As a result, the molecules of microcystin-LR may be reduced in size through the coil effect and adsorption is, therefore, facilitated. Furthermore, increased adsorption under acidic conditions can be brought about through hydrogen bond formation between microcystin-LR and the GAC surface (Sathishkumar et al., 2010) The low statistical significance of the variable pH observed in the present study may be attributed to the small difference (1.9 units) between the pH values tested.

Revista AIDIS de Ingeniería y Ciencias Ambientales:
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Vol. 11, No.3, 319–331
6 de diciembre de 2018

Conclusions

GAC was efficient in removing microcystin-LR from dilute aqueous solutions, presenting removal efficiencies ranging from 88.8% (treatment T7) to 98% (treatment T2) and an acceptable adsorption capacity of 21.2 $\mu g.g^{-1}$. The effects of the variables initial concentration of microcystin-LR and contact time between adsorbate and adsorbent on the adsorption of toxin by GAC were strong and statistically significant from the early stage of the process (6 h) through to the end of the treatment (15 h). Process conditions involving a lower concentration of microcystin-LR (14.56 $\mu g.L^{-1}$) and a longer time of contact with the GAC (90 s) were most favorable for removal of the toxin. The influence of pH on adsorption by GAC was statistically significant at the early stage of the process (6 h), but diminished with time. In the majority of treatments studied, effluents produced during 15 h of process contained concentrations of microcystin-LR that were below the maximum value permitted by Brazilian legislation (< 1 $\mu g.L^{-1}$).

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