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Modelling adsorption equilibrium of STX and dc-STX onto GAC samples with different pore size distribution

Neuma Maria Silva Buaque[a], Jose Capelo-Neto[b,*]

[a]*Water Company of Ceara (CAGECE), Av. Dr. Lauro Vieira Chaves 1030, Vila União, Fortaleza, CE CEP: 60.420-280, Brazil, Tel./Fax: +55 85 3101 ext. 1742; email: neuma.buarque@cagece.com.br*
[b]*Australian Water Quality Centre, Federal University of Ceara, 250 Victoria Square, Adelaide SA 5000, Australia, Tel. +61 0438856254; emails: capelo_neto@sawater.com.au, capelo@ufc.br*

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ABSTRACT

Many different species of cyanobacteria have been identified worldwide as a threat to drinking water safety since they are capable of producing saxitoxins (STX), one of the most toxic non-protein substances known in nature. Although removal of these components can be accomplished by adsorption on granular activated carbon (GAC), a method to accurately model how effectively they can be removed in GAC filters has not yet been published. This research investigated adsorption equilibrium of dc-STX and STX on four coconut shell GAC samples, with positive surface charge but different pore size distribution, and experimental data were mathematically modelled providing elements for future GAC filter simulations. Adsorption of STX and dc-STX could be fitted to either Langmuir or Freundlich isotherms and the GAC sample with greater amount of mesopores, presented the largest adsorption capacity for both dc-STX and STX, although its BET area and pore volume were similar to the other GAC tested.

Keywords: Saxitoxins; Pore size distribution; Langmuir and Freundlich isotherms

1. Introduction

Paralytic shellfish poison (PSP) is a group of extremely powerful neurotoxic alkaloids, produced by cyanobacteria and marine eukaryotic dinoflagellates that prevent communication between neuron and muscle cells by blocking sodium channels [1]. Wiese et al. [2] reported that 57 analogues of PSPs have been identified all over the world, imposing a high heath risk to consumers and substantial losses in the aquaculture and fishing industries [3]. In the US alone, harmful algal blooms have been estimated to cost at least US$ 82 million per year [4]. Some of the most common PSP variants are described in Table 1.

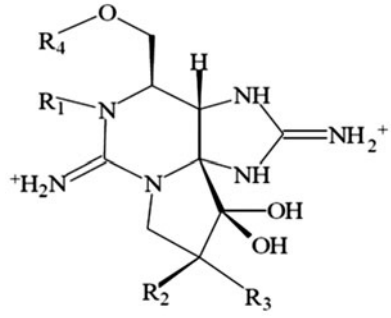
PSP-producing cyanobacteria known include *Dolichospermium circinalis* (formally described as *Anabaena circinalis*) in Australia [5], *Cylindrospermopsis raciborskii* in Brazil [6], *Lyngbya wollei* in North America [7,8], *Planktothrix* sp. in Italy [9], *Aphanizomenon* spp. in Portugal [10], North America [11] and China [12].

Since conventional water treatment plants—CWTP (Flocculation/Clarification/Filtration) are not able to remove extracellular cyanobacteria metabolites, one of the last barriers to prevent toxins from reaching households may be a granular activated carbon (GAC) filter. Until now however, there has been no way to

*Corresponding author.

Table 1
General structure, corresponding R functional groups and relative toxicity for the most common PSP variants

	R1	R2	R3	Relative toxicity
R4 = $CONH_2$ (Carbamate toxins)				
STX	H	H	H	1
neoSTX	OH	H	H	0.924
GTX1	OH	H	OSO_3^-	0.994
GTX2	H	H	OSO_3^-	0.359
GTX3	H	OSO_3^-	H	0.638
GTX4	OH	OSO_3^-	H	0.726
R4 = $CONHSO_3^-$ (N-Sulfocarbamoyl toxins)				
GTX5 (B1)	H	H	H	0.064
GTX6 (B2)	OH	H	H	–
C1	H	H	OSO_3^-	0.006
C2	H	OSO_3^-	H	0.096
C3	OH	H	OSO_3^-	0.013
C4	OH	OSO_3^-	H	0.058
R4 = H (Decarbamoyl toxins)				
dc-STX	H	H	H	0.513
dc-neoSTX	OH	H	H	–
dc-GTX1	OH	H	OSO_3^-	–
dc-GTX2	H	H	OSO_3^-	0.651
dc-GTX3	H	OSO_3^-	H	0.754
dc-GTX4	OH	OSO_3^-	H	–



Note: Adapted from [13].

accurately estimate how effectively a full-scale GAC filter would remove saxitoxins (PSP) and a tool that could help filter design, predict the moment for GAC regeneration or replacement would be extremely useful [14].

Rapid small-scale column test (RSSCT) is the most commonly used method to simulate fixed bed performance. However, RSSCT requires GAC to be crushed to a very small size, proportional to the column diameter, exposing internal pore structures and overestimating adsorption capacity [15–17]. To illustrate this phenomenon, superfine activated carbon showed a significant increase not only in adsorption capacity but also in adsorption kinetics of 2-Methylisoborneol (MIB) and geosmin when compared to the source carbon [18]. According to Matsui et al. [18], since molecules do not penetrate the particle completely, adsorbing preferentially near the outer surface, grinding the activated carbon further would increase external area, increasing also the removal capacity. Adsorption rate was also increased when the particle size was reduced due to a significant reduction of intraparticle mass transfer resistance.

To overcome these issues, Knappe et al. [16] and Gillogly et al. [17] applied the short bed adsorber (SBA) approach that, unlike the RSSCT, does not require particle diameter scaling down. Using the data obtained in their SBA experiments, the authors were able to successfully obtain design parameters and predict the performance of a real-scale GAC filter by applying the homogenous surface diffusion model (HSDM). However, in order to perform SBA tests and apply HSDM, equilibrium data such as the Langmuir or Freundlich isotherms constants must be provided.

Most studies related to adsorption of cyanotoxins by activated carbon have been conducted using microcystins [19–25]. On the other hand, investigations of saxitoxins adsorption on activated carbons are limited and unsuited for modelling [13,26–28].

Shi et al. [28] showed that STX can be effectively controlled in pH 8.2 with a powdered activate carbon (PAC) dose between 10 and 20 mg L^{-1}. Silva [29] demonstrated that PAC adsorbed high quantities of STX, reducing concentration in solution by as much as 28 μg L^{-1}. Orr et al. [27] used GAC packed columns with an empty bed contact time of 15 min and removed 100% of dc-STX, STX, GTX-2/3 and GTX-5, 94% of dc-GTX-2/3, but only partially removed N-sulfocarbamoyl-gonyautoxins 2 and 3 (C1 and C2 toxins) by 56 and 74%, respectively. Ho et al. [13] developed

experiments with PAC using two different raw waters. The first water had initial saxitoxin equivalent (STX_{equiv}) concentrations between 3.7 and 4.1 μg L^{-1} and the second one, initial concentrations between 7.5 and 9.9 μg L^{-1}. They were able to reduce the concentrations below 3.0 μg L^{-1} using a PAC dose of 10 mg L^{-1} and contact time of 15 min in the first water and with a dose of 30 mg L^{-1} and contact time of 70 min in the second water. None of the previous authors however developed their experiment or data processing in a manner that could allow further mathematical modelling.

In this context, the main objective of this study was to investigate adsorption of STX and dc-STX onto four commercially available coconut shell GAC samples and to model equilibrium data, providing elements for further experiments using SBA and HSDM. As a secondary objective, the influence of GAC pore size distribution (PSD) on the adsorption of STX and dc-STX was investigated.

2. Materials and methods

2.1. Saxitoxin production and semi-purification

The strain *Cylindrospermopsis raciborskii* T3 - CR [6] from the collection of the Federal University of Rio de Janeiro, Brazil, was used to produce saxitoxins necessary to our adsorption experiments. CR cultures were grown in ASM-1 medium [30], with pH 8.0, under a white light intensity of 75 μ mol m^{-2} s^{-1}, at a temperature of 24 ± 2°C and a 12:12 photoperiod until the end of the lag period. Although Carneiro et al. [31] demonstrated that this strain can produce STX, Neo-STX, dc-STX and dc-Neo-STX, high-performance liquid chromatography (HPLC) analysis demonstrated that in our culture only STX and dc-STX were present in measurable amounts.

To perform the extraction of intracellular saxitoxins, the CR biomass was concentrated by centrifugation at 2,700*g* for 15 min (25°C), the supernatant was discarded and the pellets were collected. The pelleted material was subjected to three freeze-thaw cycles, filtered through a 0.45-μm nitrocellulose membrane (Macherey—Nagel, UK) and the filtrate was then subjected to a semi-purification step by solid-phase extraction (SPE) on C18 cartridges (Supelco, USA), according to Lawrence et al. [32]. The semi-purified extract was acidified with 0.1 M acetic acid (Merck, Germany) to a pH of approximately 4.0 and stored at −20°C to preserve saxitoxin stability [33]. It is important to note that this semi-purified extract contained not only dc-STX and STX but also other intracellular metabolites considered hereafter as dissolved organic carbon (DOC). We believe that this approach represents more realistically the adsorption process behaviour since, in the case of an algal bloom, other dissolved intracellular compounds would be proportionally present in the filtered water.

2.2. Analytical methods

The semi-purified extract was characterized by analysing STX, dc-STX and DOC. DOC was measured using a total organic carbon analyser (Aurora 1030C, OI Analytical Co., USA). Saxitoxins analyses were performed by HPLC using an Agilent 1260 equipped with a quaternary pump, a C18 chromatography column (250 × 4 mm, 5 μm) maintained at 30°C, and a fluorescence detector (excitation = 340 nm; emission = 390 nm). As mobile phase, a 0.05 M ammonium formate aqueous solution with 5% HPLC grade acetonitrile (A) and a 0.1 M ammonium formate aqueous solution (B) with a total flow rate of 1.5 mL min^{-1} were applied. The process began with 100% mobile phase A. From 0 to 7.5 min, phase B increased from 0 to 20%. From 7.5 to 11 min, phase B increased from 20 to 80%, remaining unchanged until min 13. From 13 to 15 min, phase A returned to 100%. The above methodology was adapted from Lawrence et al. [32] and validated [34] using saxitoxins standards from the Institute for Marine Bioscience (National Research Council—Halifax, Canada).

2.3. Activated carbon characterization

Coconut shell, an agricultural by-product from renewable resources, is the most abundant and affordable raw material used to produce activated carbon in North-east Brazil [35] and therefore was the focus of this research. Four commercially available activated carbons produced with coconut shell using steam activation were utilized and named as GAC samples DD, CB, C8 and AP.

A porosimetry system (ASAP2000, Micrometrics, USA) was used to measure N_2 (at 77 K) adsorption–desorption isotherm over a relative pressure (p/p_o) range from 10^{-6} to 1. The surface area was calculated using the Brunauer–Emmett–Teller (BET) [36] equation and the total pore volume was estimated by converting the amount of adsorbed N^2 (cm^3 g^{-1} STP) to its liquid volume [37]. The PSD was obtained using density functional theory (DFT) [38]. The iodine number (mg of iodine adsorbed per g of carbon) was determined according to ASTM D 4607–86 [39]. The point of zero charge pH (pH_{pzc}), i.e. the pH above which the total net surface of the carbon particles is

negatively charged [40], was measured by the pH drift method [41].

2.4. Adsorption experiments

Virgin GAC samples were wet sieved between Tyler Standard Mesh 60 (0.25 mm) and 65 (0.21 mm). Since these experiments were meant to simulate future SBA tests in a 20 mm internal diameter (ID) column, sieving the GAC sample to this diameter (particle diameter < 50 × column ID) was necessary in order to minimize channelling and wall effect in the column [42]. Each GAC sample was washed using 10 times its volume with ultrapure water to remove fine particles, dried in a 110°C oven to constant weight and cooled in a desiccator, where it was stored prior to use [43]. The water samples were prepared using ultrapure water, with an electrolyte concentration of 0.01 M NaCl, buffered with 10 mM phosphate to a pH of 7.0 and spiked with different amounts of semi-purified toxin extract.

For the batch experiments, 3 mg of each GAC sample was placed in 12-mL amber glass vials along 10 mL of the synthetic water sample described previously. In each vial, the initial toxin concentrations (c_0) of dc-STX and STX varied from 3 to 20 μg L^{-1} and from 15 to 100 μg L^{-1}, respectively. This can be considered a worst-case scenario for dissolved saxitoxins in filtered water. DOC varied from 1 to 5 mg L^{-1}, proportional to the toxin concentration and roughly within the range (1–6 mg L^{-1}) observed in local filtered water (internal report—CAGECE, 2014).

The vials were then quickly placed into a mechanical tumbler, overturned continuously at 15 rpm in the dark, and in a controlled temperature of 28°C for 24 h. A subsample of 2 mL was removed from the collected vial, filtered through a 0.45-μm syringe filter (Acrodisc, Pall Corp., USA) and stored at −20°C until analysed. To observe if degradation or any other kind of removal besides carbon adsorption occurred, a control vial (without GAC Sample) was subjected to the same conditions.

Buarque et al. [44] developed kinetics experiments of saxitoxins onto the same GAC samples and showed that adsorption equilibrium was reached within 24 h, corroborating with the equilibrium times found by Silva [29] and Shi et al. [28] and validating the contact times applied in our study.

2.5. Adsorption modelling

The experimental data obtained was mathematically modelled using Langmuir and Freundlich isotherms. Linear regression was utilized to evaluate the models' adequacy. Statistical differences between carbons were evaluated using t-tests with a confidence level of $p_o = 0.05$. Langmuir isotherm is represented by Eq. (1) and its linearized form, by Eq. (2):

$$q_e = \frac{q_{max} c_e}{1 + k_L c_e} \tag{1}$$

$$\frac{c_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{c_e}{q_{max}} \tag{2}$$

where q_e (μg mg^{-1}) is the amount adsorbed at equilibrium, c_e (μg L^{-1}) is the concentration of adsorbate in solution at equilibrium, q_{max} (μg mg^{-1}) and k_L (L μg $^{-1}$) are the Langmuir isotherm parameters. q_{max} represents the maximum theoretical amount of toxin that can be adsorbed in a monolayer and k_L is related to the adsorption binding energy, the greater the value of k_L, the greater is the binding force between adsorbate (toxins) and adsorbent (carbons).

Eq. (3) describes the equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter [45]. R_L value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$.

$$R_L = \frac{1}{1 + k_L c_0} \tag{3}$$

where c_0 (μg L^{-1}) is the initial concentration and k_L (L μg $^{-1}$) the Langmuir Constant.

Freundlich isotherm (Eq. (4)) is an empirical equation widely used to represent adsorption systems. Its linear form (Eq. (5)) enables the determination of the parameters k_F and n:

$$q_e = k_f c_e^{1/n} \tag{4}$$

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \tag{5}$$

where q_e (μg mg^{-1}) is the amount adsorbed at a predetermined equilibrium time, c_e (μg L^{-1}) is the concentration of adsorbate in solution, and k_f [(ng mg^{-1})/(ng $L^{-1})^{1/n}$] and $1/n$ (dimensionless) are the Freundlich isotherm constants. For fixed values of c_e and $1/n$, the higher the value of k_F, the greater the adsorbent capacity and the q_e value. The parameter $1/n$ is related to the energy involved in adsorption. For a fixed c_e and k_F, the lower the value of n, the lower the strength of the adsorbate/adsorbent bond.

3. Results and discussion

3.1. GAC samples characterization and charge analysis

Carbon samples presented high surface areas and micropore volumes, except for sample DD (Table 2). GAC sample C8 has a relatively high volume of mesopores (23%), indicating a more "open" pore structure, while the other GAC samples have a smaller volume of macropore and thus a relatively "closed" pore structure. The molecular diameters of STX and dc-STX have not yet been reported in the literature, however, their molecular mass is approximately 300 and 257 Da, respectively. To give an idea how small STX and dc-STX molecules are, microcystin-LR has a molecular mass of 995.2 Da and its largest radius measures approximately 3 nm [46,47]. Therefore, it is not expected that size exclusion would significantly hinder adsorption of STX or dc-STX onto GAC samples used.

Although Iodine number have been reported in the literature to correlate well with micropore volume [48,49], no correlation was found between the samples' Iodine number and any other parameter evaluated (data not shown).

Careful examination of Table 2 shows that the pH_{pzc} of DD, CB, C8 and AP GAC samples were, respectively, 8.7, 8.8, 10.0 and 9.0 and therefore, their net surface charges are positive at pH 7.0. A large pH_{pzc} corresponds to a large content of basic groups, either in absolute or relative terms. Newcombe and Drikas [50] characterized various activated carbons surface charges utilizing only the difference between the surface titration and blank curves (pH_{pzc}). Bjelopavlic et al. [51] also relied fundamentally on surface charge (negative or positive) to explain adsorption of natural organic matter NOM onto activated carbon and proved that the intensity of the surface charge did not influence its adsorption characteristics. Therefore, we believe that, to our objectives, the PZC method is a pragmatic and appropriate tool to assess the adsorbent surface chemistry.

The molecular structures of dc-STX and STX have several amine groups that can potentially gain protons and thereby, become cationic depending on the solution pH. At pH 7.1, Shi et al. [28] observed that STX shifted to a mix of mono-cationic and di-cationic species. This same behaviour can be expected from dc-STX due to its molecular structure similarity and therefore, a weak electrostatic attraction between the few negative sites on the GAC samples and the cationic dc- STX and STX species may be the dominant mechanism of adsorption. Additionally, since the solubility of dc-STX and STX increases as they becomes more ionic, the hydrophobic driving force pushing them from the aqueous phase is reduced, reducing the GAC apparent adsorption capacity.

Bjelopavlic et al. [51] showed that at pH 4 the NOM found in surface waters is negatively charged, and at pH 7 the magnitude of the negative charge is twice as that for pH 4. It would be expected that for a positively charged activated carbon there should be a net attractive electrostatic interaction with NOM, while for the positively charged saxitoxins, toxin–surface interaction should be repulsive on average. Therefore, it is viable to assume that besides the possible micropore blockage caused by NOM, as proposed by Ding [52], a favourable adsorption of NOM would further decrease adsorption capacity of dc-STX and STX, as suggested by Shi et al. [28].

3.2. Equilibrium modelling

Experimental adsorption data of dc-STX and STX on four commercial coconut shell GAC samples were examined using Langmuir and Freundlich isotherms.

Table 2
Characteristics of four coconut shell GAC samples used

GAC samples	DD		CB		C8		AP	
Raw Material/Activation method	Coconut Shell/ Steam		Coconut Shell/ Steam		Coconut Shell/ Steam		Coconut Shell/ Steam	
BET area ($m^2\ g^{-1}$)	487		981		1,001		1,018	
Total pore vol. ($mL\ g^{-1}$)	0.215		0.446		0.494		0.525	
Micropore vol. ($mL\ g^{-1}$) (%)	0.178	83%	0.381	85%	0.374	76%	0.437	83%
Mesopore vol. ($mL\ g^{-1}$) (%)	0.024	11%	0.047	11%	0.114	23%	0.071	14%
Macropore vol. ($mL\ g^{-1}$) (%)	0.013	6%	0.018	4%	0.006	1%	0.017	3%
Average pore size (nm)	1.126		1.813		1.971		2.060	
Iodine number ($mL\ g^{-1}$)	397.5		739.4		454.7		662.3	
pH_{PCZ}	8.7		8.8		10.0		9.0	
Carbon charge at pH 7.0	+		+		+		+	
Average particle size (mm)	0.23		0.23		0.23		0.23	

Table 3
Langmuir and Freundlich isotherms coefficients for adsorption of dc-STX and STX onto GAC samples

		Langmuir isotherm			Freundlich isotherm		
GAC samples	Toxin	q_e (μg mg^{-1})	k_L (L μg^{-1})	R^2	k_f [(ng mg^{-1})/(ng L^{-1})$^{1/n}$]	n	R^2
AP	dc-SXT	0.020	3.528	0.924	0.013	3.900	0.562
	SXT	2.723	0.003	0.490	0.011	1.083	0.919
CB	dc-SXT	0.022	2.161	0.967	0.016	6.369	0.370
	SXT	0.725	0.029	0.814	0.031	1.409	0.901
C8	dc-SXT	0.253	5.947	0.954	0.201	12.531	0.150
	SXT	2.129	0.464	0.982	0.862	4.143	0.788
DD	dc-SXT	0.056	0.232	0.904	0.017	3.218	0.876
	SXT	0.289	0.016	0.735	0.008	1.379	0.964

Table 4
Experimental equilibrium capacity (q_{exper}) for dc-STX and STX onto four GAC samples

	Granular activated carbon			
q_{exper} (μg mg^{-1})	DD	CB	C8	AP
STX	0.154	0.415	2.095	0.418
dc-STX	0.049	0.023	0.255	0.024

The control samples demonstrated that no significant (p_o = 0.05) toxin removal occurred.

Based on the correlation coefficients (R^2) found in Table 3, adsorption of dc-STX on all GAC samples and adsorption of STX on C8 sample were best fitted with a Langmuir isotherm, indicating monolayer coverage. Values of k_L for sample C8 indicate that the energy involved in the adsorption of dc-SXT (5.947 L μg $^{-1}$) is one order of magnitude greater than for SXT (0.464 L μg $^{-1}$). Comparing the values of k_L for adsorption of dc-STX onto all GAC samples, the binding energy decreased in the same order as the mesopore volume and pH_{pcz} values (C8 > AP > CB > DD). Adsorption of STX on GAC samples AP, CB and DD was best described by Freundlich isotherm.

As observed in Table 4, the experimental adsorption capacities (q_{exper}), the last point of our experimental curves (Figs. 1 and 2), were very close to the Langmuir Isotherm constants q_e for adsorption of STX onto sample C8 and for dc-STX onto samples AP, CB, C8 and DD, indicating that the model was closely fitted and the time used for equilibrium was appropriate. In the case where the experimental data was best fitted by Langmuir isotherm, all R_L were between zero and one, indicating that adsorption was favourable (Table 5).

Sample C8 presented the largest experimental equilibrium capacity for both toxins (p_o = 0.05) compared to samples DD, CB and AP. GAC sample DD adsorbed the smallest amount of STX, probably due to its smaller BET area and pore volume compared to the other GAC samples tested. On the other hand, sample DD adsorbed a larger amount of dc-STX than

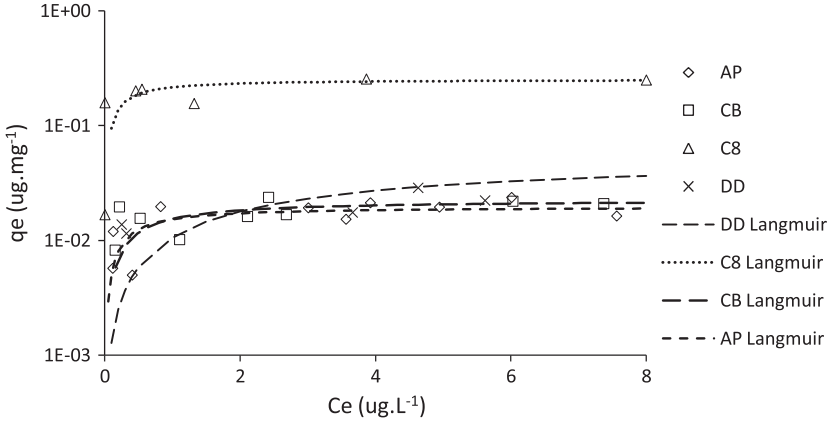


Fig. 1. Isotherm experimental data and non-linear isotherm fits for dc-STX on four GAC samples.

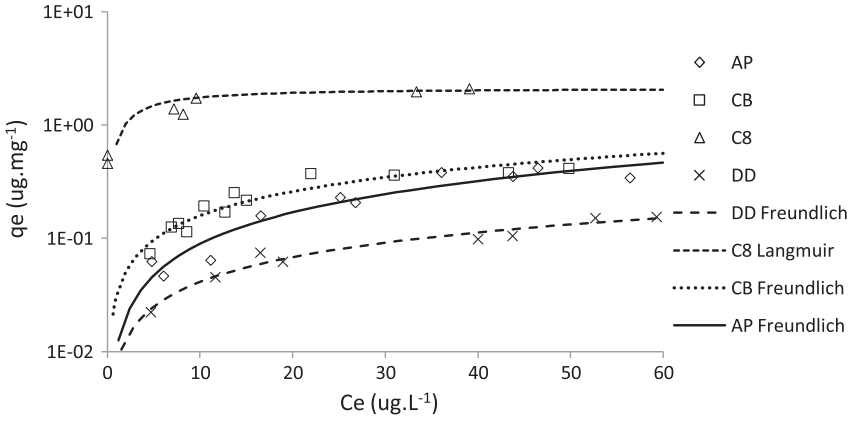


Fig. 2. Isotherm experimental data and non-linear isotherm fits for STX on four GAC samples.

Table 5
Separation factor R_L for the adsorption of dc-STX on all GAC samples and of STX on C8 GAC sample

GAC sample	STX	dc-STX
AP		
Co_1	–	0.0863
Co_2	–	0.0139
CB		
Co_1	–	0.1336
Co_2	–	0.0226
C8		
Co_1	0.1256	0.0530
Co_2	0.0211	0.0083
DD		
Co_1	–	0.5896
Co_2	–	0.1773

samples CB and AP (Table 3). Due to the smaller solid-phase concentrations of dc-STX involved at equilibrium, we believe that this behaviour, different from what happens in the case of STX, may be due to experimental or analytical errors involved.

Experimental equilibrium capacity (q_{exper}) of STX found in our study (2.095 μg mg^{-1}) represents a significant increase in adsorption capacity as compared to the value (0.625 μg mg^{-1}) found by Shi et al. [28]. Burns et al. [53] studied the adsorption of STX in different clay (kaolin, kaolinite, Ca-montmorillonite and Na-montmorillonite) suspensions with concentration of 250 mg L^{-1} and particles diameter > 38 μm, pH of 6.5 and STX concentrations ranging from 1.5 to 7.2 μg L^{-1}. Adsorption equilibrium was reached within 4 h and the data was well fitted by Freundlich isotherm. The authors found k_F values ranging from 2.6 μg mg^{-1} (n = 0.91) to 20.3 μg mg^{-1} (n = 0.58), while this work found low k_F values ranging from 0.008 μg mg^{-1} (n = 1.37) to 0.031 μg mg^{-1} (n = 1.41). Differences in the previous authors' experimental set-up, different values of n and the lack of dc-STX and STX adsorption on GAC isotherm data makes it difficult to further compare our results.

Experiments developed by Ding [53] used PAC with different PSD to remove atrazine as a trace-level contaminant in different source waters containing NOM. The author found that the greater the volume of mesopores the smaller the pore blockage (PB) by NOM and the larger amount of atrazine adsorbed. Silva [29] also found a relatively close relation between saxitoxins adsorption capacity and PAC mesoporous volume. Activated carbon PSD also played an important role in adsorption of microcystin-LR, since it is not able to enter micropores but it can easily access mesopores [20]. These observations have strong implications in our study since experimental equilibrium loadings (q_{exper}) for both toxins showed a close relation to mesoporous volume. Sample C8, with a greater amount of mesopores (23%), presented the largest adsorption capacity for both dc-STX and STX, although its BET area and pore volume were approximately the same as carbons AP and CB (p_o = 0.05).

4. Conclusions

The GAC sample with the greater amount of mesopores (C8) presented the largest adsorption capacity for both dc-STX and STX, although its BET area and pore volume were approximately the same as for GAC samples AP and CB. Adsorption of STX onto GAC sample C8 and dc-STX onto GAC samples C8, AP, CB and DD were best described with Langmuir

Isotherms and the adsorption process was considered favourable, while STX onto GAC samples AP, CB and DD were best fitted to the Freundlich model. The increase in experimental loadings (q_{exper}) for STX followed the same trend as the increase of absolute mesopore volume (C8 > AP > CB > DD). It is possible to conclude that although the GACs used in this study were produced from the same raw material (coconut shell), they presented different structural characteristics suggesting that judging adsorption efficiency solely by the raw material and surface area may be an imprecise method. Future research to understand the impact of carbon activation process and surface treatment would be of benefit, so adsorption capacity and kinetics of saxitoxins could be improved.

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References

[1] J. Roset, S. Aguayo, M.J. Munoz, Detéccion de cianobacterias y toxinas: Una revisión (Detection of cyanobacteria and toxins : A review), Rev. Toxicol. 18 (2001) 65–71.
[2] M. Wiese, P.M. D'Agostino, T.K. Mihali, M.C. Moffitt, B.A. Neilan, B.A. Brett, Neurotoxic alkaloids: Saxitoxin and its analogs, Mar. Drugs 8 (2010) 2185–2211.
[3] J. Al-Tebrineh, T.K. Mihali, F. Pomati, B.A. Neilan, Detection of saxitoxin-producing cyanobacteria and *Anabaena circinalis* in environmental water blooms by quantitative PCR, Appl. Environ. Microbiol. 76 (2010) 7836–7842.
[4] P. Hoagland, S. Scatasta. The economic effects of harmful algal blooms, in: E. Graneli, J. Turner, (Eds.) Ecology of Harmful Algae, Dordrecht, Springer-Verlag, 2006, Chap. 29. Ecology Studies Series, doi: 10.1007/978-3-540-32210-8_30.
[5] A.R. Humpage, J. Rositano, A.H. Bretag, R. Brown, P.D. Baker, B.C. Nicholson, D.A. Steffensen, Paralytic shellfish poisons from Australian cyanobacterial blooms, Aust. J. Mar. Fresh. Res. 45 (1994) 761–771.
[6] N. Lagos, H. Onodera, P.A. Zagatto, D. Andrinolo, S.M.F.O. Azevedo, Y. Oshima, The first evidence of paralytic shellfish toxins in the freshwater cyanobacterium *Cylindrospermopsis raciborskii*, isolated from Brazil, Toxicon 37 (1999) 1359–1373.
[7] Q. Yin, W.W. Carmichael, W.R. Evans. Factors influencing growth and toxin production by cultures of the freshwater cyanobacterium *Lyngbya wollei* Farlow ex Gomont. J. Appl. Phycol. 9 (1997) 55–63.
[8] F.A. Camacho, R.W. Thacker, Amphipod herbivory on the freshwater cyanobacterium *Lyngbya wollei*: Chemical stimulants and morphological defenses, Limnol. Oceanogr. 51 (2006) 1870–1875.
[9] F. Pomati, S. Sacchi, C. Rossetti, S. Giovannardi, H. Onodera, Y. Oshima, B.A. Neilan, The freshwater cyanobacterium *Planktothrix* sp. FP1: Molecular identification and detection of paralytic shellfish poisoning toxins, J. Phycol. 36 (2000) 553–562.
[10] F.M.B. Ferreira, J.M.F. Soler, M.L. Fidalgo, P. Fernández-Vila, PSP toxins from *Aphanizomenon flos-aquae* (cyanobacteria) collected in the Crestuma-Lever reservoir (Douro river, northern Portugal), Toxicon 39 (2001) 757–761.
[11] N.A. Mahmood, W.W. Carmichael, Paralytic shellfish poisons produced by the freshwater cyanobacterium *Aphanizomenon flos-aquae* NH-5, Toxicon 24 (1986) 175–186.
[12] Y. Liu, W. Chen, D. Li, Y. Shen, G. Li, First report of aphantoxins in China waterblooms of toxigenic *Aphanizomenon flos-aquae* in Lake Dianchi, Ecotoxicol. Environ. Saf. 65 (2006) 84–92.
[13] L. Ho, P. Tanis-Plant, N. Kayal, N. Slyman, G. Newcombe, Optimising water treatment practices for the removal of *Anabaena circinalis* and its associated metabolites, geosmin and saxitoxins, J. Water Health 07 (2009) 544–556.
[14] L. Ho, G. Newcombe, Granular activated carbon adsorption of 2-methylisoborneol (MIB): Pilot- and laboratory-scale evaluations, J. Environ. Eng. 136 (2010) 965–974.
[15] M.C. Carter, W.J. Weber, K.P. Olmstead, Effects of background dissolved organic matter on TCE adsorption by GAC, J. Am. Water Works Assoc. 84 (1992) 81–91.
[16] D.R.U. Knappe, V.L. Snoeyink, P. Roche, M. José Prados, M.M. Bourbigot, Atrazine removal by preloaded GAC, J. Am. Water Works Assoc. 91 (1999) 97–109.
[17] T.E.T. Gillogly, V.L. Snoeyink, J.C. Vogel, C.M. Wilson, E.P. Royal, Determining GAC bed life, J. Am. Water Works Assoc. 91 (1999) 98–110.
[18] Y. Matsui, S. Nakao, T. Taniguchi, T. Matsushita, Geosmin and 2-methylisoborneol removal using superfine powdered activated carbon: Shell adsorption and branched-pore kinetic model analysis and optimal particle size, Water Res. 47 (2013) 2873–2880.
[19] J.K. Fawell, J. Hart, H.A. James, W. Parr, Blue-green algae and their toxins—Analysis, toxicity, treatment and environmental control, Water Supply 11 (1993) 109–121.
[20] C. Donati, M. Drikas, R. Hayes, G. Newcombe, Microcystin-LR adsorption by powdered activated carbon, Water Res. 28 (1994) 1735–1742.
[21] T.W. Lambert, C.F.B. Holmes, S.E. Hrudey, Adsorption of microcystin-LR by activated carbon and removal in full scale water treatment, Water Res. 30 (1996) 1411–1422.
[22] D. Cook, G. Newcombe, Removal of microcystin variants with powdered activated carbon, Water Sci. Technol. Water Supply 2 (2002) 201–207.
[23] M. Campinas, M.J. Rosa Removal of microcystins by PAC/UF. Sep. Purif. Technol. 71 (2010) 114–120.
[24] R. Satish Kumar, D. Ragu Varman, P. Kanmani, N. Yuvaraj, K.A. Paari, V. Pattukumar, V. Arul, Isolation, characterization and identification of a potential

probiont from South Indian fermented foods (Kallappam, Koozh and Mor Kuzhambu) and its use as biopreservative, Probiotics Antimicrob. Proteins 2 (2010) 145–151.
[25] L. Ho, P. Lambling, H. Bustamante, P. Duker, G. Newcombe, Application of powdered activated carbon for the adsorption of cylindrospermopsin and microcystin toxins from drinking water supplies, Water Res. 45 (2011) 2954–2964.
[26] G. Newcombe, B. Nicholson, Treatment options for the saxitoxin class of cyanotoxins, Water Sci. Technol. Water Supply 2 (2002) 271–275.
[27] P.T. Orr, G.J. Jones, G.R. Hamilton, Removal of saxitoxins from drinking water by granular activated carbon, ozone and hydrogen peroxide-implications for compliance with the Australian drinking water guidelines, Water Res. 38 (2004) 4455–4461.
[28] H. Shi, J. Ding, T. Timmons, C. Adams, pH effects on the adsorption of saxitoxin by powdered activated carbon, Harmful Algae 19 (2012) 61–67.
[29] A.S. Silva, Avaliação da capacidade de remocao de saxitoxinas por diferentes tipos de carvão ativado em pó (CAP) produzidos no Brasil (Removal capacity assessment saxitoxins by different types of powdered activated carbon (PAC) produced in Brazil), Master Dissertation, UNB, DF, p. 115, (2005).
[30] P.R. Gorham, J. McLachlan, U.T. Hammer, W.K. Kim, Isolation and culture of toxic strains of *Anabaena flos-aquae* (Lyngb.) de Breb, Verhandlungen der Internationalen Vereinigung fur Theoretische und Angewandte Limnologie 15 (1964) 796–804.
[31] R.L. Carneiro, M.E.V. Santos, A.B.F. Pacheco, S.M.F.O. Azevedo, Effects of light intensity and light quality on growth and circadian rhythm of saxitoxins production in *Cylindrospermopsis raciborskii* (Cyanobacteria), J. Plankton Res. 1 (2009) 1–8.
[32] J.F. Lawrence, B. Niedzwiadek, C. Menard, Quantitative determination of paralytic shellfish poisoning toxins in shellfish using pre-chromatographic oxidation and liquid chromatography with fluorescence detection: collaborative study, J. AOAC Int. 88 (2005) 1714–1719.
[33] W.M. Indrasena, T.A. Gill, Thermal degradation of partially purified paralytic shellfish poison toxins at different times, temperatures, and pH, J. Food Sci. 65 (2000) 948–953.
[34] L.S. Silvino, J. Capelo-Neto, Validation of analytical method for saxitoxin detection (STX and dc-STX) by high performance liquid chromatography with fluorescence detector and pre-column derivation, Rev. AIDIS 7 (2014) 243–258.
[35] E.F. Jaguaribe, L.L. Medeiros, M.C.S. Barreto, L.P. Araujo, The performance of activated carbons from sugarcane bagasse, babassu, and coconut shells in removing residual chlorine, Braz. J. Chem. Eng. 22 (2005) 41–47.
[36] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (1938) 309–319.
[37] J. Guo, A.C. Lua, Preparation of activated carbons from oil-palm-stone chars by microwave-induced carbon dioxide activation, Carbon 38 (2000) 1985–1993.
[38] P. Kowalczyk, A.P. Terzyk, P.A. Gauden, Estimation of the pore-size distribution function from the nitrogen adsorption isotherm. Comparison of density functional theory and the method of Do and co-workers, Carbon 41 (2003) 1113–1125.
[39] ASTM D 4607-86, Standard Test Method for Determining of Iodine Number of Activated Carbon, Annual Book of ASTM Standards, Philadelphia, PA, (1994), 5.01.
[40] C.A. Leon y Leon J.M. Solar, V. Calemma, L.R. Radovic, Evidence for the protonation of basal plane sites on carbon, Carbon (1992) 797.
[41] G. Newcombe, R. Hayes, M. Drikas, Granular activated carbon: Importance of surface properties in the adsorption of naturally-occurring organics, Colloids Surf., A: Physicochem. Eng. Aspects 78 (1993) 65–71.
[42] H. Martin, Low peclet number particle-to-fluid heat and mass transfer in peaked beds, Chem. Eng. Sci. 33 (1980) 913.
[43] R.S. Summers, L. Cummings, J. DeMarco, D.J. Hartman, D.H. Metz, E.W. Howe, J.M.B. MacLeod, M. Simpson, Standardized protocol for the evaluation of GAC, Rep. Prepared for AWWA Research Foundation, Am. Water Works Assoc. (AWWA), Denver, (1992).
[44] N.M.S. Buarque, H.L.B. Buarque, J. Capelo-Neto, Adsorption kinetics and diffusion of Saxitoxins on granular activated carbon—Influence of pore size distribution, J. Water Supply Res. Technol. AQUA 64 (2015) 344–353.
[45] T.N. Webber, R.K. Chakravarti, Pore and Solid Diffusion Models for fixed bed adsorbers, J. Am. Inst. Chem. Eng. 20 (1974) 228–238.
[46] S. Doekel, M.A. Marahiel, Biosynthesis of natural products on modular peptide synthetases, Metab. Eng. 3 (2001) 64–77.
[47] K. Sivonen, G.J. Jones, Cyanobacterial Toxins, in: I. Chorus, J. Bartram (Eds.), Toxic Cyanobacteria in Water: A Guide to Their Public Health Consequences, Monitoring and Management, E & FN Spon, London, UK, 1999, pp. 41–111.
[48] A. Baçaoui, A. Yaacoubi, A. Dahbi, C. Bennouna, R.P.T. Luu, F.J. Maldonado-Hodar, J. Rivera-Utrilla, C. Moreno-Castilla, Optimization of conditions for the preparation of activated carbons from olive-waste cakes, Carbon 39 (2001) 425–432.
[49] C.A. Nunes, M.C. Guerreiro, Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers, Quím. Nova 34 (2011) 472–476.
[50] G. Newcombe, M. Drikas, Adsorption of NOM onto activated carbon: Electrostatic and non-electrostatic effects, Carbon 35 (1997) 1239–1250.
[51] M. Bjelopavlic, G. Newcombe, R. Hayes, Adsorption of NOM onto activated carbon: Effect of surface charge, ionic strength, and pore volume distribution, J. Colloid Interface Sci. 210 (1999) 271–280.
[52] L. Ding, Mechanisms of competitive adsorption between trace organic contaminants and natural organic matter on activated carbon, PhD Thesis, University of Illinois, p. 185, (2010).
[53] J.M. Burns, S. Hall, J.L. Ferry, The adsorption of saxitoxin to clays and sediments in fresh and saline waters, Water Res. 43 (2009) 1899–1904.