Effect of seawater salinity on pore-size distribution on a poly(styrene)-based resin and its adsorption of diarrhetic shellfish toxins

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Abstract :

In the present study, okadaic acid (OA) and dinophysistoxin-1 (DTX1) were spiked into artificial seawater at low, medium and high estuarine salinities (9‰, 13.5‰ and 27‰). Passive samplers (HP20 resin) used for solid phase adsorption toxin tracking (SPATT) technology were exposed in these seawaters for12-h periods. Adsorption curves well fitted a pseudo-secondary kinetics model. The highest initial sorption rates of both toxins occurred in the seawater of medium salinity, followed by seawater of low and high estuarine salinity. Pore volumes of micropores (< 2 nm) and small mesopores (2 nm < diameter < 10 nm) of HP20 resin decreased after adsorption of toxins in seawater at high and low salinity but not in seawater at medium salinity, which demonstrated that the toxin molecules entered into micropores and mesopores (below 10 m in size) in seawaters of high and low salinity. More toxin or other matrix agglomerates were displayed on the surface of resin deployed in the seawater of medium salinity. Taking into consideration the pore-size distribution and surface images, it appears that intra-particle diffusion governs toxin adsorption in seawater at high salinity while film diffusion mainly controls the adsorption process in seawater at medium salinity. This is the first study to confirm that molecules of OA and DTX1 are able to enter into micropores (< 2 nm) and small mesopores (2 - 10 nm) of HP20 resin in estuarine seawater with high salinity ($\sim$27 %).

Highlights

►HP20 resin bags were deployed in three artificial seawaters at different salinity. ►Dynamic adsorption behaviour of OA and DTX1 by these SPATT bags was explored. ►The highest initial sorption rate of toxins occurred in seawater at medium salinity. ►Resin pores below 10 nm in size governed adsorption in natural seawater. ►Toxins were retained by pores in seawaters at high and low salinity.

Keywords : Diarrhetic shellfish toxins (DST), Solid phase adsorption toxin tracking (SPATT), HP20 resin, Salinity, Pore-size distribution, Pseudo-secondary kinetics equation

1. Introduction

Micro-algal toxins potentially threaten mariculture industry and ecosystem health as toxic algal blooms occur frequently and globally in coastal waters [1, 2]. Based on their chemical structures, these micro-algal toxins are classified into total eight groups including the okadaic acid (OA), azaspiracid (AZA), yessotoxin (YTX), pectenotoxin (PTX), brevetoxin, cyclic imine, saxitoxin (STX), and domoic acid (DA) groups. They can be accumulated and transferred along food webs of marine ecosystems including cultivated shellfish [3-5]. Therefore, poisoning events and victims frequently occurred due to consumption of contaminated seafood [6-8]. For example, diarrhetic shellfish poisoning (DSP) as a familiar poisoning event is related to OA-group toxins, including OA and its derivatives dinophysistoxin-1 (DTX1) and epimer DTX2, accumulated by crabs, mussels, etc [9-12]. Although no victims were recorded by DSP events, a link was hypothesized between exposure to OA-group toxins and tumor enhancement [13-14]. Thus, it is very important to monitor and forecast the pollution of micro-algal toxins in mariculture zones in order to protect seafood safety and consumer health.

A technology referred to as Solid Phase Adsorption Toxin Tracking (SPATT) was developed to monitor the occurrence of toxic algal blooms and shellfish contamination events in seawater using porous synthetic resin [15]. Various micro-algal toxins were tentatively monitored using the SPATT method for adsorption in the laboratory or in the field [16-20]. The SPATT technology has been shown to provide reliable, sensitive, time-integrated sampling of various micro-algal toxins to

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66   monitor the occurrence of toxic algal bloom events [21]. Comparative results for

67   several different adsorbents showed that the resin DIAION®HP20 has greater

68   adsorption quantity and higher desorption rate of lipophilic toxins [15, 16]. The key

69   role played by the pore-size distribution, especially micropores of resin, for OA-group

70   toxins was hypothesized in our previous study [22]. Utility of SPATT bags packaged

71   by HP20 resin was also demonstrated to successfully monitor microcystins in

72   freshwater [23]. Presently, the range of sorbents for passive sampling of micro-algal

73   toxins was extended and assessed in laboratory and field studies [24]. However, the

74   relationship between the quantity obtained by SPATT bags and toxin content

75   accumulated by shellfish has still not been successfully modelled until now, although

76   some efforts into this direction have been made [25]. Also, knowledge on the

77   adsorption mechanism of toxins by resins and the effect of salinity on the adsorption

78   process is still limited. In the present study, the dynamic adsorption of OA and DTX1

79   toxins by HP20 resin in artificial seawater at different salinity was simulated in

80   laboratory. The pore-size distribution and surface image of resins before and after

81   adsorption toxins were explored to discuss the effect of salt matrix on the dynamic

82   adsorption of toxins by HP20 resin.

83   **2. Materials and methods**

84   *2.1. Chemicals*

85   All reagents and solvents used in the study were HPLC grade. Acetonitrile and

86   methanol were purchased from Merck Ltd. (Whitehouse Station, NJ, USA). Formic

87   acid (FA) and ammonium formate (AF) were purchased from Fisher Scientific (Fair

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88   Lawn, NJ, USA). Standard OA and DTX1 were purchased from the Certified

89   Reference Materials Program (CRMP) of the National Research Council of Canada

90   (Halifax, NS, Canada) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan),

91   respectively. Pure water was obtained from a MilliQ water purification system

92   (Millipore Ltd., Bedford, MA, USA) to 18.2 MΩ cm^{-1} quality or better.

93   *2.2. Adsorbent resin*

94   DIAION$^®$HP20 was purchased From the Mitsubishi Chemical Corporation

95   (Tokyo, Japan). It is an aromatic type adsorbent based on a cross-linked polystyrene

96   matrix. The manufacturer stated that particles of HP20 resin are 250-600 µm (more

97   than 90% particles > 250 µm).

98   *2.3. Dynamic adsorption of OA and DTX1 by HP20 resin in artificial seawaters*

99   SPATT bags were made of polyester mesh, 40 mm × 40 mm, and were packed

100   with 3.0 g of dry HP20 resin. They were immersed in methanol for 48 h to activate

101   the HP20 resin. Then they were washed three times using bulk Milli-Q water before

102   storage in pure water for use.

103   According to the manufacturer's statement, 31 g sea salt was dissolved in 1 L of

104   pure water to simulate nature seawater with the content of NaCl, $MgSO_4 \cdot 7H_2O$,

105   $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot H_2O$ and KCl at 65.0 ± 5.0, 15.0 ± 2.0, 12.0 ± 2.0, 4.0 ± 1.0, and

106   1.5 ± 1.4, respectively. In this study, 31 g, 15.5 g and 10.3 g sea salt were dissolved in

107   1 L of pure water to make the artificial seawater at high, medium, and low salinity,

108   respectively. Salinity of the artificial seawater at high salinity was approximately 27‰,

109   which was lower than that of normal natural seawater. Purified extracts of OA and

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110   DTX1 toxins (10 mL) through solid-phase extraction (SPE) were dissolved in

111   different salinity matrix and were added into the corresponding artificial seawater.

112   The initial concentrations of OA and DTX1 toxins in the adsorption system were 2.70

113   and 3.92 ng/mL, respectively. Three SPATT bags of HP20 resin were separately put

114   into the different artificial seawater strengths using a weight to hold them in the

115   middle of the container. The adsorption system was stirred continuously at 145 rpm

116   by a magnetic stirring apparatus at $25 \pm 1^{\circ}C$ in order to make toxins well-distributed.

117   Sampling time point was set at 0, 10, 20, 30, 45, 60, 90, 120, 240, 480 and 720

118   min. Triplicate of 1.5 mL seawater was taken from the adsorption system at every

119   sampling time point, respectively. These samples were purified by the Oasis[®]HLB

120   SPE cartridge (3cc, 60mg). 2 mL of methanol and 2 mL of water was successively

121   used to activate and equilibrate the cartridges, respectively, before loading 1.5 mL of

122   samples. Aliquots (2 mL) of 5% methanol (methanol/water, 5/95, v/v) were used to

123   wash and methanol (2 mL) was used to elute toxins. Finally, the eluate was dried by

124   nitrogen gas and reconstituted in 1.5 mL of methanol. Then, the samples were filtered

125   by 0.22 µm organic membrane and analyzed using LC-MS/MS. Meanwhile, the same

126   SPATT bags were deployed in different artificial seawater without micro-algal toxins

127   in a 1 L flask as blank control experiment.

128   *2.4. LC-MS/MS analysis for OA and DTX1*

129   An Agilent 6430 tandem quadrupole mass spectrometer equipped with an

130   Agilent 1290 HPLC (Palo Alta, CA, USA) using an ESI interface was used to analyze

131   all samples here. Chromatographic separation was achieved on a 50×2.1 mm i.d.,

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132 3 µm, Luna C18 column (Phenomenex) maintained at 35°C. The mobile phase

133 gradient was composed by solvent A (water) and solvent B (95% acetonitrile), each

134 containing 50 mM formic acid and 2 mM ammonium formate. A gradient was run

135 from 25% to 100% B over 7 min, holding for 3 min and back to 25% B to

136 re-equilibration for 2 min for the next run. Flow rate was set at 300 μL/min and the

137 injection volume was 5 μL. MS detection was carried out with positive ionization

138 mode. Multiple reaction monitoring (MRM) acquisition mode was used for qualitative

139 and quantitative analysis for OA (m/z 827.5 -> 809.4 / 791.3 / 723.4) and DTX1 (m/z

140 841.5 -> 823.5 / 805.5 / 737.4).

141 *2.5. Measure for surface area and porosity of resin*

142   HP20 resin was taken out from the SPATT bag after exposure in the adsorption

143 experiments. The resin was freeze-dried using a lyophilizer at -40°C. Pore volume and

144 pore-size distribution were determined by a gas sorption system (Micrometrics,

145 ASAP$^®$ 2020, USA) using nitrogen as adsorbate. About 100 mg of resin was degassed

146 at 105°C until the pressure increase rate was lower than 1.3 Pa/min within a 0.5-min

147 test interval. Helium was used as a backfill gas. In total, 106 adsorption points and 54

148 desorption points were collected from 5.63×10^{-7} to 0.995 P/P0.

149 *2.6. Scanning electron microscopy for HP20 resin*

150   The surface texture of HP20 resin in different artificial seawater spiked with or

151 without OA and DTX1 toxins were characterized by a scanning electron microscope

152 (SEM) (Hitachi, S-4800, Japan). All resin samples were freeze-dried under vacuum

153 and then were fixed on aluminum stubs and coated with gold before observation using

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154   SEM.

155   **3. Results and Discussion**

156   *3.1. Dynamic adsorption behavior of OA and DTX1 toxins by HP20 resin in different*

157   *artificial seawater*

158   Chemical structures of OA and DTX1 toxins are shown in Fig. 1. These

159   polyether toxins can be dissolved in seawater due to salt matrix but not in freshwater

160   because of their hydrophobic property. It is very difficult to arrange duplicate SPATT

161   bags for each sampling time point because of limits of toxins and experimental space.

162   The dynamic adsorption quantity of toxins on SPATT bags was calculated by the

163   concentration discrepancy between two adjacent samplings from seawater. The

164   chromatograms of OA and DTX1 toxins acquired by different transitions using

165   LC-MS/MS are shown in Fig. 2. Retention times of OA and DTX1 toxins were 5.0

166   and 6.0 min, respectively, under these chromatographic conditions. The

167   chromatograms demonstrated that no obvious matrix interferences were found due to

168   potential remaining salt matrix in the seawater samples purified by SPE cartridges.

169   Limits of quantification (LOQ, signal / noise = 10) of the LC-MS/MS method for

170   standard OA and DTX1 were measured as 0.23 and 0.07 ng/mL (injection volume 5

171   μL), respectively, using the S/N values of the lowest transitions of OA (827.5 ->

172   791.3) and DTX1 (841.5 -> 805.5).

173   Dynamic adsorption curves of OA and DTX1 toxins adsorbed by HP20 resin in

174   different artificial seawater are shown in Fig. 3. The curves showed that OA and

175   DTX1 toxins could be adsorbed fast by HP20 resin in three different artificial

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176 seawaters. The adsorption curves were close to linear type in the first 90-min time

177 period. Relatively, the adsorption rates of OA and DTX1 toxins were the slowest in

178 seawater at high salinity over the first 120-min; then they exceeded those in the

179 seawater of low salinity after this period. Totally the adsorption rates of toxins in the

180 seawater of medium salinity were the fastest in whole exposure period and there were

181 no detectable toxins in this seawater after 480-min adsorption. The adsorption curves

182 were simulated by five different dynamic adsorption models including the Elovich

183 equation, double constant equation, parabolic diffusion equation, first-order kinetics

184 equation and pseudo-secondary kinetics equation. The determination coefficient (R^2)

185 demonstrated that the dynamic adsorption curves could be well fitted by the

186 pseudo-secondary kinetics equation (Table 1). Values of R^2 fitted by the

187 pseudo-secondary kinetics equation decreased with the salinity in three different

188 artificial seawaters, which demonstrated that the salinity of seawater slightly reduced

189 the fit quality of the model.

190 Initial sorption rate h (ng/(g·min)) and equilibrium sorption quantity Q_e (ng/g)

191 could be calculated using the pseudo-secondary kinetics equation using $h = 1/a$ and

192 $Q_e = 1/b$[26]. The highest initial sorption rate occurred in the artificial seawater at

193 medium salinity, followed by the treatment with low and high salinity (Table 2). This

194 discrepancy showed that the salt matrix effectively reduced the initial sorption rates of

195 OA and DTX1 toxins by HP20 resin. The initial sorption rate of OA was also less

196 than that of DTX1 in three different artificial seawaters, which had been reported and

197 explained by the extra methyl group of DTX1 in our previous study [22]. Average

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198   linear sorption rates of OA and DTX1 toxins by HP20 resin were also directly

199   calculated using the adsorption quantity divided by time period (Fig. 4). Average

200   adsorption rates of OA and DTX1 in the seawater of low salinity slightly exceeded

201   that in seawater of medium salinity in the early 10-min period. After this period the

202   average adsorption rates in artificial seawater of medium salinity were the fastest,

203   followed by the treatments of low and high salinity. This discrepancy of average

204   linear adsorption rates also demonstrated that the salinity of seawater affected the

205   dynamic adsorption behavior of lipophilic toxins by HP20 resin. Meanwhile, the

206   average adsorption rates of OA in different seawater salinities were lower than those

207   of DTX1 due to the difference of chemical structure. However, the equilibrium

208   sorption quantities of OA and DTX1 toxins calculated by the pseudo-secondary

209   kinetics equation increased with the salinity in three different artificial seawaters

210   although the experimental sorption quantities were similar in all treatments (Table 2).

211   The concentrations of OA (2.70ng/mL) and DTX1 (3.92 ng/mL) used in this

212   study were several hundreds of times higher than the dissolved OA concentration

213   ranging from 4.24 to 9.64 ng/L in coastal seawater of Qingdao City, China [27].

214   Theoretically the experimental quantities of OA and DTX1 were 900 and 1307 ng/g

215   resin, respectively, if the toxins spiked into seawater were completely adsorbed by

216   resin in the whole experimental period. The adsorption percentage of OA and DTX1

217   spiked into three different seawaters was over 96% and 98%, respectively, when the

218   adsorption experiment was finished in the study. These high percentages demonstrated

219   that OA and DTX1 toxins were almost completely adsorbed by SPATT bags in the

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220 experimental period. Therefore, the calculated equilibrium sorption quantities of OA

221 and DTX1 in the artificial seawater increased with salinity because the salinity

222 reduced the fit of the equation for adsorption. This point has been demonstrated by the

223 values of determination coefficient R^2. Totally, the dynamic adsorption process could

224 be well fitted by the pseudo-secondary kinetics equation which suggests that either

225 film diffusion or intra-particle diffusion controls the overall rate of adsorption [26].

226 Usually the dynamic adsorption process simultaneously depends on the large specific

227 surface area and small size pores in the adsorbent. It means that the film diffusion

228 governs adsorption process if the specific surface area plays dominant role; reversely

229 it means the intra-particle diffusion governs the adsorption process. The intra-particle

230 diffusion was hypothesized to govern the capacity and equilibration rate of toxin

231 adsorption by HP20 resin in seawater of micro-algal cultures [16]. The important

232 roles caused by micropores (< 2 nm) of HP20 resin in 90% methanol solution were

233 also suggested in our previous study [22]. The dynamic adsorption behaviors of OA

234 and DTX1 toxins by HP20 resin in different seawaters also comply with this rule in

235 this study.

236 *3.2. Change of pore-size distribution of HP20 resin after adsorption for toxins*

237　　In order to explore the mechanism by which salt affects the dynamic adsorption

238 of toxins by resin, the pore-size distribution of HP20 resin deployed in seawater with

239 or without OA/DTX1 toxins was characterized. Results showed that no obvious

240 change of the pore volumes of size between 10-20 nm was found in HP20 resin

241 deployed in three different seawaters with or without toxins (Fig. 5). However, the

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242 pore volumes of micropores (diameter < 2 nm) and small mesopores (2 nm < diameter

243 < 10 nm) decreased after toxins were adsorbed onto HP20 resin in the artificial

244 seawaters at high salinity and low salinity, which demonstrated that toxin molecules

245 entered into these small size pores. Inconsistently, the pore volumes of micropores did

246 not change whether the resin adsorbed toxins or not, and the pore volumes of small

247 mesopores (2 - 10 nm) also did not change obviously and consistently in the artificial

248 seawater at medium salinity. This phenomenon testified that the toxin molecules did

249 not enter into the micropores and small mesopores (2 - 10 nm) in the seawater of

250 medium salinity. Interestingly, the pore volumes of micropores or mesopores (2 - 10

251 nm) of HP20 resin deployed in the artificial seawater of high salinity without toxins

252 were higher than those in the artificial seawater of low salinity without toxins, which

253 showed that solely the salt matrix of seawater also changed the pore size distribution

254 of resin. Possibly, salt matrix would reconstruct these pores in some big pores of

255 HP20 resin. The largest BET surface area of HP20 resin before adsorption toxins

256 occurred in the seawater at high salinity, followed by the treatments of low and

257 medium salinity (Table 3), which demonstrated that the salt matrix changed the

258 surface area of resin. Consistently, the surface areas of resins decreased after they

259 adsorbed toxins in three different seawaters. However, the average pore volume of

260 resin deployed in the seawater at medium salinity increased after it adsorbed toxins,

261 which also demonstrated that toxin molecules did not enter into these pores of resin.

262 Therefore, the HP20 resin deployed in the seawater at medium salinity displayed the

263 highest initial sorption rate because only film diffusion governed the adsorption

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264   process.

265   In order to testify the discrepancy of adsorption behavior in different seawaters,

266   the surface images of resin deployed in artificial seawaters were characterized by

267   SEM. Results showed that the surface of resins deployed in three different seawaters

268   without toxins were very clean (Fig. 6), which demonstrated that the salt matrix did

269   not change resin surface. Some agglomerates emerged on the surface of resins

270   exposed to algal extracts in seawaters of medium and low salinity, but not on the

271   surface of resin adsorbed toxins in the seawater of high salinity (Fig. 6). More

272   agglomerates occurred on the surface of resin deployed in the seawater at medium

273   salinity comparatively to the seawater at low salinity. To our knowledge we could not

274   explain the occurrence of agglomerates on the surface of resin deployed in the low

275   salinity seawater. However, the SEM results testified that the toxins were mainly

276   adsorbed onto the surface of resin deployed in the seawater at medium salinity

277   (~13.5‰), which could explain the highest initial sorption rate due to the film

278   diffusion related with surface adsorption.

279   Based on the findings of this study, it could be safely concluded that the

280   intra-particle diffusion governs the adsorption process of HP20 resin for toxins in

281   estuarine seawater with high salinity while film diffusion controls the adsorption

282   process in seawater at medium salinity (~13.5‰). Also, the adsorption process of

283   HP20 resin for toxins is dependent on both film diffusion and intra-particle diffusion

284   in seawater of low salinity (~9‰). The different adsorption mechanisms for HP20

285   resin in seawaters with different salinity suggest that the adsorption behavior of toxins

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286   by SPATT deployments in estuaries with low salinity should be different to those in

287   natural seawater.

288   **4. Conclusions**

289   In this study, purified extract containing OA and DTX1 toxins from

290   *Prorocentrum lima* was spiked into three artificial seawaters at different salinity (27‰,

291   13.5‰ and 9‰) and SPATT samplers of HP20 resin were deployed in these seawaters

292   for 720-min exposure. Adsorption curves of toxins in seawater of three different

293   salinities well fitted the pseudo-secondary kinetics equation. However, the pore-size

294   distribution and specific surface area of HP20 resins deployed in seawater with or

295   without toxins were affected and not linearly related to the salinity of seawater.

296   According to the findings of this study, it is confirmed that the molecules of OA and

297   DTX1 are able to enter into the micropores and small mesopores (2 - 10 nm) of HP20

298   resin in estuarine seawater at high salinity (~27‰). The intra-particle diffusion

299   governs the adsorption process of HP20 resin for toxins in seawater with high salinity

300   (~27‰), while film diffusion controls the adsorption process in seawater at medium

301   salinity (~13.5‰). Further studies should clarify whether the effect of salinity on

302   adsorption kinetics is sufficiently significant at the naturally low concentrations of

303   toxins in seawater to play a role during daily or weekly monitoring.

304   **Supplementary materials**

305   Extraction and purification methods for OA and DTX1 toxins could be found in

306   the supplementary file.

307   **Acknowledgement**

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311   **Conflict of interest statement**

312   All authors declare that there are no conflicts of interest.

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313   **References**

314   [1] L. Botes, A.J. Smit, P.A. Cook, The potential threat of algal blooms to the abalone

315   (*Haliotis midae*) mariculture industry situated around the South African coast,

316   Harmful Algae 2 (2003) 247-259.

317   [2] T.G. Park, W.A. Lim, Y.T. Park, C.K. Lee, H.J. Jeong, Economic impact,

318   management and mitigation of red tides in Korea, Harmful Algae 30S1 (2013)

319   S131-S143.

320   [3] L.F. Leandro, G.J. Teegarden, P.B. Roth, Z. Wang, G.J. Doucette, The copepod

321   *Calanus finmarchicus*: A potential vector for trophic transfer of the marine algal

322   biotoxin, domoic acid, J. Exp. Mar. Biol. Ecol. 382 (2010) 88-95.

323   [4] R.W.M. Kwong, W.-X. Wang, P.K.S. Lam, P.K.N. Yu, The uptake, distribution and

324   elimination of paralytic shellfish toxins in mussels and fish exposed to toxic

325   dinoflagellates, Aquat. Toxicol. 80 (2006) 82-91.

326   [5] V.M. Lopes, M. Baptista, T. Repolho, R. Rosa, P.R. Costa, Uptake, transfer and

327   elimination kinetics of paralytic shellfish toxins in common octopus (*Octopus*

328   *vulgaris*), Aquat. Toxicol. 146 (2014) 205-211.

329   [6] A.P. Sierra-Beltrán, A. Cruz, E. Núñez, L.M. Del Villar, J. Cerecero, J.L. Ochoa,

330   An overview of the marine food poisoning in Mexico, Toxicon 36 (1998)

331   1493-1502.

332   [7] A. Furey, S. O'Doherty, K. O'Callaghan, M. Lehane, K.J. James, Azaspiracid

333   poisoning (AZP) toxins in shellfish: Toxicological and health considerations,

334   Toxicon 56 (2010) 173-190.

17

335   [8] L.E. Fleming, B. Kirkpatrick, L.C. Backer, C.J. Walsh, K. Nierenberg, J. Clark, A.

336   Reich, J. Hollenbeck, J. Benson, Y.S. Cheng, J. Naar, R. Pierce, A.J. Bourdelais,

337   W.M. Abraham, G. Kirkpatrick, J. Zaias, A. Wanner, E. Mendes, S. Shalat, P.

338   Hoagland, W. Stephan, J. Bean, S. Watkins, T. Clarke, M. Byrne, D.G. Baden,

339   Review of Florida red tide and human health effects, Harmful Algae 10 (2011)

340   224-233.

341   [9] T. Torgersen, J. Aasen, T. Aune, Diarrhetic shellfish poisoning by okadaic acid

342   esters from Brown crabs (*Cancer pagurus*) in Norway, Toxicon 46 (2005)

343   572-578.

344   [10] E. Prassopoulou, P. Katikou, D. Georgantelis, A. Kyritsakis, Detection of okadaic

345   acid and related esters in mussels during diarrhetic shellfish poisoning (DSP)

346   episodes in Greece using the mouse bioassay, the PP2A inhibition assay and

347   HPLC with fluorimetric detection, Toxicon 53 (2009) 214-227.

348   [11] A. Li, J. Ma, J. Cao, P. McCarron, Toxins in mussels (*Mytilus galloprovincialis*)

349   associated with diarrhetic shellfish poisoning episodes in China, Toxicon 60

350   (2012) 420-425.

351   [12] A. Li, G. Sun, J. Qiu, L. Fan, Lipophilic shellfish toxins in *Dinophysis caudata*

352   picked cells and in shellfish from the East China Sea, Environ. Sci. Pollut. Res.

353   xxx (2014) xxx. Doi: 10.1007/s11356-014-3595-z

354   [13] S. Cordier, C. Monfort, L. Miossec, S. Richardson, C. Belin, Ecological analysis

355   of digestive cancer mortality related to contamination by diarrhetic shellfish

356   poisoning toxins along the coasts of France, Environ. Res. 84 (2000) 145-150.

18

357 [14] E. Manerio, V.L. Rodas, E. Costas, J.M. Hernandez, Shellfish consumption: A

358   major risk factor for colorectal cancer, Med. Hypotheses 70 (2008) 409-412.

359 [15] L. MacKenzie, V. Beuzenberg, P. Holland, P. McNabb, A. Selwood, Solid phase

360   adsorption toxin tracking (SPATT): a new monitoring tool that simulates the

361   biotoxin contamination of filter feeding bivalves, Toxicon 44 (2004) 901-918.

362 [16] E. Fux, C. Marcaillou, F. Mondeguer, R. Bire, P. Hess, Field and mesocosm trials

363   on passive sampling for the study of adsorption and desorption behaviour of

364   lipophilic toxins with a focus on OA and DTX1, Harmful Algae 7 (2008)

365   574-583.

366 [17] E. Fux, R. Bire, P. Hess, Comparative accumulation and composition of

367   lipophilic marine biotoxins in passive samplers and in mussels (*M. edulis*) on the

368   West Coast of Ireland, Harmful Algae 8 (2009) 523-537.

369 [18] T. Rundberget, E. Gustad, I.A. Samdal, M. Sandvik, C.O. Miles, A convenient

370   and cost-effective method for monitoring marine algal toxins with passive

371   samplers, Toxicon 53 (2009) 543-550.

372 [19] P. Rodríguez, A. Alfonso, E. Turrell, J.-P.Lacaze, L.M. Botana, Study of solid

373   phase adsorption of paralytic shellfish poisoning toxins (PSP) onto different

374   resins, Harmful Algae 10 (2011) 447-455.

375 [20] A. Caillaud, P. de la Iglesia, E. Barber, H. Eixarch, N. Mohammad-Noor, T.

376   Yasumoto, J. Diogène, Monitoring of dissolved ciguatoxin and maitotoxin using

377   solid-phase adsorption toxin tracking devices: Application to *Gambierdiscus*

378   *pacificus*in culture, Harmful Algae 10 (2011) 433-446.

19

379   [21] L.A. MacKenzie, *In situ* passive solid-phase adsorption of micro-algal biotoxins

380   as a monitoring tool, Curr. Opin. Biotech. 21 (2010) 326-331.

381   [22] A. Li, F. Ma, X. Song, R. Yu, Dynamic adsorption of diarrhetic shellfish

382   poisoning (DSP) toxins in passive sampling relates to pore size distribution of

383   aromatic adsorbent, J. Chromatogr. A 1218 (2011) 1437-1442.

384   [23] H. Zhao, J. Qiu, H. Fan, A. Li, Mechanism and application of solid phase

385   adsorption toxin tracking for monitoring microcystins, J. Chromatogr. A 1300

386   (2013) 159-164.

387   [24] Z. Zendong, C. Herrenknecht, E. Abadie, C. Brissard, C. Tixier, F. Mondeguer, V.

388   Séchet, Z. Amzil, P. Hess, Extended evaluation of polymeric and lipophilic

389   sorbents for passive sampling of marine toxins, Toxicon xxx (2014) xxx. Doi:

390   10.1016/j.toxicon.2014.03.010

391   [25] G. Pizarro, A. Moroño, B. Paz, J.M. Franco, Y. Pazos, B. Reguera, Evaluation of

392   passive samplers as a monitoring tool for early warning of *Dinophysis* toxins in

393   shellfish, Mar. Drugs 11 (2013) 3823-3845.

394   [26] Q. Gao, C. Pan, F. Liu, F. Lu, D. Wang, J. Zhang, Y. Zhu, Adsorption

395   characteristics of malic acid from aqueous solutions by weakly basic

396   ion-exchange chromatography, J. Chromatogr. A 1251 (2012) 148-153.

397   [27] X. Li, Z. Li, J. Chen, Q. Shi, R. Zhang, S. Wang, X. Wang, Detection, occurrence

398   and monthly variations of typical lipophilic marine toxins associated with

399   diarrhetic shellfish poisoning in the coastal seawater of Qingdao City, China,

400   Chemosphere 111 (2014) 560-567.

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403 **Table1** Dynamic adsorption equations for OA and DTX1 toxins by HP20 resin simulated using different mathematical models.

Salinity of seawater	Toxins	Elovich equation $q=a+b \times Lnt$	Double constant equation $Lnq=b \times Lnt+Lna$	Parabolic diffusion equation $q=a+b \times \sqrt{t}$	First order kinetic equation $Lnq=a+b \times t$	Pseudo-secondary kinetics equation $t/q=a+b \times t$
High salinity (27‰)	OA	y=134.8 x-306.1 R^2=0.9199	y=0.558x+3.43 R^2=0.9215	y=38.62 x+31.46 R^2=0.8993	y=0.0158x+4.16 R^2=0.9588	y=0.00091x+0.1153 R^2=0.9776
	DTX1	y=333.5x-790.1 R^2=0.9502	y=0.684 x+3.28 R^2=0.9517	y=56.74 x+40.54 R^2=0.8923	y=0.0043x+5.61 R^2=0.5324	y=0.00062x+0.0816 R^2=0.9832
Medium salinity (13.5‰)	OA	y=116.2 x-166.5 R^2=0.9474	y=0.449x+4.29 R^2=0.9305	y=44.51 x+106.73 R^2=0.8816	y=0.0027x+5.84 R^2=0.5225	y=0.00098x+0.0534 R^2=0.9957
	DTX1	y=302.2 x-488.3 R^2=0.9597	y=0.438 x+4.70 R^2=0.9371	y=63.45 x+153.12 R^2=0.8858	y=0.0027x+6.20 R^2=0.5452	y=0.00069x+0.0374 R^2=0.9951
Low salinity (9‰)	OA	y=99.1 x-125.0 R^2=0.9573	y=0.329 x+4.20 R^2=0.9476	y=31.97 x+139.03 R^2=0.8995	y=0.0083x+4.97 R^2=0.9440	y=0.0011x+0.0668 R^2=0.9964
	DTX1	y=263.1x-406.5 R^2=0.9761	y=0.383x+4.81 R^2=0.9456	y=48.06 x+195.47 R^2=0.8963	y=0.0027x+6.10 R^2=0.6148	y=0.00072x+0.0454 R^2=0.9979

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405 **Table2** Comparison of experimental values and theoretical values of adsorption of OA

406 and DTX1 toxins by HP20 resin simulated by the Pseudo-secondary kinetics equation.

Salinity of seawater	Toxins	Pseudo-secondary kinetics equation	h	Q_e,cal	Q_e,exp
High salinity (27‰)	OA	y=0.00091x+0.1153	8.67	1100	901
	DTX1	y=0.00062x+0.0816	12.25	1610	1310
Medium salinity (13.5‰)	OA	y=0.00098x+0.0534	18.73	1020	900
	DTX1	y=0.00069x+0.0374	26.74	1450	1290
Low salinity (9‰)	OA	y=0.0011x+0.0668	14.97	909	868
	DTX1	y=0.00072x+0.0454	22.03	1390	1280

407 Note: h(=1/a) means the initial sorption rate (ng/(g·min)); Q_e,cal (=1/b) means the

408 theoretical values were calculated according to the Pseudo-secondary kinetics

409 equations; Q_e,exp means the actual values were tested in the adsorption experiments.

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411 **Table3** Specific surface areas and average pore volumes of HP20 resins before and

412 after adsorption for OA and DTX1 toxins in seawaters of different salinity.

Salinity of seawaters	Characteristic index	Before adsorption for toxins	After adsorption for toxins	Changing ratio (%)
High salinity (27‰)	Specific surface area (m^2/g)	654.7	539.3	-17.6
	Average pore volume (cm^3/g)	1.30	1.18	-9.2
Medium salinity (13.5‰)	Specific surface area (m^2/g)	558.3	546.0	-2.2
	Average pore volume (cm^3/g)	1.01	1.18	+16.8
Low salinity (9‰)	Specific surface area (m^2/g)	604.5	552.3	-8.6
	Average pore volume (cm^3/g)	1.11	0.97	-12.6

413 Note: specific surface area was calculated by the BET model; average pore volume
414 (pore size 1.7 - 300 nm) was calculated by the BJH model.

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Legends of figures

415

416   Fig.1. Chemical structures of OA and its analogue DTX1.

417   Fig.2. LC-MS/MS chromatograms of OA and DTX1 in one sample collected from the

418   artificial seawater at low salinity after 30-min exposure in adsorption experiment.

419   Three different transitions of parent ions m/z 827.5 and 841.5 were used to

420   qualify OA and DTX1, respectively. The concentrations of OA and DTX1 in this

421   sample were tested as 1.85 and 2.77 ng/mL, respectively.

422   Fig.3. Dynamic adsorption curves of OA (a) and DTX1 (b) toxins by HP20 resin in

423   seawaters with different salinity.

424   Fig.4. Average linear adsorption rates of OA (a) and DTX1 (b) toxins by HP20 resin

425   in seawaters with different salinity calculated in different time period.

426   Fig.5. Accumulative pore volumes for different interval pore size of HP20 resin

427   before and after adsorption for OA and DTX1 toxins in seawaters with different

428   salinity.

429   Fig.6. Scanning electron microscopes (SEM) of HP20 resin before and after

430   adsorption under different salinity conditions. SEM of high salinity blank (a) and

431   high salinity (b), medium salinity blank (c) and medium salinity (d), low salinity

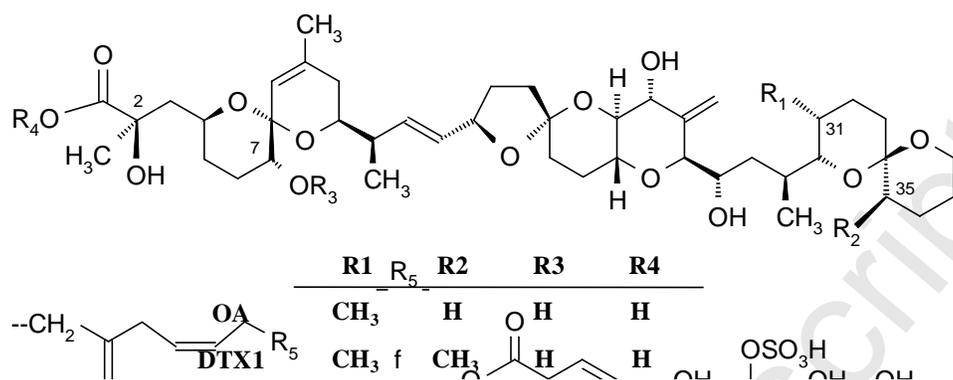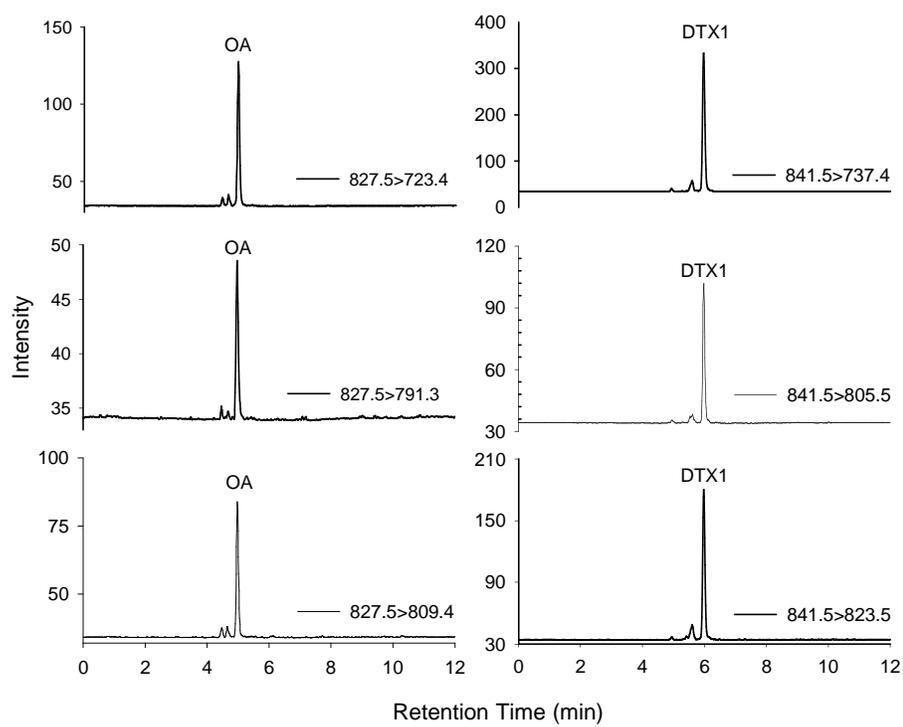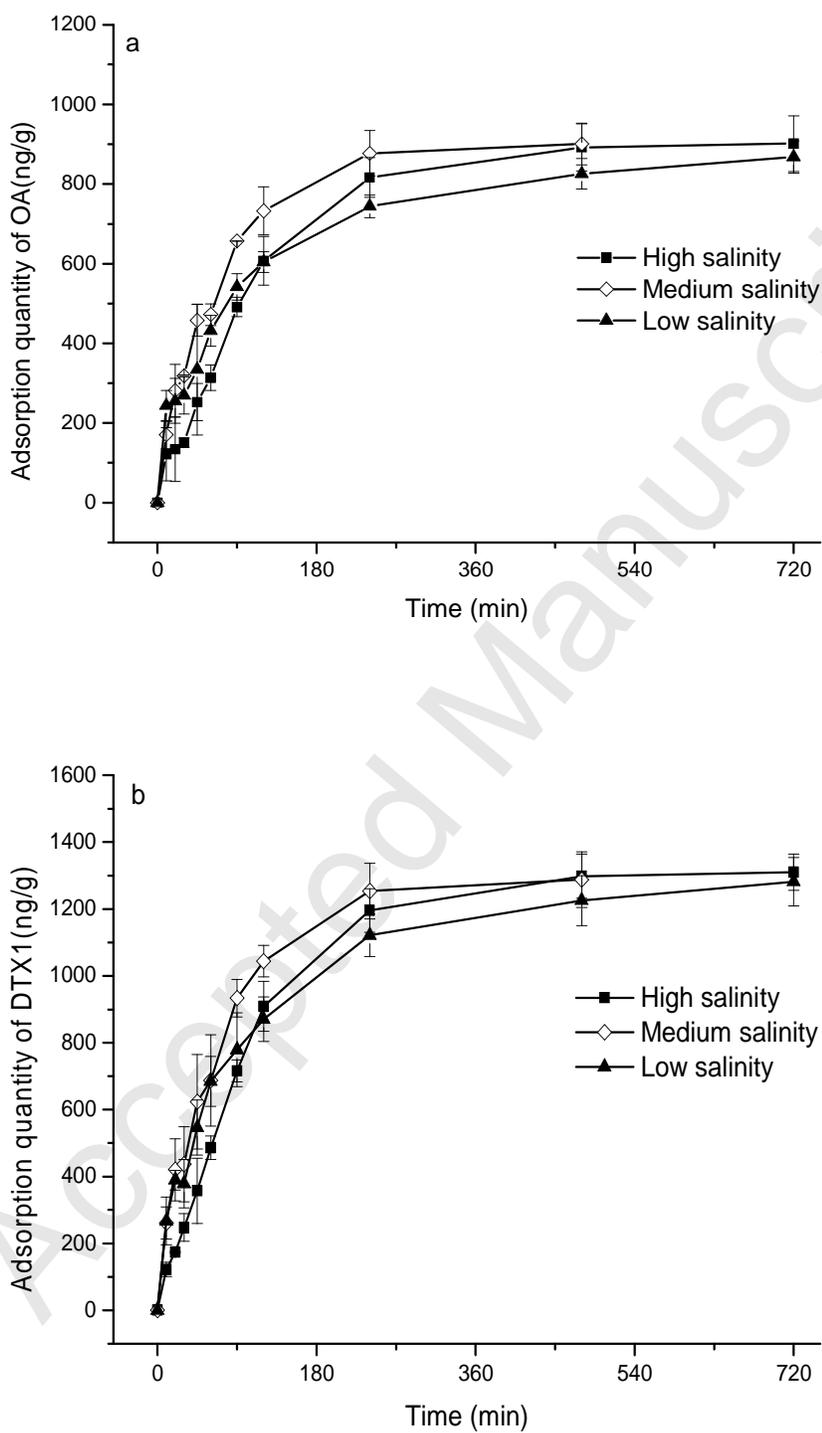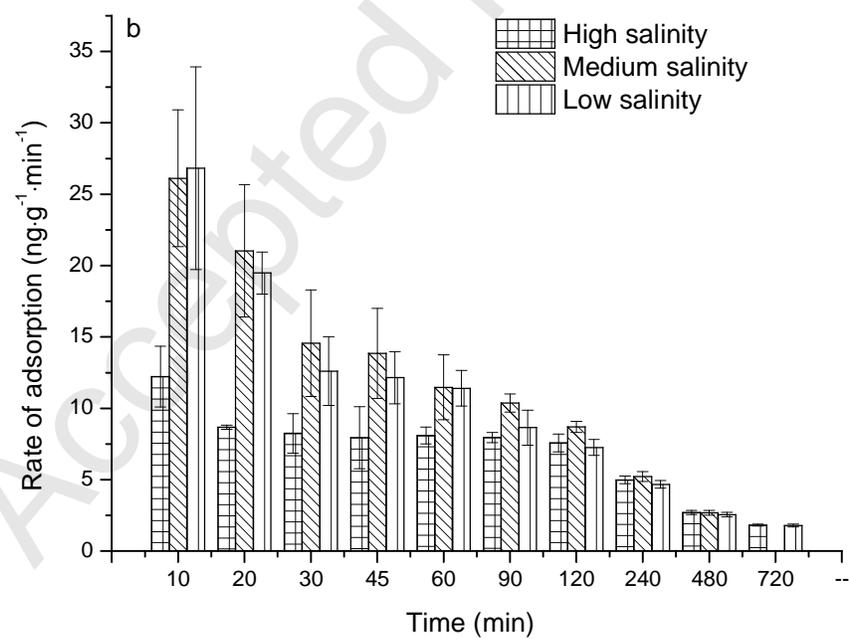432   blank (e) and low salinity (f) are compared separately.

25

	R1		R2	R3	R4
	R5				
	CH₃		H	H	H
DTX1	CH₃	f	CH₃	H	H

Fig. 1

Fig.2

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Fig. 3

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Fig. 4

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Fig. 5

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Fig. 6

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