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Application of activated carbon to accelerate detoxification of paralytic shellfish toxins from mussels *Mytilus galloprovincialis* and scallops *Chlamys farreri*

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ABSTRACT

Contamination of economic bivalves with paralytic shellfish toxins (PST) occurs frequently in many parts of the world, which potentially threatens consumer health and the marine aquaculture economy. It is the objective of this study to develop a suitable technology for accelerating detoxification of PST from shellfish using activated carbon (AC). The adsorption efficiency of PST by eight different AC materials and by different particle sizes of wood-based AC (WAC) were tested and compared. Then WAC particles (37–48 μm) were fed to mussels *Mytilus galloprovincialis* and scallops *Chlamys farreri* previously contaminated with PST through feeding with dinoflagellate *Alexandrium tamarense* ATHK. Results showed that the maximum adsorption ratio (65%) of PST was obtained by WAC. No significant differences in adsorption ratios were found between different particle sizes of WAC. The toxicity of mussels decreased by 41% and 68% after detoxification with WAC for 1 d and 3 d, respectively. Meanwhile, the detoxification ratio of mussels was approximately 3 times higher than that of scallops. This study suggests that the WAC could be used to accelerate the detoxification of PST by shellfish.

1. Introduction

Human poisoning events occur frequently worldwide due to consumption of paralytic shellfish toxins (PST) (Nicolas et al., 2017). A total of 57 analogues of PST have been identified until now (Wiese et al., 2010). These are produced by marine dinoflagellates of *Alexandrium*, *Gymnodinium* and *Pyrodinium* genera and some strains of freshwater cyanobacteria. Chemical structures of the most common congeners of PST are shown in Table 1. The three main categories are grouped as follows: carbamate toxins (STX, NEO, GTX1-4), decarbamoyl toxins (dcSTX, dcNEO, dcGTX1-4), and *N*-sulfocarbamoyl toxins (GTX5-6, C1-4). The toxicity of PST ranks from carbamate toxins, decarbamoyl toxins to *N*-sulfocarbamoyl toxins (Oshima, 1995; EFSA, 2009). The action potentials in excitable cells cannot be generated normally because Na^+ influx is blocked by PST molecules binding to the voltage-gated sodium channels (Cestèle and Catterall, 2000). Currently, the toxicities of only the common analogues of PST have been determined. More and more new metabolites of PST have been found in shellfish and standard reference materials are not available for testing toxicity (Dell'Aversano et al., 2008; Li et al., 2012). Therefore, it is difficult to accurately predict the toxicity of PST in seafood, which further increases risk to human health.

The contamination of shellfish with PST and especially the occurrence of toxic events can lead to severe economic losses of the marine aquaculture industry. PST can be accumulated by molluscan bivalves and transferred to higher trophic level organisms along food chains. Mass mortality of multispecies marine fishes, birds and mammals were linked to a PST-producing dinoflagellate bloom in the St. Lawrence Estuary (Starr et al., 2017). PST is responsible for seafood-borne illness with symptoms including nausea, vomiting, tingling of the mouth, fever, tachycardia, muscular paralysis, respiratory failure and death. A dose of as low as one mg of STX can cause human death due to shellfish consumption (Wiese et al., 2010). A regulatory limit 800 μg STX diHCl eq. kg^{-1} shellfish meat has been adopted in many countries in order to ensure that the commercially available seafood is safe for consumption. A new regulatory limit of 75 μg STX eq. kg^{-1} shellfish meat has recently been recommended by European Food Safety Authority, based on the acute reference dose of 0.5 μg STX eq. kg^{-1} body weight (EFSA,

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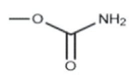
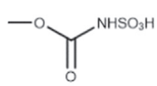
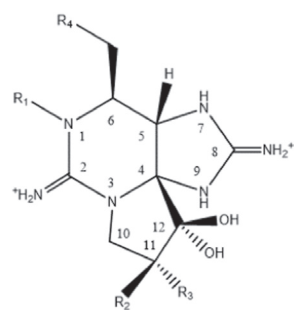
Table 1
Chemical structures and relative toxicity of some common analogues of PST (Botana et al., 2017).

Toxin	R1	R2	R3	R4	Relative toxicity*
Carbamate toxins					
STX	H	H	H		1
NEO	OH	H	H		2
GTX1	OH	H	OSO_3^-		1
GTX2	H	H	OSO_3^-		0.4
GTX3	H	OSO_3^-	H		0.6
GTX4	OH	OSO_3^-	H		0.7
N-sulfocarbamoyl toxins					
GTX5	H	H	H		0.1
GTX6	OH	H	H		0.05
C1	H	H	OSO_3^-		0.01
C2	H	OSO_3^-	H		0.1
C3	OH	H	OSO_3^-		0.01
C4	OH	OSO_3^-	H		0.1
M1	H	OH	H		—
M3	H	OH	OH		—
M7	OH	OH	H		—
Decarbamoyl toxins					
dcSTX	H	H	H		0.5
dcNEO	OH	H	H		0.2
dcGTX1	OH	H	OSO_3^-	—OH	—
dcGTX2	H	H	OSO_3^-		0.2
dcGTX3	H	OSO_3^-	H		0.4
dcGTX4	OH	OSO_3^-	H		—



*Relative toxicity from Botana et al. (2017).

2009).

In order to protect human health, some researchers have tried to develop technologies that could eliminate PST including treatment by ozone, hydrogen peroxide (Orr et al., 2004), chlorine (Zamyadi et al., 2012), bacteria (Donovan et al., 2009; Vasama et al., 2014), clay (Burns et al., 2009; Lu et al., 2015), chitin and oyster shell powder (Melegari and Matias, 2012), and activated carbon (AC) (Orr et al., 2004). Ozone alone, or combination with hydrogen peroxide, failed to destroy STX and GTX2/3 and only partially destroyed dcSTX, and C-toxins and GTX-5 (Orr et al., 2004). PST was very resistant to oxidation by ozone and it was still necessary to treat with further methods (Rositano et al., 2001). Removal of PST with chlorination increased the risk of disinfection by-product formation (Zamyadi et al., 2012). The use of ozone, hydrogen peroxide and chlorine is not suitable for detoxification of shellfish as this results in shellfish death. Xie et al. (2013) reported chitosan had a remarkable effect on PST removal in the oysters (*Ostrea rivularis* Gould) during depuration.

Adsorption by AC has been proven to be an effective and inexpensive removal process for trace contaminants from water without generating transformations (Newcombe and Nicholson, 2002; Orr et al., 2004; Silva, 2005; Ho et al., 2009; Shi et al., 2012). Orr et al. (2004) reported that granular coal-based AC could remove all of STX, dcSTX and GTXs, but only partially removed C-toxins. Silva (2005) demonstrated that AC powder extensive removal of NEO and STX. Adsorption equilibrium model, kinetics and diffusion behavior of STX and dcSTX onto different AC have also been studied (Buarque et al., 2015; Buaque and Capelo-Neto, 2015; Capelo-Neto and Buarque, 2016). To date, there have been no studies on the application of AC to accelerate the detoxification of PST from shellfish. Scallops and mussels are economically important bivalves that have been found to be contaminated by PST in many coastal countries (James et al., 2010; Ujević et al., 2012; Li et al., 2012; Turner et al., 2014; Michalski and Osek, 2016; Liu