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Modelling and understanding the competitive adsorption of microcystins and tannic acid

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ARTICLE INFO

Article history:
Received 18 December 2012
Received in revised form
14 June 2013
Accepted 26 June 2013
Available online 5 July 2013

Keywords:
Microcystins
NOM
PAC
Competitive adsorption models
HSDM

ABSTRACT

A predictive model integrating adsorption kinetics and competitive isotherm models (Homogeneous Surface Diffusion Model, Freundlich-type and Fritz & Schlünder isotherms) was developed to describe and understand the competing mechanism(s) and the ionic strength (IS) role on microcystins (MC) and tannic acid (TA) competitive adsorption. The developed model showed good agreement with the experimental data obtained from batch adsorption tests and isotherms conducted with MC extracts and TA model solutions (single-solute and multicomponent, IS presence and absence) using a mesoporous powdered activated carbon (PAC). Results confirm that similar size molecules such as MC and TA are strong competitors and tannin-rich waters may severely affect MC residuals in the treated water. Unlike usually considered, both direct site and pore blockage mechanisms seem relevant. Competition effects appear to be more dependent on the competitor/contaminant molar ratio than on the initial concentrations. The IS affects the extent and the mechanisms of MC-TA competitive adsorption, reducing PAC dose for safe control of MC residuals. The developed model, including a D_s analysis, is an important tool to understand the competitive adsorption of similar size adsorbates.

1. Introduction

Biospheric environmental perturbations, including nutrient enrichment and climate changes, strongly affect cyanobacterial growth and bloom potentials in freshwater and marine ecosystems and may act synergistically to promote cyanobacterial dominance and persistence (Paerl and Paul, 2012), therefore increasing the human and animal health risks associated to the cyanotoxins. The hepatotoxic and liver-tumour promoting microcystins (MCs) are the most commonly found cyanotoxins in surface water reservoirs. The World Health Organisation (WHO) issued a drinking water guideline-value of 1.0 μg/L for MC-LR, one of the most toxic and frequently occurring microcystins.

Extracellular microcystins are extremely stable and resistant to conventional water treatment. The hybrid process of powdered activated carbon (PAC) adsorption and ultrafiltration is a promising option for controlling both the cell-bound and the extracellular cyanotoxins, but its success relies on an efficient PAC adsorption of the latter (Lee and Walker, 2006; Campinas and Rosa, 2010).

The NOM negative effect on MC adsorption onto activated carbon is widely reported (Pendleton et al., 2001; Lee and Walker, 2006; Wang et al., 2007; Cook and Newcombe, 2008; Ho et al., 2011), yet the competition mechanisms were not fully addressed or was concluded as direct competition based on previous assumptions. Direct competition for the adsorption sites is nowadays considered the dominant competition

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0043-1354/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2013.06.048

mechanism between NOM and low molecular weight (MW) compounds (Kilduff et al., 1998; Matsui et al., 2003) and pore blockage the major contributor under high NOM and contaminant loading conditions (Kilduff et al., 1998; Li et al., 2003). According to Matsui et al. (2011), NOM molecules, particularly high MW NOM, do not completely penetrate the PAC particles and instead preferentially adsorb near the outer surface; hence only a NOM fraction penetrates the PAC internal structure and may cause pore blockage or direct site competition. It is often assumed that pore blockage mainly occurs during advanced phases of granular activated carbon filters' preloading (Kilduff et al., 1998; Wang et al., 2007), but the limit beyond which the loading is enough to make the pore blockage dominant is still unknown. Moreover, the micropollutants usually studied are <300 Da (e.g. trichloroethylene, 2-methylsioborneol (MIB), geosmin and atrazine (Li et al., 2003; Wigton and Kilduff, 2004; Zoschke et al., 2011), and as so preferentially adsorb on micropores, where most NOM does not access, rendering the competing mass only a small fraction of the bulk NOM. For instance, Zoschke et al. (2011) calculated the DOC of the competing NOM fraction for geosmin and MIB to be, respectively, only 2 μgC/L and 13 μgC/L out of the 1.8 mg C/L water DOC.

However, microcontaminants around 1 kDa, such as microcystins, preferentially adsorb on mesopores (Zhang et al., 2011), where a great NOM fraction can access – NOM average MW is often 1.1–2.4 kDa (Li et al., 2003; Cook and Newcombe, 2008; Ho et al., 2011). Therefore, NOM mass competing with MCs is expected to be much higher, especially for NOM-rich waters, a feature which may change the competition approaches usually considered.

NOM fractions are often studied, but it is rather complex to quantify their contribution to direct site competition and pore blockage, as each fraction still comprises a range of MWs and may thus cause both effects. In the present study, a NOM surrogate of similar size to microcystins, e.g. tannic acid (TA), and high TA/MC molar ratios (up to about 30) were used to simulate tannin-rich waters with strong competition potential, with and without background ionic strength (IS).

As both MC and TA have hydrophobic and ionisable functional groups, hydrophobic and electrostatic interactions, and thus water IS, may play a role in their adsorption. While some authors (Pendleton et al., 2001) suggested that electrostatic interactions have minimal influence on MC adsorption, others concluded that electrostatic repulsions may explain different adsorption capacities for MC variants, not predicted by hydrophobicity (Campinas and Rosa, 2006; Cook and Newcombe, 2008; Ho et al., 2011). The IS impact onto single-solute and NOM adsorption has been studied, but research addressing its role on competitive adsorption is, as far as our knowledge goes, limited to Kilduff and Karanfil (2002) study. These authors concluded that the preload of an activated carbon with humic acid in IS presence further reduced TCE adsorption as a result of increased uptake of organic matter.

Several works have reported successful descriptions of MC single-solute adsorption isotherms onto activated carbons by a Freundlich-type equation. To predict a competitive micropollutant-NOM adsorption, a competitive sorption model is nonetheless required and the ideal adsorbed solution theory (IAST) coupled with the concept of equivalent background compound (EBC) is frequently used, where EBC represents the fraction of NOM that competes directly with the target compound for the available adsorption surface and is characterized by Freundlich isotherm parameters (Qi et al., 2007). In this approach the competing NOM concentration is used as a fitting parameter of the model, a strategy that conducts to extremely low fractions of the competing NOM (μg/L range). The IAST-EBC model has been simplified for describing trace organic compound adsorption from natural water and that simplified IAST has been used for describing MC adsorption (Wang et al., 2007; Cook and Newcombe, 2008). The same authors have successfully described carbon adsorption kinetics of MC-LR and MC-LA, both in single-solute and in competition, by the Homogeneous Surface Diffusion Model (HSDM). Nevertheless, no discussion was made regarding the competition mechanisms.

This paper aims to develop a predictive model to describe the competitive adsorption of microcystins and tannic acid, and to better understand the competition mechanism(s) and the role of background IS on MC and similar size NOM adsorption.

Freundlich non-linear models will be used to describe the single-solute isotherms and several models will be tested for the simultaneous bisolute (MC-TA) competitive adsorption equilibrium. The models will provide the input data for implementing the HSDM for describing the adsorption kinetics of both solutes and their competitive adsorption. The model developed, integrating adsorption kinetics and competitive isotherms, will be used to discuss the competing mechanism(s) and the IS role on MC-TA adsorption.

2. Experimental

2.1. Microcystins

Microcystins are cyclic heptapeptides that share a general structure containing five fixed amino acids (three D-amino acids: alanine, methylaspartic acid and glutamic acid; two unusual amino acids: N-methyldehydroalanine (Mdha) and 3-amino-9-methoxy-2,6,8,-trimethyl-10-phenyldeca-4,6-dienoic acid (Adda)) and two variable L-amino acids, designated as X and Z, which give different names to the toxin molecule (Cook and Newcombe, 2008). MCs were produced and extracted from *Microcystis aeruginosa* laboratory grown culture (Pasteur Culture Collection Cyanobacteria), as described in Campinas and Rosa (2006). Four MC variants were detected by high-performance liquid chromatography (HPLC): MC-LR, -LY, -LW and -LF (L-leucine; R-arginine; Y-tyrosine; W-tryptophan; F-phenylalanine). MC-LR was the dominant variant, accounting for ca. 75% of total MCs.

These four MCs vary between 985 Da and 1024 Da (Campinas and Rosa, 2006) and the 3D molecular dimensions of MC-LR are 1.4–2.6–2.9 nm (Sathishkumar et al., 2010; Zhang et al., 2011).

The four MC variants have two ionisable carboxyl groups, one in the methylaspartic segment and the other in the glutamic acid, which are negatively charged at neutral pH (pKa 2.19–2.2). In addition to those two carboxyl groups, MC-LR contains one ionisable amino group in arginine, with a positive charge at neutral pH (pKa 12.5) (De Maagd et al., 1999).