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Dynamic adsorption of diarrhetic shellfish poisoning (DSP) toxins in passive sampling relates to pore size distribution of aromatic adsorbent

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ABSTRACT

Solid-phase adsorption toxin tracking (SPATT) technology was developed as an effective passive sampling method for dissolved diarrhetic shellfish poisoning (DSP) toxins in seawater. HP20 and SP700 resins have been reported as preferred adsorption substrates for lipophilic algal toxins and are recommended for use in SPATT testing. However, information on the mechanism of passive adsorption by these polymeric resins is still limited. Described herein is a study on the adsorption of OA and DTX1 toxins extracted from *Prorocentrum lima* algae by HP20 and SP700 resins. The pore size distribution of the adsorbents was characterized by a nitrogen adsorption method to determine the relationship between adsorption and resin porosity. The Freundlich equation constant showed that the difference in adsorption capacity for OA and DTX1 toxins was not determined by specific surface area, but by the pore size distribution in particular, with micropores playing an especially important role. Additionally, it was found that differences in affinity between OA and DTX1 for aromatic resins were as a result of polarity discrepancies due to DTX1 having an additional methyl moiety.

1. Introduction

Contamination of shellfish with naturally occurring phycotoxins from harmful algal blooms is a serious problem for public health and the shellfish industry worldwide. In order to protect consumer health and reduce economic losses it is imperative that sensitive analytical methods and early warning systems for shellfish toxin detection be available. Many countries maintain routine monitoring programs in order to forecast toxic algae blooms and to test for toxin contamination in shellfish [1]. However, phytoplankton monitoring has some disadvantages: it is difficult to obtain spatially and temporally integrated water samples; the algal toxicity varies between species; phytoplankton monitoring is labour intensive; and definitive identification of some species is difficult [1]. Sometimes toxin production by algae varies with time, and the species present and the number of algal cells alone cannot be used as an indicator for the presence of toxins [2]. MacKenzie et al. [3] developed a solid-phase adsorption toxin tracking (SPATT) technology for use as a possible early warning tool for lipophilic shellfish toxins. The basis of the technique is passive adsorption of lipophilic toxins in seawater onto polymeric resins, with a HP20 resin being the substrate of choice from the initial work. Subsequently, numerous studies have examined the usefulness of the technique as a tool for early warning of lipophilic toxins and for profiling toxin occurrences and distributions. Turrell et al. [4] showed that SP700 resin accumulated toxins more rapidly than HP20 over short incubation periods, but after longer exposure periods there was no significant difference. Adsorption and desorption behaviors of lipophilic toxins with five different resins were compared, and results demonstrated that HP20, SP850, SP825L had similar adsorption rates, however, HP20 did not appear to reach saturation after 72 h exposure when the other resins did [5]. Recently, a correlation was shown between toxin profiles in shellfish and in SPATT sampling with the latter determined to be useful for monitoring the exposure of shellfish to the toxigenic algae of concern in northern Europe [6].

SPATT sampling has proven to be a very useful tool for tracking dissolved lipophilic toxins in seawater [2,7]. Advantages of the technique include: time and spatially integrated sampling that simulates shellfish uptake; toxins tracked by the resin are not subject to bio-transformation (as can be the case with shellfish); sample matrices are relatively clean; and it provides unique information on toxin dynamics [1]. Perhaps one of the most interesting aspects of SPATT technology is its potential for use as an early warning tool for biotoxins. However, use of SPATT for early warning is dependent on a number of things. For example the amount of toxins released from cells and the toxin profiles of the toxic species in seawater are both very important in terms of the applicability of the technique. Toxin profile is influenced by the time of sampling and the distri-

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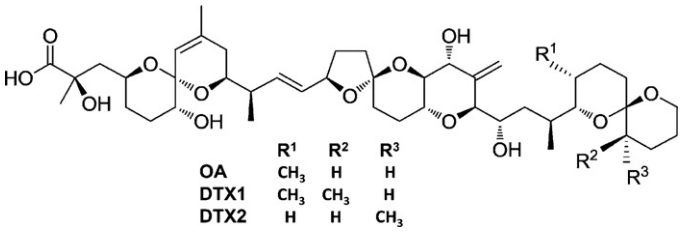

Fig. 1. Chemical structure of major DSP toxins. OA and DTX1 are primarily produced by the *Prorocentrum lima* strain used in these experiments.

bution of toxic algae, and it is necessary that the toxins adsorbed by passive samplers reflect the vertical distribution of toxic algae in the water body. Pizarro et al. [7] emphasized the need to have information on the physiological conditions and behavior of *Dinophysis* populations during different phases of the population growth and hydrodynamic scenarios. A study carried out on the West coast of Ireland showed that SPATT testing did not give an earlier warning of the presence of lipophilic shellfish toxins than that obtained from analysis of indigenous or even transplanted mussels [8]. However, a study with the hydrophilic toxin domoic acid has demonstrated the possibility for early warning of the onset of a toxic event [1]. Therefore, the potential for use of the method as an early warning system does exist.

Relationships between toxin profiles tracked by SPATT and environmental conditions including the physical parameters of seawater, physiological characters of toxic algae, accumulation rate of shellfish, etc., require further examination to fully evaluate the potential of the SPATT technique. An aspect of the methodology deserving scrutiny in terms of dynamic adsorption of lipophilic toxins is the resin characteristics. Some researchers have suggested that the adsorption capacity of lipophilic compounds by aromatic adsorbents is not related to the specific surface area [5,9]. With attention to this topic the current paper reports a study which looked at the dynamic adsorption of okadaic acid (OA) and dinophysistoxin-1 (DTX1) (Fig. 1) from solution by HP20 and SP700 resins. The pore size distribution of the adsorbents was characterized in order to explain the relationship of this parameter to toxin uptake.

2. Materials and methods

2.1. Chemicals

All reagents and solvents were LC grade materials. A certified standard of OA was purchased from the Certified Reference Materials Program (CRMP) of the National Research Council Canada (Halifax, NS, Canada). DTX1 standard was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Acetonitrile and methanol were purchased from Merck Ltd. (Whitehouse Station, NJ, USA). Formic acid, acetic acid, ammonium formate and ammonium acetate were purchased from Fisher Scientific (Fair Lawn, NJ, USA). De-ionized water was obtained from a MilliQ water purification system (Millipore Ltd., Bedford, MA, USA) to 18 mΩ quality or better.

2.2. Adsorbent resin

DIAION®HP20 and SEPABEADS®SP700 were purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). Both resins are aromatic type adsorbents based on a cross-linked polystyrenic matrix. The manufacturer stated that particles are 250–600 μm (>90% > 250 μm) and 250–700 μm (>95% > 250 μm) for the HP20 and SP700 resins, respectively. Detailed product descriptions including specific surface area, pore volume, and predominant pore radius are shown in Table 1.

2.3. Toxic algae

A strain of *Prorocentrum lima* (CCMP1996) was purchased from Provasoli-Guillard National Center for Culture of Marine Phytoplankton (CCMP, West Boothbay Harbor, Maine, USA). The algae were kept in 500 mL borosilicate flasks containing 300 mL f/2 medium. The medium was filtered (0.45 μm) and seawater taken from Huiquan Bay, Qingdao City, in the Yellow Sea was autoclaved and added to the medium. The salinity of the culture medium was approximately 31‰. Cultures were maintained at 20 °C under an irradiance of 54 $\mu E\,m^{-2}\,s^{-1}$ in a 12 h light:12 h dark cycle. The stock culture was used to inoculate larger batches in 5 L bottles to produce sufficient amounts of algae for the experiment. These large cultures were maintained under the same growth conditions for 4 weeks before harvesting (about 1.5×10^7 cells/L). The culture medium and algal cells were filtered using 10 μm silk mesh, and were centrifuged at 3000 rpm for 5 min. The algal pellet was stored at −20 °C until use.

2.4. Surface area and porosity measurements

Specific surface area, pore volume and pore size distribution were determined using nitrogen (N_2) as adsorbate with a Quantachrome Autosorb-1 automated gas sorption system (Boynton Beach, Florida, USA) [10]. Approximately 50 mg of resin was degassed at 105 °C until the pressure increase rate was lower than 1.3 Pa min^{-1} within a 0.5 min test interval. Helium was used as a backfill gas. In total 67 adsorption points and 20 desorption points were used to draw isotherms from 1.0×10^{-6} to 0.995 P/P_0. Specific surface area was calculated from the Brunauer–Emmett–Teller (BET) equation [11,12]. The cumulative pore volume was calculated during desorption phase using the Barrett–Joyner–Halenda (BJH) method for calculation of pore size distribution [13]. Pore size distribution was calculated using a density functional theory (DFT) and Monte-Carlo (MC) method [14].

2.5. LC–MS analysis for DSP

LC–MS analysis for OA and DTX1 was performed using a Thermo LTQ XL mass spectrometer equipped with an ESI interface coupled to a Finnigan Surveyor HPLC consisting of a solvent

Table 1
Specific surface area and pore size of HP20 and SP700 resins. Product description obtained from www.diaion.com (website accessed 16-08-2010).

Resin	Surface area (m^2/g)		Pore volume (cm^3/g)		Average pore radius (A)	
	Product description	Multipoint BET method	Product description	Total pore volume	Product description[a]	Average pore radius
HP20	590	588	1.30	1.43	260	49
SP700	1200	1160	2.20	2.05	85	35

[a] *Note*: radius of the predominant pores of resin.

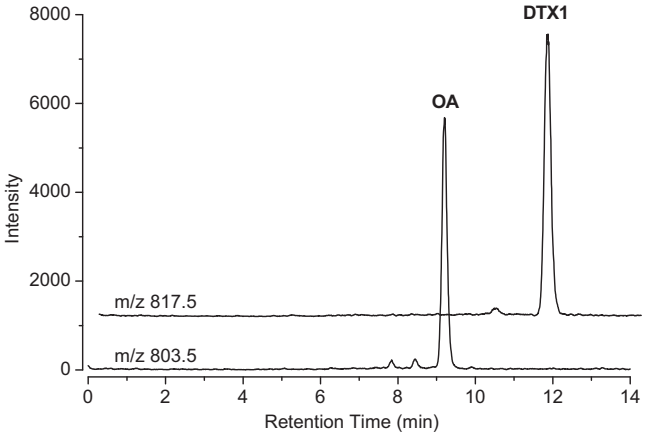

Fig. 2. Chromatogram for OA and DTX1 toxins using LC–MS analysis.

reservoir, in-line degasser, binary pump, refrigerated autosampler, and temperature-controlled column oven (Thermo Fisher Scientific, Waltham, MA, USA).

Chromatographic separation was achieved on a Phenomenex Luna C_{18} column (250 × 4.6 mm, 5 μm, 100 Å) maintained at 40 °C. Isocratic elution was with acetonitrile/0.05% acetic acid (9:1, v/v) at 0.45 mL/min. MS detection was carried out in negative ionization mode by monitoring the ions *m/z* 803.5 and 817.5 for OA and DTX1, respectively (Fig. 2).

2.6. Adsorption experiments of DSP toxins

Dry HP20 and SP700 resins were activated by immersing in methanol for 48 h after which suspended fine particles were discarded. The wet resins were washed three times with de-ionized water to remove the organic solvent. Excess water on the surface of resins was removed using hygroscopic paper before using them in the adsorption experiments.

DSP toxins extracted from the *P. lima* cultures were used in the adsorption experiments due to costs associated with using OA and DTX1 standards. In the CCMP1996 strain DTX1 and OA were the predominant toxin components, with the amount of DTX1 being approximately twice that of OA. In a strain of *P. lima* from Portugal used in a previous study, OA and DTX1 were also the predominant toxins produced, while several diol esters of both OA and DTX1 were also present [15]. In this study the algal cells were heated to 100 °C for 10 min by boiling before extraction in order to stop enzyme activity and prevent bio-transformation of diol esters. Following this the cells were extracted with a methanol/0.5 M acetic acid solution (9:1, v/v) using a sonicator for 10 min, and then placed in the fridge at 4 °C overnight. Finally, the mixture was centrifuged at 8000 rpm for 10 min and the supernatant was retained for experimentation.

The crude cell extract was used to prepare a series of DSP toxin solutions at different concentrations (OA 1.3–162 μg/mL; DTX1 2.5–470 μg/mL). The extraction solution (90% methanol solvent) was used to dilute the crude toxin solution to make DSP solutions with different concentrations. 0.1 g resin was added into 2 mL toxin solution and the mixture was shaken at 145 rpm for 5 min at room temperature (25 ± 1 °C). The 5 min adsorption time was optimized using preliminary experiments (data not shown). Every treatment level was prepared in triplicate for adsorption testing. The adsorption solutions were centrifuged at 8000 rpm for 10 min and the suspensions were filtered by 0.22 μm membrane. The concentration of DSP toxins in the suspension was analyzed by LC–MS.

The Freundlich equation was used to analyze the equilibrium adsorption isotherms of DSP toxins in order to compare the adsorption ability of different resins for OA and DTX1 toxins. Freundlich equation, $\mathrm{Lg}\, q_e = 1/n * \mathrm{Lg}\, C_e + \mathrm{Lg}\, K_f$, where q_e is adsorbate concentration on adsorbent (μg/g); C_e is equilibrium concentration of adsorbate in solution (μg/mL); n and K_f are characteristic constants. K_f is a relative indicator of adsorption capacity in the Freundlich theory [16]. The kinetics is defined as a favorable adsorption if the value of n is larger than 1. The favorable adsorption kinetics means that the adsorption rate is fast or controllable depending on the requirement of a particular application. And the maximal capacity (q_m) can be calculated by the equation, $q_m = K_f * C_o^{1/n}$, where C_o, is initial concentration of adsorbate in solution (μg/mL).

3. Results

3.1. Characteristics of resin HP20 and SP700

The experimentally determined specific surface areas and total pore volumes of the resins were similar to the data provided by the product manufacturer (Table 1). However, the average pore radius determined in this study was below the value stated in the product description regarding the predominant pores. Cumulative pore volume calculated using the BJH method showed that there were a combination of mesopores (2–50 nm) and micropores (<2 nm) in the resins. The desorption isotherms exhibited hysteresis which also demonstrated that micropores and mesopores existed in the resin. The mesopore volume in SP700 was above that of HP20 based on the results shown in Fig. 3.

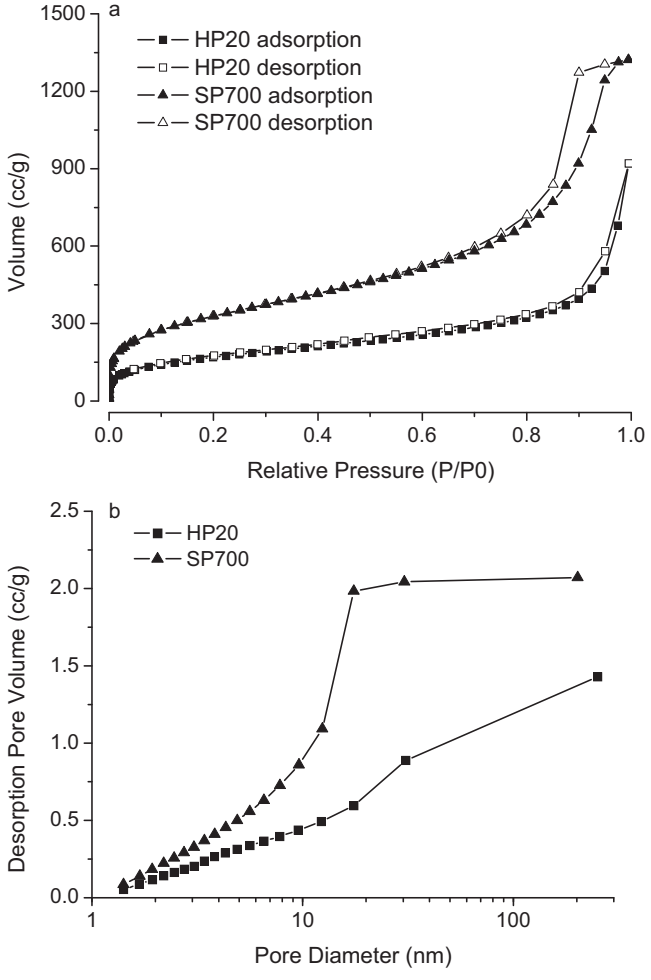

Fig. 3. Adsorption and desorption isotherms (a) and cumulative pore volume of HP20 and SP700 resins calculated using the BJH method (b).

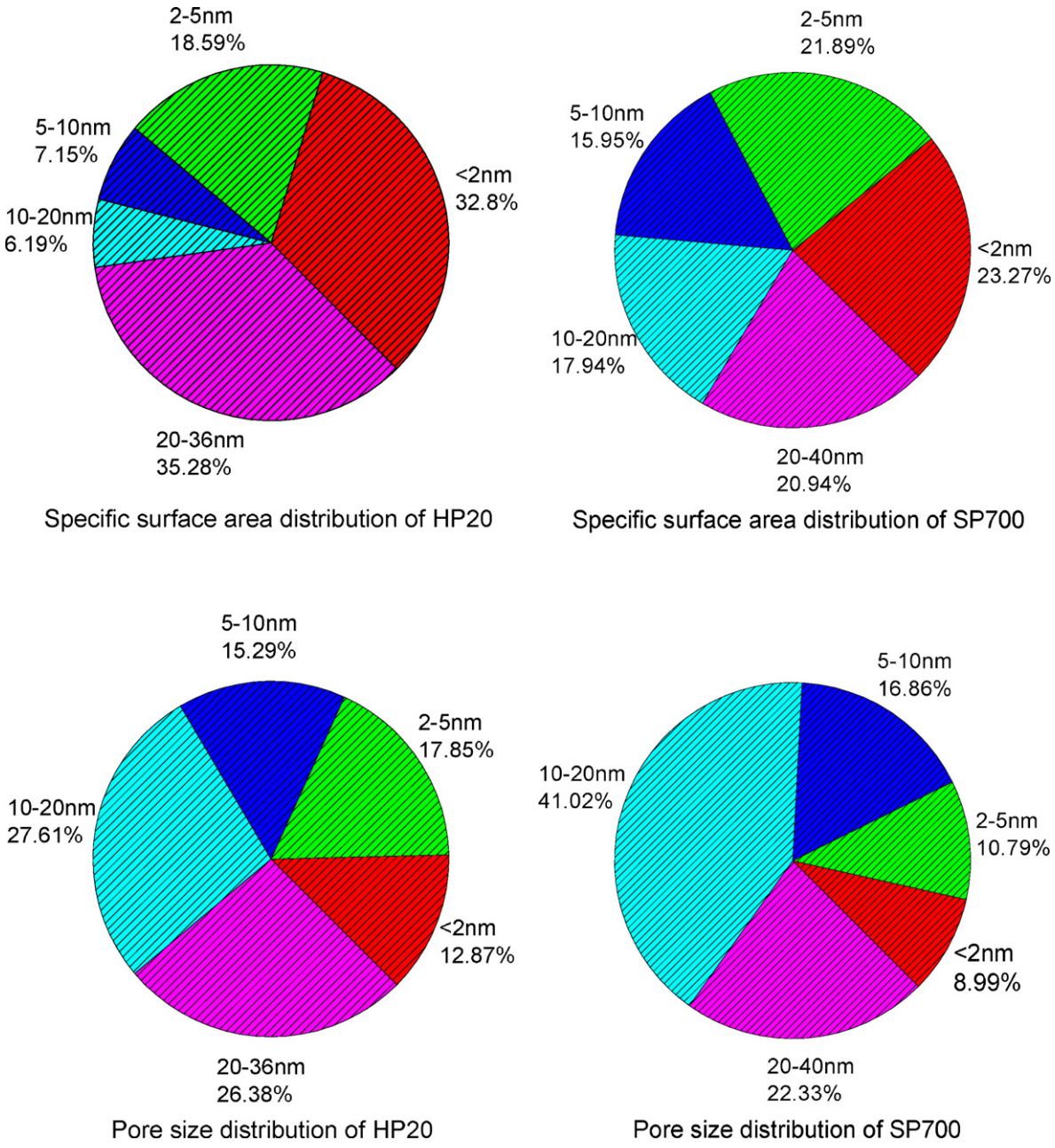

Fig. 4. Specific surface area and pore size distribution calculated by the DFT and Monte-Carlo method.

Pore size distribution was calculated by the DFT and Monte-Carlo methods in order to explain the effect of pore size on the dynamic adsorption of toxins. The percentages of varying mesopore sizes and specific surface areas calculated by the DFT and Monte-Carlo method showed differences between the two resins (Fig. 4). The percentage micropore (<2 nm) volume in HP20 and SP700 was 12.9% and 9.0%, respectively, with the percentage pore size <5 nm being 30.7% and 19.8%, respectively. The micropore (<2 nm) surface area of HP20 and SP700 was 32.8% and 23.3%, respectively. Therefore, this data clearly shows that the percentage of micropore volume and surface area in HP20 is higher than that of SP700.

3.2. Dynamic adsorption of OA and DTX1 toxins by HP20 and SP700

A series of seven different concentrations of OA and DTX1 toxin solutions were used to draw the dynamic adsorption by SP700 in the study. The adsorption isotherm was not linear, and exhibited an "S" type curve in some respects. A separate series of thirteen different concentrations of OA and DTX1 toxin solution were used for HP20 adsorption to explain the isotherm property in more detail for this resin. It was also not linear, and the "S" type curve became more obvious. These adsorption isotherms demonstrated that the adsorption velocity was not uniform.

The Freundlich adsorption isotherms of DSP toxins by resins are shown in Fig. 5. The regression equations with constants, K_f and n, and the correlation coefficient, r, are listed in Table 2. The value of K_f indicated that the adsorption capacity of HP20 was higher than that of SP700 for OA and DTX1, and the adsorption capacity (or rate) of DTX1 was higher than that of OA for the two resins. The exponent n was larger than 1 in all cases, indicating favorable adsorptions.

It was attempted to determine the maximum adsorption capacity of the DSP toxins by the resins using the Langmuir equation [17] to analyze these isotherms. Although the regression coefficients (r)

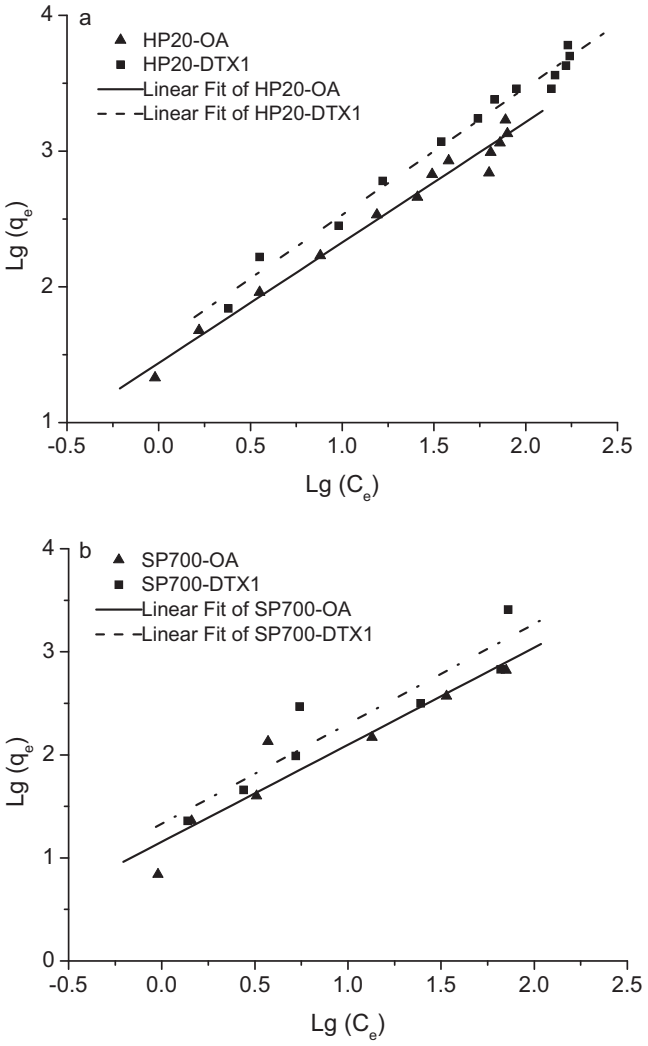

Fig. 5. Linear fit of the Freundlich isotherm equation for adsorption of DSP toxins by resins (a) HP20 and (b) SP700.

Table 2
Regression equation of Lg q_e vs. Lg C_e for Freundlich isotherms at 25 °C.

Adsorbent	Adsorbate	Regression equation	K_f	n	r
HP20	OA	$\mathrm{Lg}\,q_e = 0.8883\mathrm{Lg}\,C_e + 1.4387$	27.460	1.126	0.990
	DTX1	$\mathrm{Lg}\,q_e = 0.9359\mathrm{Lg}\,C_e + 1.5954$	39.391	1.068	0.992
SP700	OA	$\mathrm{Lg}\,q_e = 0.9397\mathrm{Lg}\,C_e + 1.1566$	14.342	1.064	0.947
	DTX1	$\mathrm{Lg}\,q_e = 0.9694\mathrm{Lg}\,C_e + 1.3343$	21.592	1.032	0.936

were all above 0.95, the regression intercept was close to zero or even a negative value. We hypothesize that the initial concentration of OA and DTX1 is 100 μg/mL to calculate the maximal capacity of toxins using the equation $q_m = K_f * C_o^{1/n}$. The maximal capacity of OA and DTX1 by HP20 is 1639 and 2934 μg/g, and OA and DTX1 by SP700 resin is 1088 and 1872 μg/g, respectively.

4. Discussion

Research in the area of physical adsorption on solid materials such as active carbons showed that the adsorption capacity is usually related to the specific surface area and pore size of the adsorbent [18]. In particular it has been noted that the adsorption capacity increases in relation to the micropores in a material with researchers paying attention to the effect of micropore abundance on adsorption or desorption behavior of adsorbent [19–21]. Technologies based on the use of N_2 and carbon dioxide as probes for determining pore volume were developed and employed for such studies [22–25]. It is known that the solute will be quickly adsorbed to the solid adsorbent due to large specific surface area. The adsorption isotherm would be linear if the solid material did not contain fine pores and if all the adsorbate easily found adsorption sites without any rearranging processes. However, this is an ideal situation, with the reality being that most adsorbents have a proportion of fine pores from manufacturing.

Based on the pore size distribution analysis, the macropore resins HP20 and SP700 used in this study were found to contain significant proportions of mesopores and micropores as part of the overall porosity. The ratio of micropore (<2 nm) volume to total mesopore volume in HP20 and SP700 was 12.9% and 9.0%, respectively (Fig. 4). The percentage micropore volume in the HP20 resin is higher than that in the SP700 resin, even though the total pore volume of HP20 is lower (Table 1). The percentage surface area of micropore (<2 nm) in HP20 and SP700 is 32.8% and 23.3% (Fig. 4), respectively, although the total surface area of SP700 is almost twice that of HP20 (Table 1). Therefore, the adsorption behavior of HP20 would be affected seriously by the presence of micropores explaining why the adsorption isotherm for the DSP toxins was not linear. Initially the adsorbate in solution was adsorbed rapidly by the resin because of the large specific surface area, with the adsorption isotherm being almost linear at this stage. The velocity would then decrease as a result of adsorption sites on the resin surface becoming occupied and the available surface area being reduced. However, the adsorbate would be rearranged due to the different affinities for the different sized pores causing an increased adsorption velocity after this rearrangement process, thus resulting in an adsorption isotherm was an "S" curve. In order to explain the non-linear dynamic adsorption, we hypothesize that the molecular shape of adsorbate OA and DTX1 is stick-shaped and they will slowly rearrange in the pores of resins resulting from different affinity. In this study, the adsorption isotherms of OA and DTX1 toxins by HP20 and SP700 demonstrated typical "S" curves thereby verifying this hypothesis. Of course the pigment, salt and other macromolecule compounds in algal cells could have an affect on the adsorption process, as these excess compounds could occupy some adsorption sites on the surface of resins. The adsorption capacity would be reduced a little. However, the adsorption curve would not be changed significantly because there were similar effects in the different concentration treatments in the experiment.

Fux et al. [5] had previously supposed that the pore size of the resin may govern the capacity and equilibration rate of toxin adsorption in a study using a variety of resins. HP20 resin had the smallest surface area and yet showed good performance for toxin adsorption. In this study the Freundlich equation parameters showed that the K_f values of OA and DTX1 adsorbed by HP20 were higher than those for SP700 (Table 2). The results showed that HP20 also has a higher capacity for DSP toxins than SP700. The data from this experiment strongly supports the idea that the non-linear desorption isotherms of OA and DTX1 toxins are due to the lagged release of adsorbate from micropores. Fux et al. [5] found that the elution of OA and DTX1 from HP20, SP825 and XAD4 resins had a similar profile with a Gaussian type peak, while the desorption of OA and DTX1 from SP850 and L493 resins did not follow this trend. This phenomenon determined by the pore size distribution also verified our hypothesis about desorption isotherm. Studies on the adsorption of phenol and three of its derivatives (*p*-cresol, *p*-chlorophenol, *p*-nitrophenol) by adsorbent resins (XAD4, MX4 and NJ8) also showed that adsorption capacity was not related to the specific surface area of adsorbent [9,26].

The K_f constants of DTX1 adsorbed by HP20 and SP700 were both higher than those for OA, showing that the affinity between DTX1 and the resins was stronger than that of OA, illustrating a

competitive adsorption process for lipophilic shellfish toxins. This difference can be explained by differences in chemical structure with DTX1 being more non-polar due to an additional methyl moiety over OA, thus having a stronger affinity for the aromatic adsorbent. This is a new finding about the difference between OA and DTX1 adsorption by resins.

However, there is a phenomenon which still could not be completely explained. The 90% methanol solution with DSP toxins was used as the solvent to explain the adsorption mechanism caused by the pore size distribution of resins. OA and DTX1 toxins were quickly adsorbed by resins in this solution despite the high percent of organic solvent. However, methanol is used to extract and release DSP toxins from resins which have accumulated lipophilic toxins in seawater in other experiments. OA and DTX1 are not soluble in freshwater but do have some solubility in seawater due to the salt matrix. The salt may play a role in the adsorption and desorption dynamic process. Other experiments will be carried out to explain this phenomenon in the future.

5. Conclusions

Two aromatic resins, HP20 and SP700, which had been reported as effective for passive sampling lipophilic shellfish toxins were evaluated in this study. The specific surface area and pore size distribution of these two resins were different. The surface area of SP700 was about two times that of the HP20 resin, however, the percentage micropore (<2 nm) of SP700 was lower than that of the HP20 resin. OA and DTX1 toxins extracted from a *P. lima* culture was used as the test adsorbate. The Freundlich equation was used to analyze the adsorption data and the K_f constant showed that HP20 had higher capacity than the SP700 resin for DSP toxins. We conclude that passive adsorption of DSP toxins is determined more significantly by the pore size distribution than the surface area based on the relationship between adsorption capacity and the pore size characteristics of the two resins. The study also determined that analyte polarity is an important factor in adsorption.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.01.043.

References

[1] L.A. MacKenzie, Curr. Opin. Biotechnol. 21 (2010) 326.
[2] E. Takahashi, Q. Yu, G. Eaglesham, D.W. Connell, J. McBroom, S. Costanzo, G.R. Shaw, Mar. Environ. Res. 64 (2007) 429.
[3] L. MacKenzie, V. Beuzenberg, P. Holland, P. McNabb, A. Selwood, Toxicon 44 (2004) 901.
[4] E. Turrell, L. Stobo, J.P. Lacaze, E. Bresnan, D. Gowland, in: Oceans'07 IEEE Aberdeen Conference Proceedings, 'Marine Challenges Coastline to Deep Sea', Paper No. 070131-028, 2007.
[5] E. Fux, C. Marcaillou, F. Mondeguer, R. Bire, P. Hess, Harmful Algae 7 (2008) 574.
[6] T. Rundberget, E. Gustad, I.A. Samdal, M. Sandvik, C.O. Miles, Toxicon 53 (2009) 543.
[7] G. Pizarro, L. Escalera, S. González-Gil, J.M. Franco, B. Reguera, Mar. Ecol. Prog. Ser. 353 (2008) 89.
[8] E. Fux, R. Bire, P. Hess, Harmful Algae 8 (2009) 523.
[9] A. Li, Q. Zhang, G. Zhang, J. Chen, Z. Fei, F. Liu, Chemosphere 47 (2002) 981.
[10] K. Sing, Colloids Surf. A 187 (2001) 3.
[11] G.F. Cerofolini, L. Meda, Surf. Sci. 416 (1998) 403.
[12] C. Scherdel, G. Reichenauer, M. Wiener, Micropor. Mesopor. Mater. 132 (2010) 572.
[13] E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373.
[14] P.I. Ravikovitch, A.V. Neimark, Langmuir 18 (2002) 1550.
[15] P. Vale, V. Veloso, A. Amorim, Toxicon 54 (2009) 145.
[16] F.L. Slejko, Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application, Marcel Dekker, New York, 1985, p. 13.
[17] P. Lafrance, M. Mazet, D. Villessot, J.-C. Thomes, War. Res. 20 (1986) 123.
[18] M. Jaroniec, K.P. Gadkaree, J. Choma, Colloids Surf. A 118 (1996) 203.
[19] K. Nam, M. Alexander, Environ. Sci. Technol. 32 (1998) 71.
[20] X. Yu, G. Ying, R.S. Kookana, J. Agric. Food Chem. 54 (2006) 8545.
[21] C. Mikutta, F. Lang, M. Kaupenjohann, Geochim. Cosmochim. Acta 70 (2006) 595.
[22] P.I. Ravikovitch, G.L. Haller, A.V. Neimark, Adv. Colloid Interface Sci. 76 (1998) 203.
[23] P.I. Ravikovitch, B.W. Bogan, A.V. Neimark, Environ. Sci. Technol. 39 (2005) 4990.
[24] K.C. Makris, D. Sarkar, R. Datta, P.I. Ravikovitch, A.V. Neimark, Environ. Sci. Technol. 40 (2006) 7732.
[25] A.V. Neimark, Y. Lin, P.I. Ravikovitch, M. Thommes, Carbon 47 (2009) 1617.
[26] A. Li, Q. Zhang, G. Zhang, J. Chen, Z. Fei, C. Long, W. Li, React. Funct. Polym. 49 (2001) 225.