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Simulation of saxitoxins adsorption in full-scale GAC filter using HSDM

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

[a] Federal University of Ceara – DEHA, Bloco 713 – 1, Andar CEP 60451-970, Brazil
[b] Water Company of Ceara (CAGECE), Av. Dr. Lauro Vieira Chaves, 1030 – Vila União, Fortaleza, CE CEP 60.420-280, Brazil

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ABSTRACT

Many different species of cyanobacteria capable of producing saxitoxins have been identified as a threat to the safety of drinking water supplies worldwide. Removal of these contaminants can be accomplished by adsorption on granular activated carbon (GAC) but little is yet known about the kinetics of this process. This research investigated adsorption kinetics and diffusion behaviour of decarbomoyl saxitoxin (dc-STX) and carbamate saxitoxin (STX) on a GAC sample and simulated a full-scale GAC filter using batch experimental data and the homogeneous surface diffusion model (HSDM). HSDM was able to successfully describe batch adsorption of STX and dc-STX onto GAC sample and the surface diffusion coefficient was identified as the main adjustment parameter for this model. Different scenarios of STX and dc-STX removal in a GAC filter were simulated, offering engineers and scientists an option for the design of GAC full-scale filters, bench or pilot-scale experiments.

1. Introduction

Humans may be exposed to cyanotoxins through the ingestion of contaminated drinking water and food, inhalation or dermal adsorption during recreational activities in waters affected by a toxic bloom (Merel et al., 2013). Saxitoxins, also known as paralytic shellfish poisons (PSPs), have been associated with multiple human intoxications mainly through seafood consumption, resulting in numbness, paralysis and even death (Kuiper-Goodman et al., 1999). Wiese et al. (2010) reported that 57 analogues of PSPs have been identified all over the world. Furthermore, the molecular structures of PSPs have several amine groups (Table 1) that can gain protons and become cationic depending on the pH and therefore, saxitoxin (STX), the most toxic PSP compound for example, may present up to 10 different species (Hilal et al., 1995).

PSP-producing cyanobacteria have been increasingly reported in fresh and brackish water worldwide (Humpage et al., 1994; Kaas and Henriksen, 2000; Sevcik et al., 2003; Liu et al., 2006; Ballot et al., 2010; Berry and Lind, 2010; Clemente et al., 2010). According to Shi et al. (2012) the concentrations of extracellular PSPs reported could reach up to 15 μg $STX_{equiv}.L^{-1}$ in natural waters, with intracellular concentrations ranging from 5 to 3400 μg STX_{equiv} per gram of dry cell weight. Paerl and Paul (2012) suggested that frequency and intensity of harmful cyanobacteria blooms are expected to increase globally because of climate change. Australia adopted a PSP health alert level of 3 μg $STX_{equiv}.L^{-1}$ for drinking water (NHMRC, 2011), while a maximum PSP concentration of 1 and 3 μg $STX_{equiv}.L^{-1}$ is currently required by the New Zealand and Brazilian Ministry of Health, respectively (Orr et al., 2004; Portaria, 2914, 2011).

Since conventional water treatment plants – CWTP (coagulation/flocculation/sedimentation/filtration) are not able to remove extracellular cyanotoxins and other dissolved metabolites, two of the simplest barriers available to prevent these substances from reaching households are granular activated carbon (GAC) filter and post-chlorination.

Senogles-Derham et al. (2003) showed that a pH greater than 8 is most effective for saxitoxin destruction by chlorine. Experiments using raw water spiked with *Anabaena cirlinalis* cells, chlorine doses of 2 and 5 mg L^{-1} and pH of 8, demonstrated that for both chlorine doses extracellular STX were degraded from initial concentrations of 4–10 μg L^{-1} to a final concentration below 1 μg L^{-1} after a CT of over 60 mg.min.L^{-1} (Zamyadi et al., 2012). The problem of using chlorination solely to control STX is that dissolved organic matter (DOM) present in filtered water competes with the toxin for

* Corresponding author.
E-mail addresses: zecapelo@hotmail.com (J. Capelo-Neto), neuma.buarque@cagece.com.br (N.M. Silva Buarque).
URL: http://hcapelo@ufc.br

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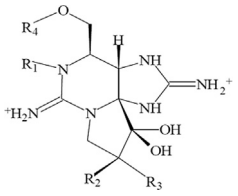
Table 1
General structure, corresponding R functional groups, and relative toxicity for the most common PSP variants.

	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	–



Adapted from Ho et al. (2009).

chlorine, increasing the risk of disinfection by-product formation. So adsorption of STX with activated carbon would present an advantage over post-chlorination. Until now, however, there is no accurate way to predict how effectively a full-scale GAC filter will remove compounds such as PSPs (Ho and Newcombe, 2010).

A few researchers have studied adsorption of PSPs on activated carbons in aqueous solutions (Bailey et al., 1999; Newcombe and Nicholson, 2002; Orr et al., 2004; Ho et al., 2009; Shi et al., 2012). Shi et al. (2012) showed that STX can be effectively controlled at a pH of 8.2 with a PAC dose between 10 and 20 mg L^{-1}. Orr et al. (2004) 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 reduced C1 and C2 toxins by 56% and 74%, respectively. Ho et al. (2009) developed experiments with PAC using two Australian raw waters (HV and MP). HV water had initial STX_{equiv} concentrations between 3.7 and 4.1 μg L^{-1} and MP water between 7.5 and 9.9 μg L^{-1}. They were able to decrease concentrations below 3.0 μg $STX_{equiv}.L^{-1}$ with a powder activated carbon (PAC) dose of 10 mg L^{-1} and 30 mg L^{-1}, respectively. These studies, however, presented neither appropriate equilibrium nor kinetic modelling adsorption data, making it difficult to extend their findings to full-scale treatment situations.

Models developed to describe adsorption kinetics can normally be classified as adsorption reaction or diffusion models (Qiu et al. 2009). First-order and second-order kinetic equations (adsorption reaction models) do not describe adsorption and diffusion mechanisms individually. Rather, they assume that the overall rate of adsorption is exclusively controlled by adsorption rate, while intraparticle diffusion and external mass transport are neglected (Qiu et al. 2009; Ocampo-Perez et al. 2012). On the other hand, adsorption diffusion models, like the homogeneous surface diffusion model – HSDM (Crittenden and Weber, 1978a) for example, assume that mass transfer is controlled by external film and surface diffusion and that pore diffusion and adsorption resistances are negligible (Baup et al. 2000).

The HSDM has been effectively used over the last few decades to determine the surface diffusion coefficient (D_s) and the film mass transfer coefficient (K_f). These parameters were used to predict adsorption dynamics of microcystin LR and LA onto PAC and GAC (Cook and Newcombe, 2008; Campinas et al., 2013; Viegas et al., 2014), of 2-methylisoborneol (MIB), of geosmin onto PAC (Cook et al., 2001; Matsui et al., 2009) as well as other micro-contaminants onto different types of activated carbon (Crittenden and Weber, 1978b; Fritz et al., 1980; Schideman et al., 2007; Worch, 2008; Kalalova et al., 2013). However, no data have yet been published on the use of HSDM to model adsorption kinetics of PSPs onto GAC, predominantly because of the large amount of toxin required to conduct column experiments. To overcome the limitations of cost and logistics of purchasing or purifying enough toxin to complete GAC column tests, we have put together a series of experimental and mathematical procedures that, although individually not novel, should allow an initial assessment of the efficiency of a full scale GAC filter removing STX and dc-STX.

Therefore, the aims of this study were to model the adsorption kinetic data of two PSPs (STX and dc-STX) onto GAC using HSDM, to develop a sensitivity analysis using variations of the model's diffusion parameters (D_s, K_f) and to apply this data to simulate a hypothetical full-scale GAC filter.

2. Materials and methods

2.1. PSP production and semi-purification

The strain *Cylindrospermopsis raciborskii* T3 – CR (Lagos et al., 1999) from the collection of the Federal University of Rio de Janeiro, Brazil, was used to produce small amounts of PSP for the adsorption experiments. CR cultures were grown in ASM-1 medium, with pH of 8.0, under a white light intensity of 75 μ.mol m^{-2} s^{-1}, at a temperature of 24 ± 2 °C, with aeration and a photoperiod of 12:12 (light/dark) until they reached the end of lag period. Although Carneiro et al. (2009) demonstrated that this strain can produce STX, Neo-STX, dc-STX and dc-Neo-STX, HPLC analysis showed that our culture only produced STX and dc-STX in a sufficient amount to be used in the experiments.

To perform the extraction of intracellular PSP, the culture's biomass was concentrated by centrifugation at 2700 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. (2005). The semi-purified extract was acidified with 0.1 M acetic acid (Merk, Germany) to a pH of approximately 4.0 and stored at −20 °C to preserve saxitoxin stability (Indrasena and Gill, 2000). It is important to note that this semi-purified extract contained not only dc-STX and STX but other intracellular metabolites considered here as dissolved organic matter (DOM). It is assumed that this approach more realistically represents the behaviour of the adsorption process in full-scale plants since, in the case of an algal bloom, other dissolved intracellular compounds, apart from PSP, would also be present in the water matrix.

2.2. Analytical methods

The semi-purified extract was characterized by analysing STX, dc-STX and DOM. DOM was measured with a TOC analyser (Aurora 1030C, OI Analytical Co., USA). STX and dc-STX analysis were performed by high performance liquid chromatography (HPLC) using an Agilent 1260 equipped with a quaternary pump, a C18 chromatography column (250 × 4 mm, 5 μm) maintained at 30 °C, a manual injector with a loop of 20 μL, and a fluorescence detector – FLD with excitation of 340 nm and emission of 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 13 min. From 13 to 15 min it returned to 100% of A. The above methodology was adapted from Lawrence et al. (2005) and validated by Silvino and Capelo-Neto (2014) using standards from the Institute for Marine Bioscience (National Research Council—Halifax, Canada).

2.3. GAC samples characterization

A commercial coconut shell based GAC was used in this investigation because of its mesopore volume, PSP adsorption capacity and kinetics and, as described previously in more detail by Buarque et al. (2015).

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 of 10^{-6} to 1. The surface area was calculated using the Brunauer—Emmett—Teller (BET) 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 (Guo and Lua, 2000). The pore size distribution (PSD) was obtained using density functional theory (DFT) (Kowalczyk et al., 2003). The point of zero charge (PCZ) pH was measured by the pH drift method (Newcombe et al., 1993).

2.4. Adsorption experiments

A batch system was used to study the adsorption kinetics and equilibrium of STX and dc-STX in aqueous solution onto the GAC sample. A virgin GAC sample was wet sieved between Tyler Standard Mesh 60 (0.25 mm) and 65 (0.21 mm), washed with 10 times its volume with ultrapure water, then dried in a 110 °C oven to constant weight and cooled in a desiccator where it was stored prior to use (Summers et al., 1992). The water samples were prepared using ultrapure water, with an electrolyte concentration of 0.01 M NaCl, buffered with 10 mM phosphate to pH of 7.0 and spiked with semi-purified PSP extract. To maintain the same DOM characteristics and to control the amount of DOM added throughout the experiments, we chose to use this artificial water samples instead of real treated water spiked with semi-purified PSP extract.

For the batch experiments, 3 mg of GAC was placed in 12-mL amber glass vials along with 10 mL of the water sample described previously. For the kinetics experiments, the initial toxin concentrations (C_0) were ~7 μg L^{-1} for dc-STX and ~60 μg L^{-1} for STX. For the equilibrium experiments, the initial toxin concentrations (C_0) of dc-STX and STX varied from ~3 to ~12 μg L^{-1} and from ~15 to ~60 μg L^{-1}, respectively. This can be considered a worst-case scenario for dissolved PSP in treated water from CWTP prior to GAC filtration. DOM varied from 1 to 5 mg L^{-1}, proportionally to the toxins concentration and roughly between the range (1 and 6 mg L^{-1}) observed in treated water from CWTP prior to GAC filtration (internal report – CAGECE, 2014).

The vials were then quickly placed into a tumbler, and overturned continuously in the dark at 15 rpm, in a temperature-controlled chamber at 28 °C. For the equilibrium experiments, vials were collected after 24 h Buarque et al. (2015) developed experiments with STX and dc-STX onto the same GAC sample and showed that adsorption equilibrium was reached within 24 h, corroborating with the equilibrium times found by Shi et al. (2012). For the kinetic experiments vials were collected hourly up to 8 h and then with less frequency until 24 h.

A subsample of 2 mL was removed from each collected vial, filtered through a 0.45 μm syringe filter (Acrodisc, Pall Corp.) and stored at −20 °C until analysis. HPLC analysis occurred 24 h after the first vial was collected for equilibrium and kinetics experiments, respectively. To observe if degradation or any other kind of removal besides carbon adsorption occurred, control vials (without GAC) were submitted to the same conditions.

2.5. Adsorption modelling

The HSDM was used to describe the process of adsorption onto GAC (Mathews and Weber, 1976; Crittenden and Weber, 1978b; Traegner and Suldan, 1989). The non-linear equations involved (Table 2), which include physical and kinetic parameters, are solved numerically.

Experimental equilibrium data was mathematically modelled using Langmuir and Freundlich isotherms and linear regression to evaluate their adequacy. The adsorption equilibrium parameters were than fed into the HSDM to simulate the experimental adsorption kinetics of dc-STX and STX onto the GAC. HSDM calculations were performed using the software FAST 2.1 (Sperlich et al., 2008). By minimizing the difference between the model calculations and experimental concentrations, two kinetic parameters, K_f and D_s, were obtained. After finding K_f and D_s that provided the best fit, each parameter was varied individually to observe the effect they had on fitting to the experimental curve.

2.6. Filter design

With the HSDM coefficients determined using bench experiment data, HSDM was used again, this time to simulate GAC filter breakthrough curves using an effluent concentration limit of 3 μg $STX_{equiv.}.L^{-1}$, different input concentrations and empty bed contact times (EBCT). The flow inside the simulated GAC filter was assumed to have the same turbulent regime applied to the bench-scale experiments and consequently, the filter's film diffusion coefficient (K_f) was the same to the one found experimentally.

3. Results and discussions

3.1. GAC samples characterization and charge analysis

GAC sample presented a pH_{PCZ} of 10.0, indicating it has a net positive charge in the working solution pH (7.0). Examination of Table 3 shows that GAC sample has a relatively high mesopore volume (23%), indicative of an “open” pore structure. The molecular structure 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. (2012) observed that STX shifted to a mix of mono-cationic and di-cationic species (65 and 35%, respectively). This same behaviour can be extrapolated to dc-STX due to their molecular structure similarity. Hence, electrostatic repulsion may have been an important mechanism influencing the adsorption process due to the cationic nature of the GAC sample and to the cationic speciation of dc-STX and STX as described by Buarque et al. (2015).

3.2. Equilibrium modelling

Adsorption equilibrium data was examined using Langmuir and Freundlich models. The control samples demonstrated that until 24 h, no significant ($p_o = 0.05$) toxin decrease occurred. Based on the correlation coefficients (R^2) found in Table 4, adsorption of dc-STX and STX on GAC was best described by Langmuir isotherm, indicating monolayer coverage. Values of K_L for GAC sample indicate that the energy involved in adsorption of dc-STX (5.947 L μg^{-1})

Table 2
Basic equations for the HSDM.

Equation no.	Equation	Role
1	$\frac{dC_b}{dt} = -M\frac{dq_{avg}}{dt}$	Mass balance for batch
2	$q_{avg} = \frac{3}{(d_p/2)^3}\int_0^{d_p/2} q(r,t)r^2 dr$	Average carbon load
3	$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right)$	Diffusion equation for a spherical particle
4	$q(r,0) = 0$	Initial condition
5	$\frac{\partial q}{\partial r} = 0 f or r = 0$	Boundary condition at r = 0
6	$\rho_p D_s \frac{\partial q}{\partial r} = K_f(C_b - C_s)$	Boundary condition at r = dp/2
7	$q_s = K_f C_s^{1/n}$	Freundlich isotherm
8	$q_s = \frac{q_{max}C_s}{1+K_L C_s}$	Langmuir isotherm

(Adapted from Roy et al., 1993).

Table 3
Characteristics of the coconut shell GAC sample used.

GAC samples	GAC	
Raw Material/Activation method	Coconut Shell/Steam	
BET area ($m^2\ g^{-1}$)	1001	
Total pore vol. ($mL\ g^{-1}$)	0.494	
Micropore vol. ($mL\ g^{-1}$/%)	0.374	76%
Mesopore vol. ($mL\ g^{-1}$/%)	0.114	23%
Macropore vol. ($mL\ g^{-1}$/%)	0.006	1%
Average pore size (nm)	1.971	
pH_{PCZ}	10.0	
Carbon charge at pH 7,0	+	
Avarage particle size (mm)	0.23	
Particle density ($g\ cm^{-3}$)	1.45	

is one order of magnitude greater than for STX (0.464 L μg^{-1}). The experimental adsorption capacity (q_{exper}), considered here as the last point of our experimental isotherms (Fig. 1), was approximate to the calculated Langmuir constant q_e for both STX and dc-STX (Table 4), indicating that the model was closely adjusted. The experimental adsorption capacity (q_{exper}) of STX found in this study (2.1 $\mu g\ mg^{-1}$) represents a significant increase compared to the one (0.625 $\mu g\ mg^{-1}$) found by Shi et al. (2012), making it technically viable to continue the modelling effort using the selected GAC sample.

3.3. Kinetic modelling

In this case also, no significant ($p_o = 0.05$) toxin decrease occurred in the control samples until 24 h. The close agreement between the model fittings and the experimental data shows that HSDM could successfully describe the adsorption of both STX and dc-STX onto GAC sample, making it possible to obtain realistic K_f and D_s (Table 5). It can be observed also that the best K_f and D_s found for STX ($K_f = 5 \times 10^{-3}$ cm min^{-1}; $D_s = 5 \times 10^{-16}\ cm^2\ min^{-1}$) and dc-STX ($K_f = 10^{-3}$ cm min^{-1}; $D_s = 5 \times 10^{-16}\ cm^2\ min^{-1}$) can be considered practically equal.

K_f and D_s were found to be independent of initial concentration for adsorption of MC-LR (Campinas et al., 2013), MIB and geosmin (Gillogly et al., 1998; Cook et al., 2001) onto powder activated carbon (PAC). Similarly, the proximity of STX and dc-STX parameters K_f and D_s displayed in Table 5 indicates that diffusion kinetics, and consequently adsorption kinetics, of both toxins onto our GAC sample are similarly and independent of initial concentration.

We are currently unaware of similar studies that have proposed K_f and D_s for STX onto activated carbon. Melegari and Matias (2012) showed that STX adsorption kinetics onto chitin and oyster shell were best adjusted to pseudo-first-order and pseudo-second-order models respectively. Buarque et al. (2015) investigated adsorption kinetics of dc-STX and STX onto four coconut shell-based GAC. They observed that equilibrium concentration was reached within 24 h and that a pseudo-second-order model best represented experimental data. No attempt however, was made by these authors to apply HSDM to the kinetic data. Ho et al. (2009) and Dixon et al. (2011) studied saxitoxin removal using PAC adsorption but their results were expressed in terms of relative removal. Orr et al. (2004) investigated the removal of saxitoxins by GAC, but considered only the implications of residual toxicity for compliance with the Australian drinking water standards.

Fig. 2 through 5 show simulations of STX and dc-STX adsorption sensitivity analysis using HSDM. It is observed in those Figures that the variation of D_s contributed significantly ($p_o = 0.05$) to the model adjustment, while variations of K_f by one order of magnitude showed no significant ($p_o = 0.05$) effects and that the best fitting parameters were equal for both STX and dc-STX. This finding is consistent with other authors' results, which considered D_s as the main HSDM adjustment parameter (Cook and Newcombe, 2008; Campinas et al., 2013; Viegas et al., 2014) and reinforces the idea that STX and dc-STX can be considered as a single component when diffusing onto our GAC sample.

3.4. Filters simulation

Typically, the drinking water industry uses GAC with a 8 × 30 mesh (size range of 2.38–0.55 mm) or a 12 × 40 mesh (size range of 1.41–0.35 mm) (Kennedy et al., 2015). For this simulation, therefore, a GAC particle size with diameter of 2.2 mm was used. The empty bed contact time (EBCT) and the STX and dc-STX influent concentration were varied according to Table 6. The STX/dc-STX concentration ratio used was the same as in the experimental

Table 4
Langmuir and Freundlich coefficients and experimental equilibrium capacity for adsorption of dc-STX and STX onto GAC sample.

GAC sample	Toxin	Langmuir isotherm				Freundlich isotherm		
		q_{exper} ($\mu g\ mg^{-1}$)	q_{max} ($\mu g\ mg^{-1}$)	K_L ($L\ \mu g^{-1}$)	R^2	K_F ($ng\ mg^{-1}$)/($ng\ L^{-1}$)$^{1/n}$	n	R^2
	dc-STX	0.255	**0.253**	5.947	**0.954**	0.201	12.531	0.150
	STX	2.095	**2.129**	0.464	**0.982**	0.862	4.143	0.788

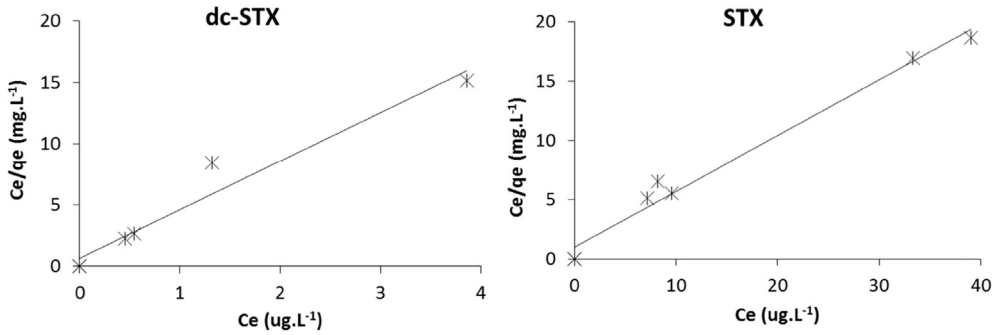


Fig. 1. Linear Langmuir adsorption isotherm fits for dc-STX and STX on GAC sample.

Table 5
STX and dc-STX experimental and calculated concentrations in solution using best K_f and D_s found.

T (h)	STX		Dc-STX	
	Exp. conc. (μg/L)	HSDM. conc. (μg/L)[a]	Exp. conc. (μg/L)	HSDM. conc. (μg/L)[b]
0.0	59.81	59.81	6.67	6.67
1.0	33.32	39.20	3.73	4.15
2.0	31.23	34.24	2.98	3.47
4.0	27.43	25.81	2.93	2.54
6.0	23.93	19.86	2.39	1.78
9.5	16.45	11.99	1.46	0.93
24.0	6.34	2.57	0.00	0.17
	$R^b = 0.97$		$R^b = 0.96$	

[a] $K_f = 5 \times 10^{-3}$ cm min^{-1}; $Ds = 5 \times 10^{-16}$ cm^2 min^{-1}.
[b] $K_f = 10^{-3}$ cm min^{-1}; $Ds = 5 \times 10^{-16}$ cm^2 min^{-1}.

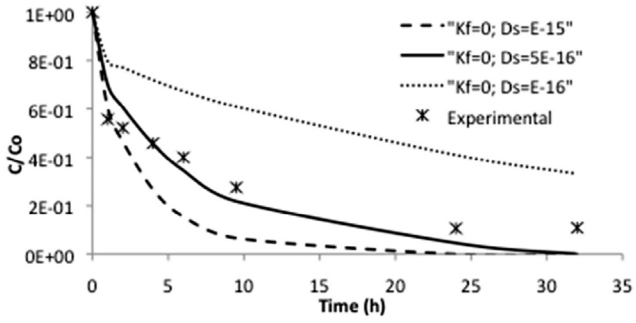


Fig. 2. Adsorption of STX onto GAC – HSDM sensitivity analysis varying Ds and maintaining Kf constant.

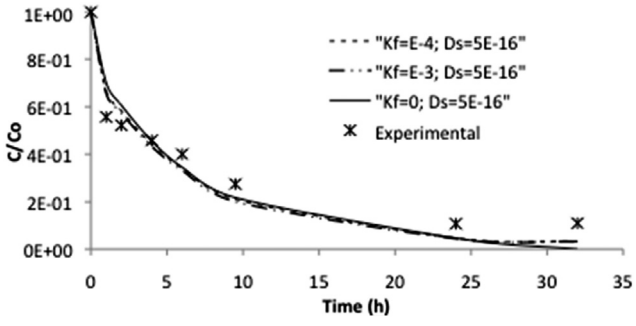


Fig. 3. Adsorption of STX onto GAC – HSDM sensitivity analysis varying Kf and maintaining Ds constant.

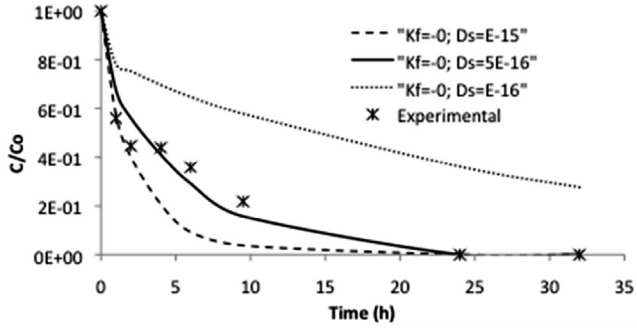


Fig. 4. Adsorption of dc-STX onto GAC – HSDM sensitivity analysis varying Ds and maintaining Kf constant.

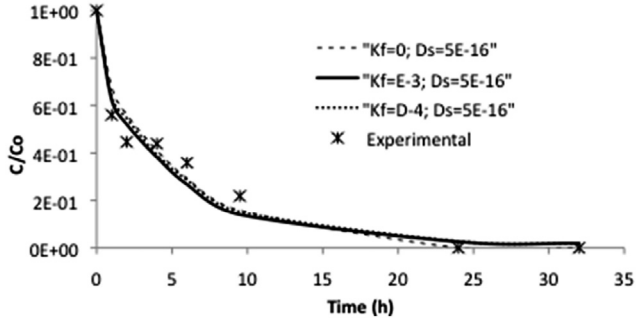


Fig. 5. Adsorption of dc-STX onto GAC – HSDM sensitivity analysis varying Kf and maintaining Ds constant.

solution and the model was run individually for each toxin with a specific STX or dc-STX concentration and EBCT. The STX equivalent concentration in the effluent – C_{out} ($\mu g_{stxeq}.L^{-1}$) was obtained by summing up the two results considering the dc-STX relative toxicity of 0.513. A 3 $\mu g_{stxeq}.L^{-1}$ horizontal line was also plotted (Fig. 6) in order to visualize when C_{out} would exceed this limit.

Table 6
Time for C_{out} to reach 3 $\mu g_{stxeq}.L^{-1}$ using different empty bed contact time (EBCT) and STX and dc-STX influent concentration (Co).

		Run ID					
		10 min10 + 2	5 min10 + 2	10 min20 + 4	15 min20 + 4	15 min50 + 10	20 min50 + 10
Time (d) for C_{out} to reach 3 $\mu g_{stxeq}.L^{-1}$		138	39	42	87	18	31.5
EBCT (min)		10	5	10	15	15	20
Co ($\mu g.L^{-1}$)	STX	10	10	20	20	50	50
	dc-STX	2	2	4	4	10	10

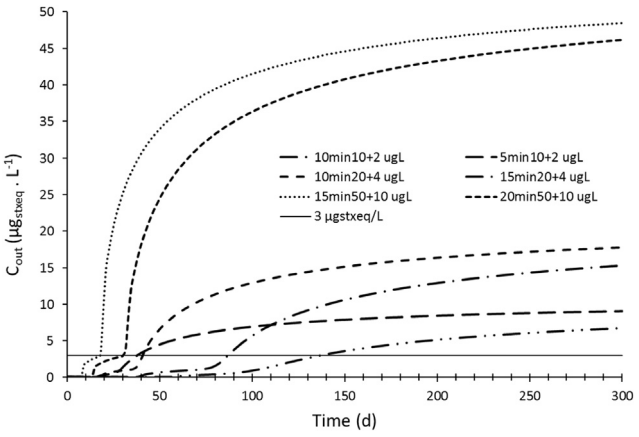


Fig. 6. Simulation of STX equivalent concentration (C_{out}) in the GAC filter's effluent over time (days), using different EBCT and influent STX and dc-STX concentrations (Note that Run ID = 10min10 + 2 µg L means EBCT = 10 min, 10 µg L^{-1} of STX and 2 µg L^{-1} of dc-STX).

Fig. 6 shows that, in the simulation using EBCT of 10 min, concentrations of STX = 10 µg L^{-1} and dc-STX = 2 µg L^{-1}, C_{out} would exceed 3 $\mu g_{stxeq}.L^{-1}$ after 138 days of continue use. This indicates, for example, that a water treatment plant with a flow rate of 30 ML d^{-1} containing 10 µg L^{-1} of STX and 2 µg L^{-1} of dc-STX could comply with Australian and Brazilian guidelines using a total GAC filter volume of 208 m^3 for 138 consecutive days before the activated carbon needed to be changed or regenerated. This limited lifetime could represent an operational problem for utilities if these metabolites were constantly present in the raw water, which, according to Newcombe et al. (2010), that is not the case. Besides, GAC filters are expected to remove occasional episodes of cianobacteria metabolites and therefore, filter may be put offline avoiding the decrease of its removal capacity.

Higher DOM can substantially reduce GAC adsorption capacity (Newcombe et al., 2002; Zoschke et al., 2011) and therefore, the applicability of our modelled results may be limited by higher DOM in the influent water to the full-scale GAC filter. Other point that might decrease the theoretical breakthrough time may be the water quality influent water to the full-scale GAC filter. Higher turbidity was shown to decrease geosmin and MIB removal by PAC (Cook and Newcombe, 2008). Therefore, low quality filtered water may decrease the GAC filter efficiency and toxin breakthrough time.

Biological removal of other cyanotoxins has been reported in GAC filters (Newcombe and Nicholson, 2002; Newcombe et al., 2003; Ho and Newcombe, 2010; Wang et al., 2007; Drogui et al., 2012), offering the advantage of two removal mechanisms, adsorption and biodegradation, and thus increasing breakthrough time. In the case of PSP, however, biological activity seams not to play an important role in water treatment. The fate of five PSP variants through biologically active laboratory filters was assessed by Kayal et al. (2008). They found that an increase in the concentrations of the more toxic variants coincided with a decrease of the less toxic variants suggesting that organisms within the biofilm had the ability to biotransform the PSP. The lack of STX biological removal indicates that defining precisely the GAC filter adsorption capacity for is even more crucial than for other cyanotoxins.

The simulated breakthrough curves and the horizontal line over the x-axis representing the 3 $\mu g_{stxeq}.L^{-1}$ limit are displayed in Fig. 4. C_{out} ($\mu g_{stxeq}.L^{-1}$) is zero at the beginning of the simulation, followed by two fast increases and finally a concentration levelling off at the influent concentration. The first fast increase, the smaller one, represents the contribution of dc-STX and the second and larger one, represents the contribution of the STX concentration to the C_{out}. Although both toxins have demonstrated practically the same adsorption kinetics on the GAC tested, dc-STX experimental adsorption capacity (q_{exper}) is smaller than STX's, as defined by the equilibrium isotherms, explaining therefore the curves configuration.

4. Conclusions

Homogenous surface diffusion model was used to simulate batch and full-scale adsorption kinetics of STX and dc-STX onto a GAC sample. Adsorption kinetics and isotherms lab-scale experiments data were used in the simulation to find the HSDM constants K_f and D_s. Conclusions from this study were:

- Adsorption of dc-STX and STX on the GAC sample was best described by Langmuir isotherm, energy involved in adsorption of dc-STX was one order of magnitude greater than for STX but the experimental adsorption capacity (q_{exper}) was one order of magnitude greater for STX than for dc-STX;
- HSDM could successfully describe adsorption of STX and dc-STX onto the GAC sample and the proximity of STX the dc-STX parameters indicates that diffusion of both toxins behaves in a similar way;
- Variations of D_s significantly altered the model adjustment whereas variations of K_f by one order of magnitude showed no significant effect. Therefore, Ds can be considered as the main HSDM adjustment parameter;
- With the data obtained in the experimental procedures and with the model adjustment, it was possible to simulate a full-scale GAC filter treating water containing STX, dc-STX and dissolved organic matter.

The methodology presented in this paper may offer an option not only as a first approach to GAC filter projects but also for bench and pilot scale experimental designs. To test the validity of our methodology and the accuracy of our determinations however, column adsorption experiments should be conducted as soon as STX and dc-STX are sufficiently available.

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References

Bailey, D., Bowen, B., Goodwin, L., Procter, L., 1999. An organic removal strategy for Grahamstown WTP. In: Proceedings 18th AWWA Federal Convention, Adelaide, April 11–14.

Ballot, A., Fastner, J., Wiedner, C., 2010. Paralytic shellfish poisoning toxin-producing cyanobacterium Aphanizomenon gracile in Northeast Germany. Appl. Environ. Microbiol. 76, 1173–1180.

Baup, S., Jaffre, C., Wolbert, D., Laplanche, A., 2000. Adsorption of pesticides onto granular activated carbon: determination ofsurface diffusivities using simple batch experiments. Adsorption 6, 219–228.

Berry, J.P., Lind, O., 2010. First evidence of paralytic shellfish toxins and cylindrospermopsin in a Mexican freshwater system, Lago Catemaco, and apparent bioaccumulation of the toxins in tegogolo snails (Pomacea patula catemacensis). Toxicon 55, 930–938.

Buarque, N.M.S., Buarque, H.L.B., Capelo-Neto, J., 2015. Adsorption kinetics and diffusion of saxitoxins on granular activated carbon – influence of pore size distribution. J. Water Supply Res. Tech. – AQUA 64, 344–353.

CAGECE – Companhia de Água e Esgoto do Ceará, 2014. Dissolved organic matter in post-filtered water from conventional water treatment plants in the State of Ceará – Brazil. In: Internal Report Centro de Pesquisa da ETA Gavião.

Campinas, M., Viegas, R.M.C., Rosa, M.J., 2013. Modelling and understanding the competitive adsorption of microcystins and tanni acid. Water Res. 47, 5690–5699.

Carneiro, R.L., Santos, M.E.V., Pacheco, A.B.F., Azevedo, S.M.F.O., 2009. Effects of light intensity and light quality on growth and circadian rhythm of saxitoxins production in Cylindrospermopsis raciborskii (Cyanobacteria). J. Plankton Res. 1 (1), 1–8.

Clemente, Z., Busato, R.H., Oliveira Ribeiro, C.A., Cestari, M.M., Ramsdorf, W.A., Magalhães, V.F., Wosiack, A.C., Silva de Assis, H.C., 2010. Analyses of paralytic shellfish toxins and biomarkers in a southern Brazilian reservoir. Toxicon 55, 396–406.

Cook, D., Newcombe, G., Sztajnbok, P., 2001. The application of powdered activated carbon for MIB and Geosmin removal: predicting PAC dose in four raw waters. Water Res. 35 (5), 1325–1333.

Cook, D., Newcombe, G., 2008. Comparison and modelling of the adsorption of two microcystin analogues onto powdered activated carbon. Environ. Technol. 29, 525–534.

Crittenden, J.C., Weber, W.J., 1978a. Predictive model for design of fixed-bed absorbers: single component model verification. J. Environ. Eng. Div., Am. Soc. Civ. Eng. 104, 433–443.

Crittenden, J.C., Weber, W.J., 1978b. Predictive model for design of fixed-bed adsorbers: parameter estimation and model development. J. Envir. Engrg. Div. – ASCE 104 (2), 185–197.

Dixon, M.B., Richard, Y., Ho, L., Chow, C.W.K., O'Neill, B.K., Newcombe, G., 2011. A coagulation–powdered activated carbon–ultrafiltration – multiple barrier approach for removing toxins from two Australian cyanobacterial blooms. J. Hazard. Mat. 186 (2–3), 1553–1559.

Drogui, P., Daghrir, R., Simard, M.C., Jean, C.S., Blais, F., 2012. Removal of microcystin-LR from spiked water using either activated carbon or anthracite as filter material. Environ. Tech. 33 (4), 381–391.

Fritz, W., Merk, W., Schlunder, E.U., 1980. Competitive adsorption of two dissolved organics onto activated carbon. Chem. Engin. Sci. 36, 743.

Gillogly, T., Snoeyink, V., Elarde, J., Wilson, C., Royal, E., 1998. C^{14}-MIB adsorption on PAC in natural water. J. Am. Water Works Assoc. 90 (1), 98–108.

Guo, J., Lua, A.C., 2000. Preparation of activated carbons from oil-palm-stone chars by microwave-induced carbon dioxide activation. Carbon 38 (14), 1985–1993.

Hilal, S., Karickhoff, S.W., Carreira, L.A., 1995. A rigorous test for SPARC's chemical reactivity models: estimation of more than 4300 ionization pK_a's. Quant. Struct.–Activity Relat. 14, 348–355.

Ho, L., Newcombe, G., 2010. Granular activated carbon adsorption of 2-methylisoborneol (MIB): pilot- and laboratory-scale evaluations. J. Environ. Eng. 9, 965–974.

Ho, L., Tanis-Plant, P., Kayal, N., Slyman, N., Newcombe, G., 2009. Optimizing water treatment practices for the removal of anabaena circinalis and its associated metabolites, geosmin and saxitoxins. J. Water Health 7, 544–556.

Humpage, A.R., Rositano, J., Bretag, A.H., Brown, R., Baker, P.D., Nicholson, B.C., Steffensen, D.A., 1994. Paralytic shellfish poisons from Australian cyanobacterial blooms. Aust. J. Mar. Freshw. Res. 45, 761–771.

Indrasena, W.M., Gill, T.A., 2000. Thermal degradation of partially purified paralytic shellfish poison toxins at different times, temperatures, and pH. J. Food Sci. 65 (6), 948–953.

Kaas, H., Henriksen, P., 2000. Saxitoxins (PSP toxins) in Danish lakes. Water Res. 34, 2089–2097.

Kalalova, L., Knappe, D.R.U., Lehnberg, K., Kazner, C., Hollender, J., 2013. Removal of highly polar micropollutants fom wastewater by powdered activated carbon. Environ. Sci. Pol. Res. 20, 3607–3615.

Kayal, N., Newcombe, G., Ho, L., 2008. Investigating the fate of saxitoxins in biologically active water treatment plant filters. Environ. Toxic. 23, 751–755.

Kennedy, A.M., Reinert, A.M., Knappe, D.R.U., Ferrer, I., Summers, R.S., 2015. Full- and pilot-scale GAC adsorption of organic micropollutants. Water Res. 68, 238–248.

Kowalczyk, P., Terzyk, A.P., Gauden, P.A., 2003. 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 (6), 1113–1125.

Kuiper-Goodman, T., Falconer, I., Fitzgerald, J., 1999. In: Chorus, I., Bartram, J. (Eds.), Toxic Cyanobacteria in Water: a Guide to Their Public Health Consequences, Monitoring and Management, pp. 113–153. London.

Lagos, L., Onodera, H., Zagatto, P.A., Andrinolo, D., Azevedo, S.M.F.O., Oshima, Y., 1999. The first evidence of paralytic shellfish toxins in the freshwater cyanobacterium cylindrospermopsis raciborskii, isolated from Brazil. Toxicon 37, 1359–1373.

Lawrence, J.F., Niedzwiadek, B., Menard, C., 2005. 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 (6), 1714–1719.

Liu, Y., Chen, W., Li, D., Shen, Y., Li, G., Liu, Y., 2006. First report of aphantoxins in China—waterblooms of toxigenic Aphanizomenon flos-aquae in Lake Dianchi. Ecotox. Environ. Saf. 65, 84–92.

Matsui, Y., Ando, N., Sasaki, H., Matsushita, T., Ohno, K., 2009. Branched pore kinetic model analysis of geosmin adsorption on super-powdered activated carbon. Water Res. 43, 3095–3103.

Mathews, A.P., Weber, W.J.J., 1976. Effects of external mass transfer and intraparticle diffusion on adsorption rates in slurry reactors. AIChE Symp. Ser. 166, 91–107.

Melegari, S.P., Matias, W.G., 2012. Preliminary assessment of the performance of oyster shells and chitin materials as adsorbents in the removal of saxitoxin in aqueous solutions. Chem. Cent. J. 6 (86), 1–8.

Merel, S., Walker, D., Chicana, R., Snyder, S., Baurès, E., Thomas, O., 2013. State of knowledge and concerns on cyanobacterial blooms and cyanotoxins. Environ. Int. 59, 303–327.

Newcombe, G., Hayes, R., Drikas, M., 1993. Granular activated carbon: Importance of surface properties in the adsorption of naturally-occurring organics. Coll. Surf. 78, 65–71.

Newcombe, G., House, J., Ho, L., Peter Baker, P., Burch, M., 2010. Management Strategies for Cyanobacteria (Blue-Green Algae): a Guide for Water Utilities. Water Quality Research Australia Limited (WQRA). Research Report No 74.

Newcombe, G., Nicholson, B., 2002. Treatment options for the saxitoxin class of cyanotoxins. Water Sci. Technol. Water Supply 2 (5–6), 271–275.

Newcombe, G., Cook, D., Brooke, S., Ho, L., Slyman, N., 2003. Treatment options for microcystin toxins: similarities and differences between variants. Environ. Tech. 24, 299–308.

NHMRC – National Health and Medical Research Council, 2011. Australian Drinking Water Guidelines (ADWG) Updated December 2014. Available at: https://www.nhmrc.gov.au/guidelines-publications/eh52. accessed (05.03.15).

Ocampo-Perez, R., Abdel Daiem, M.M., Rivera-Utrilla, J., Mendez- Dıaz, J., Sanchez-Polo, M., 2012. Modelling adsorption rate of organic micro pollutants present in landfill leachates onto granular activated carbon. J. Colloid Interface Sci. 385, 174–182.

Orr, P.T., Jones, G.J., Hamilton, G.R., 2004. 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, 4455–4461.

Paerl, H.W., Paul, V.J., 2012. Climate change: links to global expansion of harmful cyanobacteria. Water Res. 46 (5), 1349–1363.

Portaria 2914 de 12, December of 2011, Brasília: Ministry of Health, Brazil.

Qiu, H., Lu, L.V., Pan, B.C., Zhang, Q.J., Zhang, W.M., Zhang, Q.X., 2009. Critical review in adsorption kinetic models. J. Zhejiang Univ. Sci. A 10, 716–724.

Roy, D., Wang, G.T., Adrian, D.D., 1993. A simplified solution technique for carbon adsorption model. Water Res. 27, 1033–1040.

Schideman, L.C., Snoeyink, V.L., Marinas, B.J., Ding, L., Campos, C., 2007. Application of three-component competitive adsorption model to evaluate and optimize granular activated carbon systems. Water Res. 41, 3289–3298.

Senogles-Derham, P.-J., Seawright, A., Shaw, G., Wickramisingh, W., Shahin, M., 2003. Toxicological aspects of treatment to remove cyanobacterial toxins from drinking water determined using the heterozygous P53 transgenic mouse model. Toxicon 41, 979–988.

Sevcik, C., Noriega, J., D'Suze, G., 2003. Identification of Enterobacter bacteria as saxitoxin producers in cattle's rumen and surface water from Venezuelan Savannahs. Toxicon 42, 359–366.

Shi, H., Ding, J., Timmons, T., Adams, C., 2012. pH effects on the adsorption of saxitoxin by powdered activated carbon. Harm. Algae 19 (64), 61–67.

Silvino, L.S., Capelo-Neto, J., 2014. 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 (3), 243–258.

Summers, R.S., Cummings, L., DeMarco, J., Hartman, D.J., Metz, D.H., Howe, E.W., MacLeod, J.M.B., Simpson, M., 1992. Standardized Protocol for the Evaluation of

GAC. Rep. Prepared for AWWA Research Foundation. American Water Works Association (AWWA), Denver.
Sperlich, A., Schimmelpfennig, S., Baumgarten, B., Genz, A., Amy, G., Worch, E., Jekel, M., 2008. Predicting anion breakthrough in granular ferric hydroxide (GFH) adsorption filters. Water Res. 42 (8–9), 2073–2082.
Traegner, U.K., Suidan, M.T., 1989. Evaluation of surface and film diffusion coefficients for carbon adsorption. Water Res. 23, 267–273.
Viegas, R.M.C., Campinas, M., Costa, H., Rosa, M.J., 2014. How do the HSDM and Boyd's model compare for estimating intraparticle diffusion coefficients in adsorption process. Adsorption 20, 737–746.
Wang, H., Ho, L., Lewis, D.M., Brookes, J.D., Newcombe, G., 2007. Discriminating and assessing adsorption and biodegradation removal mechanisms during granular activated carbon filtration of microcystin toxins. Water Res. 41, 4262–4270.
Wiese, M., D'Agostino, P.M., Mihali, T.K., Moffitt, M.C., Neilan, A., Brett, B.A., 2010. Neurotoxic alkaloids: saxitoxin and its analogs. Mar. Drugs 8, 2185–2211.
Worch, E., 2008. Fixed-bed adsorption in drinking water treatment: a critical review on models and parameter estimation. J. Water Supply Res. Technol. – AQUA 57 (3), 171–183.
Zamyadi, A., Ho, L., Newcombe, G., Bustamante, H., Prévost, M., 2012. Fate of toxic cyanobacterial cells and disinfection by-products formation after chlorination. Water Res. 46, 1524–1535.
Zoschke, K., Engel, C., Bornick, H., Worch, E., 2011. Adsorption of geosmin and 2-methylisoborneol onto powdered activated carbon at non-equilibrium conditions: Influence of NOM and process modeling. Water Res. 45, 4544–4550.