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Specifications of the Quality of Granulated Activated Charcoal Used in Water Systems Treatment in Hemodialysis Centers in Brazil


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Brazil

1. Introduction

According to the Brazilian Nephrology Society, in 2009, Brazil had approximately 600 Hemodialysis clinical centers. Currently, more than 77,000 Brazilians, who resort to specialized Hemodialysis services, are exposed to a volume of water of 18,000 to 36,000 L/year (Silva et al., 1996). Therefore, if the water used in these centers during the service is not duly treated, many chemical, toxic and bacteriological contaminants may be transferred to the patients, eliciting adverse effects, sometimes lethal (Buchanan et al., 1982; Arvanitidou et al., 2000).

The water used in these Hemodialysis centers come mainly from the public supply, and it is known that in many water reservoirs that are aimed for the population supply and consume, as the ones located in the Brazilian states like São Paulo, Paraná and Pernambuco, there is a propensity towards cyanobacteria toxic growing (Mendonça et al., 1999). The first report of human death from hepatotoxins of cyanobacteria, more specifically the microcystins -LR, -YR and -AR, happened in intravenous exposition in a Hemodialysis clinic in the city of Caruaru, Pernambuco, in 1996 (Carmichael et al., 2001).

In 2001, another incident involving Hemodialysis water contamination by microcystins was reported. Toxic growths of cyanobacteria with preponderance of the Microcystis sp. and Anabaena sp. were identified in the Funil reservoir and in the Guandu River, both used as water resources for the public supply in the city of Rio de Janeiro, RJ, Brazil. Thus, from that episode, microcystins concentration of the order of 4 μg/L and 0.32 μg/L, respectively were detected in the water and in the activated charcoal filter, used by the water treatment station of the Hemodialysis Center of the Clementino Fraga Filho Hospital of the Federal University of Rio de Janeiro, which is supplied by the water reservoir of Funil and the Guandu river.

As a consequence of this incident, a total of 44 uremic patients who had received care in this Hemodialysis Center, were believed to be exposed to the microcystins found in the water used in the preparation of the dialysate, being until the present time, monitored as to evaluate a possible chronic exposition to those toxins (Soares et al., 2006).

Considering thus the need to define the minimal criteria for the functioning and assessment of the public and private services which perform dialysis in outpatients, bearers of chronic
renal insufficiency, as well as the mechanisms of their monitoring, moreover the need of risk reduction to which the dialysis patients are submitted, the ANVISA (The National Agency of Sanitary Surveillance) has established as resolution (RESOLUÇÃO-RDC nº 154, of June 15th, 2004, republished in May 31, 2006) which foresees the technical regulation for the functioning of these services in Brazil.

It was established from that resolution’s publication, that the water used in the preparation of dialysate, must have its quality guaranteed in all phases of the treatment, storage and distribution through the monitoring of the microbiological and physic-chemical parameters, as well as the procedures for the treatment themselves. Therefore, the water provision of the dialysis services from the public supply, from wells and any other sources must have its drinking standard as provisioned in the Act MS Nr. 518 of March 25th, 2004, (Brazilian Health Ministry) or of any legal instrument which may replace that one. Regarding the cyanotoxins, according to the art. 14 of this regulation, it was established that the upper limit allowed of microcystins in water for public supply be of 1 µg/L, it was also recommended that the analysis for the cyanotoxins included the determination of cylindrospermopsin and saxitoxins (STX), taking into consideration, respectively, the value limits of 15.0 µg/L e 3.0 µg/L of STX/L equivalents.

A good example of cyanotoxins monitoring is being made in the systems of water collection which supply the city of São Paulo, Brazil (systems Rio Grande, Alto Tiête and Guarapiranga) by the Basic Sanitation Company and water treatment of São Paulo-SABESP. It has been noticed that despite the microcystin levels are below the standard established by the MS 518/2004, many Hemodialysis clinics, in where this water is used, are at alert, as the water used by them for the Hemodialysis treatment needs to be with microcystins concentration equal to zero.

In Brazil, according to the Brazilian Society of Nephrology, in order to guarantee the water quality used for renal patients, more than 80% of the Hemodialysis centers have water treatment systems which use reverse osmosis, deionization, integrated system of reverse osmosis + deionization, besides activated charcoal.

The granulated activated charcoal (GAC) is an adsorbent used in processes of water treatment (activated charcoal filters) to remove micropollutants present in water, as pesticides, industrial chemical agents, cyanobacterial secondary metabolites such as geosmin and 2-methyl isoborneol (MIB) which give taste and odor to water, and toxins like hepatotoxins (microcystins) and neurotoxins (Newcombe, 1999).

The adsorption capacity of activated carbons (AC) by compounds in the water is mainly influenced by the physical structure and chemical characteristics of the surface of these adsorbents, their previous material, and their preparation condition (Newcombe, 1999; Karanfil et al., 1999). Different research groups have shown that the ACs with pore volume developed in the regions of mesopores and secondary micropores can be very effective in the removal of microcystins (Falconer et al., 1989; Donati et al., 1994; Pendleton et al. 2001; Campinas & Rosas, 2010a, 2010b). Therefore, it is indispensable to estimate the distribution of pores in these regions, whether by means of adsorbing in liquid phase by using the methylene blue solution or in gaseous phase using N₂.

The Hemodialysis Centers are concerned with the correct quality parameters which would indicate from those parameters which is the best charcoal to be used in their water treatment, as the activated charcoal, associated with other technologies, is commonly used by water treatment stations in Hemodialysis Centers. Thus, in this Chapter, are discussed the adsorption techniques in liquid and gaseous phase which were used aiming to assess the
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adsorption capacity of the GAC commonly used by water treatment stations in the Brazilian Hemodialysis Centers, providing indicators which may be used as to purchase these adsorbents.

2. Sampling of activated charcoals

Activated charcoals used in two Brazilian Hemodialysis Centers, located in the city of Recife/Pernambuco, Brazil - Hemodialysis Center of the Clinical Hospital of the Federal University of Pernambuco, coordinates 08°03’15.40”S 34°52’52.52”W (termed A) - and in the city of Campinas/São Paulo, Brazil - Hemodialysis Center of the Clinical Hospital of the State University of Campinas, coordinates 22°54’25.58”S 47°03’47.66”W (termed B) - were used in this study. Besides that, sugarcane bagasse (CA-R-H) and dry coconut shell (CA-R-G) based-activated charcoal were specially produced for this work and used as reference charcoals (termed R) (Table 1). These charcoals were activated with water steam at temperature close to 900 ºC. The raw material preparation conditions, the carbonization and activation, besides those charcoals full characteristics, in liquid and gaseous phase, are thoroughly described by Albuquerque Junior et al. (2005)*.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Origin</th>
<th>Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-A-A</td>
<td>Unknown</td>
<td>Coconut Tree wood</td>
</tr>
<tr>
<td>AC-A-B</td>
<td>Calgon®, EUA</td>
<td>Coconut Shell</td>
</tr>
<tr>
<td>AC-A-C</td>
<td>Calgon®, EUA</td>
<td>Coconut Shell</td>
</tr>
<tr>
<td>AC-A-D</td>
<td>Criciúma, Brazil</td>
<td>Coal</td>
</tr>
<tr>
<td>AC-B-E</td>
<td>Carboleste, Brazil</td>
<td>Babaçu coconut endocarp</td>
</tr>
<tr>
<td>AC-B-F</td>
<td>Bahia Carbon®, Brazil</td>
<td>Coconut shell</td>
</tr>
<tr>
<td>AC-R-G</td>
<td>Author*</td>
<td>Coconut shell</td>
</tr>
<tr>
<td>AC-R-H</td>
<td>Author*</td>
<td>Sugar Cane Bagasse</td>
</tr>
</tbody>
</table>

Table 1. Assessed Activated Charcoals

2.1 Characterization of activated charcoals

For the characterization in liquid phase by means of use of methylene blue solution and in gaseous phase by N₂, the charcoals were marked in mortar and pestle, grinded in a sieve with nominal opening mesh of 0.075mm. Whereas the ones used in the experiments in fixed bed column were grinded in sieves with nominal opening mesh of 0.50mm and 0.35mm, being the obtained material in this last sieve collected for the referred experiment. The charcoals were then dried in greenhouse at 150 ºC by 3 hours minimally, and then cooled in desiccators with silica gel until reached room temperature for its posterior use.

2.1.1 Adsorption in gaseous phase: Specific surface area and distribution of pores size

As the analysis procedures, all the ACs were degasified in vacuum at 150 ºC for 24 h. A software in interface with a gas analyzer (model NOVA-1200, Quantachrome Corp.) was used in the measures of specific surface area and distribution of pores size. Equilibrium data obtained from the isothermal of adsorption / desorption of gaseous nitrogen at 196 ºC were used to determine the specific surface area by means of application of the method developed by Brunauer, Emmet and Teller (BET). The micropores area was obtained by the “t-plot” method. The total volume of the pores was determined converting in liquid volume the
nitrogen aborted volume in the saturation point \((P/P_0 \sim 0.99)\). The micropores and primary micropores were calculated from the intercept point of the t-plot linear region after the saturation of the micropores and primary micropores respectively. The volume of the mesopores was calculated from the difference between the total volume of the pores and the volume of the micropores, also, the volume of the secondary micropores was calculated by the difference between the volume of the mesopores and the volume of the primary micropores. The distribution of the size of the pores in the micropore and mesopore regions in the ACs was obtained from the methods developed by Horvath-Kawazoe (HK) and Barrett-Joyner-Halenda (BJH), respectively (Webb & Orr, 1997).

2.1.2 Adsorption in liquid phase: Methylene blue index and \([\text{D-Leucine}^1]\text{microcystin-LR}\)

2.1.2.1 Batch experiments

An isotherm study of adsorption equilibrium is important as to describe an interaction between adsorbate and adsorbents, and it is critical in the optimization of these materials for both studies in continuous or in batch process. Information regarding the distribution of the sizes of the AC pores were obtained from comparison of the adsorption characteristic for three different adsorbates: methylene blue and \([\text{D-Leucine}^1]\text{microcystin-LR}\) (\([\text{D-Leu}^1]\text{MCYST-LR}\)). The choice of these molecules is justified by their properties, forms and polarities, being the first commonly used for foretelling the capacity of the activated charcoal in adsorbing micropollutants in industrial effluents (Hsieh & Teng, 2000; Lussier et al., 1994), besides providing an estimate of the volumes in secondary micropores + mesopores, as foretold in previous works by Albuquerque Junior et al. (2005).

The trihydrate methylene blue (99.95%, Merck, EUA) analytical grade was used in the solution preparation as to determine the Methylene Blue Index (MBI). The adsorption experiments were made in accordance with the norm JIS (Japanese Industrial Standard), JIS-K 1474 (1991). The methylene blue concentrations in the liquid phase after the equilibrium were determined indirectly from molecular adsorption spectrophotometry (spectrophotometer GBC UV/VIS – 911 A) in the wave length of 665 nm. The experimental data were adjusted to the Freundlich’s model, and the quantity of the methylene blue adsorbed by the charcoals \((q)\) was calculated according to the equation 1.

\[
q = \frac{(C_0 - C)}{m} V
\]

For the foretelling of the capacity and removal of microcystine in water by activated charcoal, an aqueous extract of \([\text{D-Leu}^1]\text{MCYST-LR}\) of concentration around to 6000 \(\mu\)g/L, prepared in drinkable water exempt of chloride, was used as adsorbate. This toxin has been already identified in growths in Lagoa dos Patos, Rio Grande do Sul, Brazil, (coordinates 31º 9'56.93"S 51º25'51.45"W) by Matthiensen et al. (2001) and in Lagoa de Jacarepaguá, Rio de Janeiro, Brasil (22º59'10.69"S 43º23'57.95"W) by Oliveira et al. (2004). The preparation of the respective extract, as in the quantification model of the referred toxin by High Performance Liquid Chromatography (HPLC) was fully discussed by Kuroda et al. (2005). The experimental data were adjusted to the Langmuir’s model and the quantity of adsorbed toxin by the activated charcoals was measured from the equation 1.
2.1.2.2 Experiments in fixed bed columns: Adsorption of [D-leucine]\MCYST-LR

In order to evaluate the microcystin dynamics in experiments in fixed bed column, an acrylic column was used of 2.5 cm de d, and height of up to 25 cm, adjusted by means of a piston. A distributor plate with five orifices of 1mm openings, made of stainless steel, was inserted in the base of this column. A net of 60 μm was used below the distributor and in the entrance of the piston through which the fluid that passed the column flowed, avoiding that possible loss of adsorbent by reflux (Fig. 1).

Fig. 1. The column scheme used in this work (a) o-ring, (b) distributor (perforated plate), (c) net (60 μm), (d) screw, (e) rule, (f) piston. Source: Santos et al., 2002.

The charcoal bed was continuously percolated by a solution having [D-Leu]\MCYST-LR of varied concentration, from which effluent samples were intermittently collected until the bed saturation. The toxin concentration in the liquid phase was determined by HPLC and the evaluation of the continuous process of adsorption was made by means of breakthrough curves sizing, which is the relation between the ration of the initial concentration by the toxin concentration in the column effluent (C/C₀) vs time (t).

3. Results

3.1 Textual characteristics of activated charcoals

The activated charcoals are formed by an interconnected net of pores, which according to IUPAC (International Union of Pure and Applied Chemistry) may be classified according to its diameters in different categories: macropores (di > 50 nm), mesopores (2 nm < di < 50 nm), primary micropores (di < 0.8 nm) and secondary micropores(0.8 nm < di < 2nm) (Everett, 1988).

The activated charcoal porosity may be estimated from the form of the isotherm of Nitrogen adsorption according to the Brunauer, Deming, Deming and Teller (BDDT) (Gregg & Sing, 1982) classification. Therefore, from that classification, it was observed that the AC-B-F, AC has presented an isotherm characteristic of the type I, typical of micropores material, with relatively small external surface area. Nevertheless, loops characteristic from hysteresis in partial pressures (P/P₀) above 0.4 in other ACs, which indicate that these charcoals must present a small band of pores in the secondary micropore region and mesopores. Thus, these other charcoals have presented a combination between the isotherms I and II, the same observed for charcoals taken as reference (fig. 2).
Fig. 2. Nitrogen adsorption/desorption Isothermes at -196°C. (a) AC-A-A, (b) AC-A-B, (c) AC-A-C, (d) AC-A-D, (e) AC-B-E, (f) AC-B-F, (g) AC-R-G and (h) AC-R-H.
The adsorption isotherms could also be analyzed from the hysteresis loop format according to the standard classification, which contains 4 types: H1–H4 (Girgis & Hendawy, 2002). The hysteresis loops appear in multilayer regions of isothermal of physisorption, and are considered as being associated to capillary condensation. The hysteresis loop style found for the analyzed charcoals was of the H4 type, which was originated from the influence, even small, of the existing secondary micropores and mesopores in these materials.

The charcoal sample AC-A-D has presented an unusual behavior from the obtained isothermal data of N₂ adsorption/desorption, as it has shown a very low Nitrogen adsorbed volume, around 0.27 cm³/g, when compared with those obtained by other sampled charcoals, which then Nitrogen adsorbed volumes were above 248 cm³/g (Figure 2d). By the adsorption behavior of that charcoal, it is assumed that the same is an activated charcoal and, thus, could not be used in the water treatment station in the Hemodialysis Centers A (HC Campinas) for the removal of contaminants.

The used ACs in the water treatment station of the Hemodialysis Center A have presented BET area (S\textsubscript{BET}) between 764.9 m²/g e 1,017.4 m²/g, whereas the ones used in the Hemodialysis Center B have presented S\textsubscript{BET} between 632.8 m²/g and 789.5 m²/g (Table 2).

<table>
<thead>
<tr>
<th>REF.</th>
<th>Surface area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Primary micropore (%)</th>
<th>Secondary micropore (%)</th>
<th>Mesopore (%)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET</td>
<td>Micro</td>
<td>Meso</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC-A-A</td>
<td>764.9</td>
<td>756.2</td>
<td>8.7</td>
<td>0.16 (44.7)</td>
<td>0.21 (55.3)</td>
<td>0.01 (2.6)</td>
</tr>
<tr>
<td>AC-A-B</td>
<td>871.2</td>
<td>857.6</td>
<td>13.6</td>
<td>0.12 (31.9)</td>
<td>0.32 (68.1)</td>
<td>0.03 (6.4)</td>
</tr>
<tr>
<td>AC-A-C</td>
<td>1017.4</td>
<td>967.9</td>
<td>49.5</td>
<td>0.08 (31.9)</td>
<td>0.38 (69.1)</td>
<td>0.09 (16.4)</td>
</tr>
<tr>
<td>*AC-A-D</td>
<td>4.6</td>
<td>4.5</td>
<td>0.015</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AC-B-E</td>
<td>632.8</td>
<td>610.2</td>
<td>22.6</td>
<td>0.17 (55.9)</td>
<td>0.15 (44.1)</td>
<td>0.02 (5.9)</td>
</tr>
<tr>
<td>AC-B-F</td>
<td>789.5</td>
<td>772.0</td>
<td>17.5</td>
<td>0.14 (37.5)</td>
<td>0.30 (62.5)</td>
<td>0.04 (8.3)</td>
</tr>
<tr>
<td>AC-R-G</td>
<td>1079.5</td>
<td>1014.2</td>
<td>65.3</td>
<td>0.08 (50.0)</td>
<td>0.29 (50.0)</td>
<td>0.20 (34.5)</td>
</tr>
<tr>
<td>AC-R-H</td>
<td>1174.3</td>
<td>1097.3</td>
<td>77.3</td>
<td>0.10 (22.3)</td>
<td>0.35 (77.7)</td>
<td>0.39 (41.8)</td>
</tr>
</tbody>
</table>

* The very low adsorption capacity has not allowed the calculation of these parameters.

Table 2. Activated Charcoals textural properties.

A first observation of these results would imply in the choice of charcoals of any of the two centers, however, according to Quinlivan et al. (2005), the BET area (SBET) is a poor indicator of the adsorption capacity of activated charcoals, hence, the sampled charcoals quality cannot be assessed only by their BET (SBET) area data, so, other effectiveness parameters must be taken into consideration in order to choose a charcoal for a determined aim. Thus, beyond that parameter, the secondary micropores and mesopores volumetric fractions must also be considered in the choice of an activated charcoal for the use in water treatment, as these pores are significantly important in the adsorption of organic micropollutants like the microcystins by the activated charcoals according to Donati et al. (1994) and Pendleton et al. (2001). According to Donati et al. (1994), there is no correlation between the adsorption capacity of activated charcoals by microcystins and the BET area, the micropores volume and the number of Iodine. However, the mesopores presence in these adsorbents may favor the adsorption of the cyanobacterium toxin. Moreover, Pendleton et al. (2001), have shown that besides the mesopores volume, the adsorption capacity of that toxin, was also influenced by the
volumetric fraction correspondent to the secondary micropores. In these charcoals, the secondary micropores and mesopores volumetric fractions have exceeded 37% e 28%, respectively, favoring the adsorption of microcystin in 200.0 μg/mg.

The activated charcoals of the water treatment in the hemodialysis Center (A and B) have presented secondary micropores and mesopores volumetric portions of 0.15 to 0.38 cm³/g (44.1 to 69.1%) and of 0.01 to 0.09 cm³/g (2.6 to 16.4%), respectively. These charcoals have presented secondary micropores portions higher than those found by Pendleton et al. (2001), however, they have also presented very low mesopores volumetric fractions, around 8% in average, which characterizes microporous charcoals. Nevertheless, those commercial activated charcoals obtained as reference by the authors, have presented secondary micropores volumetric fractions and mesopores of 59.2 to 63.6% and of 34.5 to 41.8%, respectively, which can be characterized as a good indicator for the AC for the treatment water use.

A visualization of the pores size distribution can be obtained from the distribution function calculated by the HK and BJH (Figure 3) methods. The (A), (B) and (C) charcoals have shown a distribution function HK/BJH, with dW/dLo of 0.04; 0.07 and 0.06 cm³/nm/g consisting of pores average diameters of 3.81, 3.80 and 3.28 nm, respectively. Due to the low adsorption capacity of the D charcoal, it was not possible to obtain its distribution of the pores sizes. For the E charcoal, the distribution function dW/dLo has presented two peaks with 0.02 and 0.01 cm³/nm/g a 2.53 and 4.15 nm in pores average diameter; while the AC-B-F has presented dW/dLo ≈ 0.06 cm³/nm/g to an average pore diameter of 2.7 nm. In contrast with these results, the standards AC-R-G and AC-R-H have shown a distribution function a little higher: (AC-R-G) dW/dLo ≈ 0.3 cm³/nm/g with 1.61 nm of pore average diameter, and AC-R-H has presented two peaks with dW/dLo ≈ 0.17 and 0.08 cm³/nm/g with pore average diameter of approximately 1.71 and 3.00 nm, respectively.

**Fig. 3.** Function distribution HK/BJH: (■) AC-A-A; (□) AC-A-B; (△) AC-A-C; (●) AC-B-E; (★) AC-B-F; (Ө) AC-R-G; (О) AC-R-H.

According to Lanaras et al. (1991) the MCYST-LR when dissolved in water, has a solvated volume of 2.63 nm, length of 1.9nm, height of 1.5nm, thickness of 1.1nm, and solvated area of 1.8 nm². The [D-Leu¹]MCYST-LR has an amino acid residue, D-Leucine, which has replaced the amino acid residue, D-Alanine, of MCYST-LR, that confers the [D-Leu¹]MCYST-LR more hydrophobicity than the MCYST-LR. But, these differences between their chemical structures are not so significant regarding their heights, solvated volume and transversal section area, enabling that approximate dimensions of the first MCYST-LR might
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be taken as referential of the latter. Thus, taken the approximate dimensions of the MCYST-LR it is presumed that the [D-Leu']MCYST-LR is adsorbed in the activated charcoal pores with an internal diameter close to 2-3 nm.

The distribution of the pores size (Figure 3) estimated from the HK/BJK has allowed to observe that the sampled charcoals have a pores average diameter between 2.5-4 nm, which would make these charcoals potential adsorbents for their use in the removal of the water microcystin, but the low volume of the pores observed in this 2.5-4 nm band is smaller than 0.07 cm³/g, which makes these charcoals adsorbents of low adsorption capacity for such aim.

3.2 Adsorption on liquid phase

3.2.1 Batch experiments

Knowing the adsorption equilibrium represents the first step in investigating the possibilities for using an adsorbent in a determined separation process. Besides, additional information regarding the distribution of the sizes of the activated charcoal pores can be obtained by comparing the adsorption characteristics of adsorbate by taking those obtained from adsorption data in gaseous phase.

Methylene blue (MB) has been widely used as an adsorbate to estimate the adsorption capacity of CA from continuous in fixed bed or batch experiments (Kumar & Sivanesan, 2006; Macedo et al., 2006; Zhang et al., 2006). Studies on MB adsorption equilibrium in activated charcoal can provide important information about the selectivity of these adsorbents regarding this molecule, given that the MB is accessible to the charcoal pores with an inner diameter greater than 1.5 nm, being important for the characterization of the secondary micropores (0.8 <di <2.0 nm) and mesopores (2 nm < di < 50 nm) mainly, besides being a model compost used for predicting the adsorption of organic contaminants found in industrial effluents such as textile dye and microcystines (Barton, 1987; Baçaoui et al., 2001).

According to the JIS norm (1994), the Methylen Blue Index is operationally defined as the adsorbed amount of that molecule when its residual concentration in liquid phase after equilibrium is of 0.24 mg/L. This adsorption capacity was obtained from an equilibrium isotherm where the experimental data were adjusted to Freundlich’s adsorption model. The correlation coefficients for linear regression from the adjustment of the experimental data to the respective linearized model along with its empirical parameters, K and 1/n, besides the charcoals’ Methylen Blue Index (MBI), are displayed on Table 3.

<table>
<thead>
<tr>
<th>Reference</th>
<th>K (L/mg)</th>
<th>1/n</th>
<th>r²</th>
<th>MBI (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-A-A</td>
<td>9.2</td>
<td>0.13</td>
<td>0.91</td>
<td>7.6</td>
</tr>
<tr>
<td>AC-A-B</td>
<td>40.7</td>
<td>0.07</td>
<td>0.98</td>
<td>36.6</td>
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<tr>
<td>AC-A-C</td>
<td>43.4</td>
<td>0.02</td>
<td>0.95</td>
<td>42.1</td>
</tr>
<tr>
<td>* AC-A-D</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AC-A-E</td>
<td>35.4</td>
<td>0.1</td>
<td>0.97</td>
<td>32.5</td>
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<tr>
<td>AC-A-F</td>
<td>85.6</td>
<td>0.05</td>
<td>0.99</td>
<td>79.2</td>
</tr>
<tr>
<td>AC-A-G</td>
<td>104.5</td>
<td>0.08</td>
<td>0.94</td>
<td>92.6</td>
</tr>
<tr>
<td>AC-A-H</td>
<td>271.4</td>
<td>0.16</td>
<td>0.99</td>
<td>217.5</td>
</tr>
</tbody>
</table>

*This charcoal has a very low adsorption capacity (close to zero) for methylene blue, which makes it impossible to calculate the MBI.

Table 3. Freundlich’s model adsorption parameters.
Standard international and national norms regarding the quality of activated charcoal for water treatment bring specifications primarily concerning the minimal iodine adsorption limit (iodine number), 600 mg/g (ABNT - EB-2133, 1991 and AWWA – B600-05) and 900 mg/g (ASTM - D 4607-96), making no mention to the minimal limits of methylene blue adsorption. It is known that iodine is a small molecule of approximately 0.8 nm and being thus associated with micropore adsorption. Therefore, the iodine number cannot be the sole specification of quality standard adopted for an activated charcoal destined for water treatment, because it is a well-applied parameter for microporous charcoals.

In Morroco, the activated charcoals destined for water treatment have in their specifications the minimal limits established for the methylene blue adsorption capacity of 180.0mg/g (Baçaoui et al., 2001). Thus, if we consider this minimal limit as a specification for the activated charcoal sampled in both the Hemodialysis Centers, we would see that none of these charcoals could be used for water treatment, because they are specifically microporous activated charcoals.

3.2.1.1 Adsorption of [D-Leucine]$^1_1$MCYST-LR

From results obtained in the characterization of the hemodialysis centers AC regarding the pore volume and methylene blue adsorption, it was possible to choose the best AC in each center and use it in the adsorption studies with the cyanobacteria toxin. The adsorption kinetics of the [D-Leucine]$^1_1$MCYST-LR on the charcoals was studied, from which we could estimate the efficiency of the removal of this cyanobacteria toxin by those adsorbents. Other two activated charcoals produced by Albuquerque et al. (2005) (AC-R-G and AC-R-H, originating from the sugarcane bagasse and coconut tree endocarp) were also studied regarding their removal efficiencies for [D-Leu]$^1_1$MCYST-LR on water.

![Fig. 4. Adsorption kinetics of [D-Leucine]$^1_1$MCYST-LR on the activated charcoals: (a) □ AC-B-F, ■ AC-A-B, and (b) ○ AC-R-G and Δ AC-CP - F.](image-url)

After 15 seconds of contact between the [D-Leu]$^1_1$MCYST-LR and the charcoals, removal efficiencies of 7.40% (AC-R-G) and 26.47% (AC-R-H) were observed, compared to the very low results obtained by the AC-A-B and AC-B-F with removal efficiency of 1.96 and 2.26%, respectively. The adsorption kinetics evolved gradually with time until the adsorption balance was reached in around 30 minutes for the AC-R-G and AC-R-H, and of 60 minutes for the AC-A-B and AC-B-F (Figure 4). The removal efficiencies by these AC in the respective equilibrium times were of 62.31% (AC-R-G), 98.73% (AC-R-H), 4.3% (AC-B-F)
and 3.7% (AC-A-B). Still in the equilibrium, toxin adsorption in the charcoals of 30 µg/mg (AC-R-G), 32 µg/mg (AC-R-H), 1.4 µg/mg (AC-A-B) and 1.7 µg/mg (AC-B-F) were observed. The low removal efficiency of the two last charcoals (from hemodialysis centers) can be explained by their low mesopore volumes, around 0.04 cm³/g in average, when compared to those of other charcoals taken as standards, AC-R-G and AC-R-H (0.20-0.39 cm³/g).

3.2.2 Experiments in fixed bed column

In the dynamic adsorption dynamic of the [D-Leu¹]MCYST-LR in a fixed bed of activated charcoal, the latter removed that toxin from a solution until the saturation of the bed, wherein the performance of this continuous adsorption process is affected, among other parameters, by the concentration of the entry solution (Gomes et al., 2001) and by operational conditionals such as particle size and fluid flow in the column (Inglezakis et al., 2002). According to Sag & Aktay (2001) and Barros et al. (2001), the solutions which are more concentrated saturate the bed faster, and small particles diminish the resistance to mass transfer. It is also known that an increase in the flow of the solution on the bed reduced its adsorption capacity, increasing the length of the mass transfer zone, because the phenomenon of mass transfer necessary for adsorption of [D-Leu¹]MCYST-LR might not be able to continue in higher mass transfer rates, brought forth by an increase in the flow of the fluid (Watson, 1999). Besides, the bed flow can be deviated from the ideal because of the flow channeling due to insufficient material wettability. Those problems can reduce the adsorption process efficiency, because it is important that the column operates as close as possible to the flow/runoff conditions as the one observed for a tubular-type “plug flow” reactor. Hence, in order to correctly plan and operate the continuous adsorption process of that toxin in a AC fixed bed, as the one found in many water treatment stations of hemodialysis centers, it is necessary to study the kinetics and adsorption equilibrium for that toxin, besides knowing its adsorption dynamics in a fixed bed through the sizing of the breakthrough curves. The first step in a adsorption project for [D-Leu¹]MCYST-LR in fixed bed column is the establishment of optimal conditions for preparing the process, that is, those that minimize the diffusional resistances both in the film and in the interior of adsorbent particles, thus favoring a greater interaction between the charcoals’ active sites, accessible to adsorption, and the adsorbate.

In this experiment, the previous studies of methylene blue adsorption in activated charcoal fixed bed have shown flows between approximately 8 and 12 mL/min and average particle size of 0.425 mm would be conditions that could reduce to minimum those mass transfer resistances without significant increase in charge loss on the bed, and thus be taken as a starting point for the planning of a continuous adsorption process for that toxin. Under these conditions, one should expect that the breakthrough curves come closer to a perfect degree, which is desirable (McCabe et al., 2001). Thus, taking such conditions like particle size, flow and height of the bed, new experiments with solutions [D-Leu¹]MCYST-LR were carried out aiming to evaluate the removal of this toxin from the treated water using fixed bed columns of AC-A-B charcoals and AC-B-F, besides the AC taken as standards AC-R-G and AC-R-H (Table 4).

Aiming to recover the solution initially containing [D-Leu¹]MCYST-LR kept in contact in a continuous fashion with an activated charcoal bed initially free from it, the concentration of this toxin in the exit of the bed was monitored, in function of the time, producing curves as shown in Figure 5 denominated breakthrough curves.
### Table 4. Experimental conditions and adsorption results in continuous regime

<table>
<thead>
<tr>
<th>REF.</th>
<th>(C_0) ((\mu g/L))</th>
<th>Flow (mL/min)</th>
<th>H(_{\text{bed}}) (cm)</th>
<th>m(_Z) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-A-B</td>
<td>12,779.6</td>
<td>11.1</td>
<td>2.4</td>
<td>8.3</td>
</tr>
<tr>
<td>AC-B-F</td>
<td>12,460.6</td>
<td>8.5</td>
<td>2.3</td>
<td>8.1</td>
</tr>
<tr>
<td>AC-R-G</td>
<td>13,496.4</td>
<td>10.5</td>
<td>2.4</td>
<td>9.2</td>
</tr>
<tr>
<td>AC-R-H</td>
<td>19,153.5</td>
<td>12.2</td>
<td>2.3</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Initially, the adsorbent layer located in the inferior part of the bed adsorbs the solution quickly and effectively thus reducing the concentration of that toxin in the exit of the column. The effluent on the top of the bed is practically free of solute. In this situation, the inferior layer of the bed is practically saturated and the adsorption occurs in an adsorption zone (Z\(_{\text{ad}}\)) that is relatively narrow and the concentration changes rapidly. Continuing with the solution flow, the Adsorption Zone flow (Z\(_{\text{ad}}\)) moves in an ascendant way like a wave, at an ordinarily much slower rate than the linear fluid velocity through the bed. In a certain time, practically half of the bed is saturated with the solute, but the concentration in the effluent is still substantially zero. When the adsorption zone (Z\(_{\text{ad}}\)) has reached the top of

![Graphical representation of breakthrough curves (a) AC-R-H, (b) AC-A-B, (c) AC-B-F, (d) AC-R-G.](www.intechopen.com)
the bed, and the solute concentration in the effluent increases sensibly, the system is said to initiate rupture, so the solute concentration in the effluent increases rapidly when the adsorption zone (Zad) passes through the bed bottom and the solute concentration is substantially equated to the concentration value in the initial solution (C₀).

Based on the data obtained from the Breakthrough curves, it was possible to estimate the needed time for the C/C₀ = 0.05 ratio to be reached in the exit of the column, which denominated breakthrough time (tₜ).

With the continuous adsorption process until the exhaustion of each bed in 282 min (AC-B-F) and 310 min (AC-A-B), the C/C₀ = 1 ration was achieved in the column exit, it was possible to estimate the [D-Leu¹]MCYST-LR mass adsorbed by the bed in those times. Under this conditions, each bed showed an adsorbed mass of [D-Leu¹]MCYST-LR of 29,868.05 μg (282 min × 0.0085 L/min = 2.237 L; 2.237 L × 12,460.6 μg/L = 25,818.35 μg), corresponding to 3.678 μg/mg.

Comparing the performance of the beds above with those composed by the activated charcoals AC-R-G and AC-B-F, adsorbed masses of [D-Leu¹]MCYST-LR of 1,017.29 μg (7.5 min × 0.01005 L/min = 0.0754 L; 0.0754 L × 13,496.4 μg/L) and 2,072.02 μg (9 min × 0.01202 L/min = 0.1082 L; 0.1082 L × 19,153.5 μg/L) were observed, which corresponds to 0.113 μg/mg and 0.296 μg/mg, respectively.

<table>
<thead>
<tr>
<th>REF.</th>
<th><em>tₜ</em> (min)</th>
<th>tₑ (min)</th>
<th>tₙ (min)</th>
<th>tₛ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-A-B</td>
<td>7.0</td>
<td>320</td>
<td>45.7</td>
<td>593.2</td>
</tr>
<tr>
<td>AC-B-F</td>
<td>24</td>
<td>282</td>
<td>153.5</td>
<td>615.6</td>
</tr>
<tr>
<td>AC-R-G</td>
<td>7.5</td>
<td>132</td>
<td>59.2</td>
<td>276.1</td>
</tr>
<tr>
<td>AC-R-H</td>
<td>9.0</td>
<td>165</td>
<td>56.6</td>
<td>384.9</td>
</tr>
</tbody>
</table>

*tₜ* is the breakthrough time, tₑ exhaustion time, tₙ utile time and tₛ stoichiometry time.

Table 5. Properties of the activated charcoal beds.

Comparing the results obtained from the activated charcoals AC-R-G and AC-R-H with the Bernezeau (1994) data (50 μg microcystin-LR/12 mg Powdered Activated Charcoal - PAC), the sugarcane bagasse based-activated charcoal showed an adsorption capacity 1.3 times bigger than the PAC studied by the aforementioned researcher, remembering that in our studies we have used an extract with four microcystins.

According to Zambon (2002), qualitative information regarding the resistance to mass transfer can be obtained from the form of breakthrough. If the mass transfer zone is narrow,
the breakthrough curve will be more inclined, whereas if the zone is wider, the curve will be more elongated. From Figure 6, it is possible to see that such zones differed from charcoal to charcoal according to the operational parameters established in each experiment such as initial concentration, flow and bed height. Hence, in the case of the Breakthrough curves obtained for the AC-R-G, AC-A-B and AC-R-H beds, a narrower S-shaped curve indicating a narrower mass transfer zone and, therefore, with mass transfer resistance to be considered. Nonetheless, the breakthrough curve obtained from the bed packaged with charcoal AC-B-F (Hemodialysis Center B) displayed a more elongated S-shaped curved, as seen on Figure 5, indicating a broader mass transfer zone and, therefore, little resistance to mass transfer. The supposition of the adsorption zone provides the basis for a method for a much simpler project, which makes it possible to scale up the experiments from a small laboratory scale. However, besides the Mass Transfer Zone (MTZ) concept, the estimative of parameters such as average residence time and dimensionless variance can help in the design of an adsorption column (activated charcoal filter).

4. Conclusion

Granulated Activated charcoals are largely used in adsorption continuous processes in fixed bed for the water treatment in Hemodialysis Centers. The quality of the water used in these centers is intrinsically associated with the quality of these charcoals. As in Brazil, there are no norms, and neither, entities which control the quality of these adsorbents; it is each day more important to find the correct parameters indicators of quality. Activated charcoals used in two water treatment stations in hemodialysis centers were sampled as to assess their qualities. The Specific Surface Area ($S_{\text{BET}}$) of the charcoal sampled in the water treatment stations in the two centers have presented values between 600 and 1000 m$^2$/g approximately. $S_{\text{BET}}$ values around 800 m$^2$/g are usually taken as reference value, for those who acquire such adsorbents, mainly those destined to the water treatment. From that principle, it is verified that the sampled charcoals of both Hemodialysis Centers are in accordance with this parameter, however, it was also observed, that the same charcoals have mesopores volume of (0.01-0.09 cm$^3$/g), which are significantly below from those specified in the literature (0.40 cm$^3$/g), thus, the charcoals from both centers must be rejected for such aim or used with caution. The blue methylene adsorption was proposed as adsorption capacity measure of activated charcoals, as this molecule has been used as to estimate the charcoal mesopores volume. It was observed that the activated charcoals which have presented higher mesopores+ secondary micropores volume have more adsorption capacity to that molecule, and, hence, may be taken as a model to estimate the referred pores region, which is important for the charcoals used in the water treatment.

Regarding the first estimate of the adsorption capacity in batch of the activated charcoal in both hemodialysis centers for the cyanobacterium toxin [D-Leu$^1$]MCYST-LR, low removal efficiencies for that toxin were observed (close to 4%), compared with the activated charcoal from sugarcane bagasse (close 99%). The behavior in the adsorption of the sampled charcoals in the hemodialysis centers is associated with its low mesopores volumes, smaller than 0.04 cm$^3$/g, contrary to the sugarcane bagasse based-activated charcoal whose mesopores volume is around 0.40 cm$^3$/g.

Preliminary studies regarding the dynamic adsorption of the [D-Leu$^1$]MCYST-LR in fixed beds of the activated charcoals in the Hemodialysis Centers have shown low adsorption capacity between 3.67 and 5.31 µg/mg. Regarding the coconut shell and the sugarcane...
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It was observed a 2.07 and 5.43 μg/mg adsorption capacity of the respective beds.

5. Acknowledgment

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This book provides an overview of technical aspects in treatment of hemodialysis patients. Authors have contributed their most interesting findings in dealing with hemodialysis from the aspect of the tools and techniques used. Each chapter has been thoroughly revised and updated so the readers are acquainted with the latest data and observations in the area, where several aspects are to be considered. The book is comprehensive and not limited to a partial discussion of hemodialysis. To accomplish this we are pleased to have been able to summarize state of the art knowledge in each chapter of the book.

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