



Adsorption mechanisms of microcystin variant conformations at water–mineral interfaces: A molecular modeling investigation

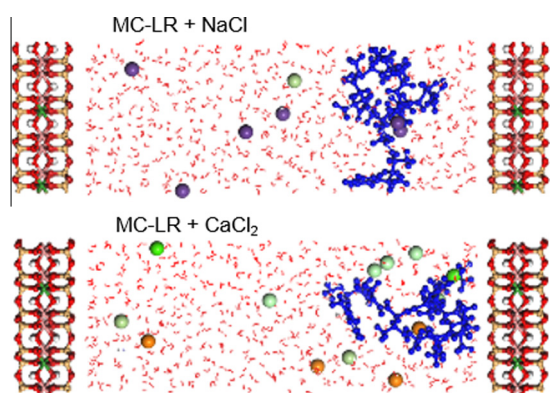


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GRAPHICAL ABSTRACT



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ABSTRACT

Microcystins (MCs) are potent toxins released during cyanobacterial blooms. Clay minerals are implicated in trapping MCs within soil particles in surface waters and sediments. In the absence of molecular characterization, the relevance of previously proposed adsorption mechanisms is lacking. Towards obtaining this characterization, we conducted Monte Carlo simulations combined with molecular dynamics relaxation of two MC variants, MC-leucine-arginine (MC-LR) and MC-leucine-alanine (MC-LA), adsorbed on hydrated montmorillonite with different electrolytes. The resulting adsorbate structures revealed how MC conformations and aqueous conditions dictate binding interactions at the mineral surface. Electrostatic coupling between the arginine residue and a carboxylate in MC-LR excluded the participation of arginine in mediating adsorption on montmorillonite in a NaCl solution. However, in a CaCl₂ solution, the complexation of Ca by two carboxylate moieties in MC-LR changed the MC conformation, which allowed arginine to mediate electrostatic interaction with the mineral. By contrast, due to the lack of arginine in MC-LA, complexation of Ca by only one carboxylate in MC-LA was required to favor Ca-bridging interaction with the mineral. Multiple water-bridged H-bonding interactions were also important in anchoring MCs at the mineral surface. Our modeling results offer molecular insights into the structural and chemical factors that can control the fate of MCs at water–mineral interfaces.

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1. Introduction

Due to increasing nutrient loads, harmful algal blooms are proliferating in surface waters worldwide [1,2]. Many cyanobacterial blooms release toxic compounds such as microcystins (MCs), which are potent liver toxins [1–4]. Due to their toxicity, lakes and rivers with high MC concentrations are not adequate for drinking water production or recreational use [5]. In addition, MCs are reported to be both toxic to fish and disruptive to aquatic food webs [6]. Therefore, understanding the mechanisms that control the fate of MCs is of great importance both to public and environmental health. In addition to biodegradation [3–5,7–9] and photodegradation [10,11], adsorption of MCs to particles in waters and sediments [3,9,12–16] is considered to be one of the major processes responsible for the removal of MCs from contaminated surface waters. Of special interest is the elucidation of the mechanisms that drive the adsorption of different MC variants to minerals in suspended particles and sediments.

There are over 80 variants of MCs, which are monocyclic heptapeptides with two variable amino acids. The cyclic peptide in MCs contains a mixture of charged, polar, and nonpolar amino acid residues; all MCs also contain an Adda (3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid) group attached to the peptide ring (Fig. 1). The most toxic MC is MC-LR, which has a leucine (Leu) and an arginine (Arg) in the variable amino acid positions (Fig. 1) [7]. Other common MCs include MC-RR with two Arg residues, MC-LW with a Leu and a tryptophan (Trp), and MC-LA with a Leu and an alanine (Ala) in the variable positions. Previous studies have reported of high retention of various MC variants in sediments enriched with clay content implied that clay minerals

are important adsorbents of MCs [14,16,17]. In fact, because current cyanobacterial bloom treatments include the application of algacides and chlorination, which can cause cell death and thus lead to the release of high levels of MCs [18–20], silicate minerals have been touted as efficient adsorbents for the removal of MCs [12,21,22] and MC-containing cells [20,23]. The adsorption mechanisms have not yet been elucidated via spectroscopic or other molecular-scale techniques. However, previous macroscopic studies have led to several proposed mechanisms.

Previous adsorption studies [13,15] have reported higher adsorption of MC-RR than MC-LR on natural sediments and the clay mineral montmorillonite. The positively-charged guanidinium in the Arg residues is primarily implicated for the affinity of Arg-containing MCs for the negatively-charged mineral surfaces [15]. In addition to this electrostatic interaction, amino acid residues in the MC peptide ring are proposed to facilitate H-bonding and cation-bridging interactions [12–15]. Moreover, electrolytes in solution are suggested to affect the conformation of MCs whereby changes in conformation seemed to be dependent on whether monovalent or divalent cations were in solution [24,25]. However, the MC conformation required to enable favorable adsorption mechanisms under different aquatic chemistry conditions remains unknown.

Molecular modeling simulations have proven to be a powerful tool for obtaining complementary insights towards improving or adding to experimental interpretations of contaminant-clay interactions [26–32]. The objective of the present study is to employ this tool to elucidate the adsorbate structures and adsorption mechanisms responsible for the trapping of MC variants by clay minerals under different aquatic chemistry. The results from the aforementioned macroscopic adsorption studies have led us to the following hypotheses: (1) MC complexation with metal cations in the aqueous environment can induce specific MC conformation, (2) favorable MC conformation is required for optimal binding mechanisms to clay minerals, and (3) H-bonding and metal complexation are the prevailing adsorption interactions for MC variants lacking a positive Arg residue. To evaluate these hypotheses, Monte Carlo simulations coupled with molecular dynamics relaxation were conducted to model the adsorption of two different MC variants, MC-LR and MC-LA (Fig. 1), on montmorillonite. Montmorillonite (MONT) was chosen because it is an expandable clay mineral commonly found in soils and sediments. The simulations were performed in a fully-hydrated environment populated with either NaCl or CaCl₂ in order to examine the effects of different electrolytes. The findings from this work provide mechanistic insights about the role of aquatic chemistry, MC chemistry, and MC conformation in the interaction of MCs with clay nanoparticles, thus allowing for better predictions of the potential of MCs to be trapped within soil particles in contaminated waters and sediments.

2. Computational methods

2.1. Modeling platform

Simulations were conducted using the all-atom Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS; Accelrys, San Diego, CA, USA) [33] force field as implemented in the Materials Studio software package [34]. All atom descriptions including bonding and nonbonding terms were assigned by the COMPASS forcefield [33], except that partial charges for the water atoms were according to the extended simple point charge water model [35] and partial charges for the MONT atoms were according to the CLAYFF model [36]. The COMPASS force field [33,37] previously demonstrated accurate simulations

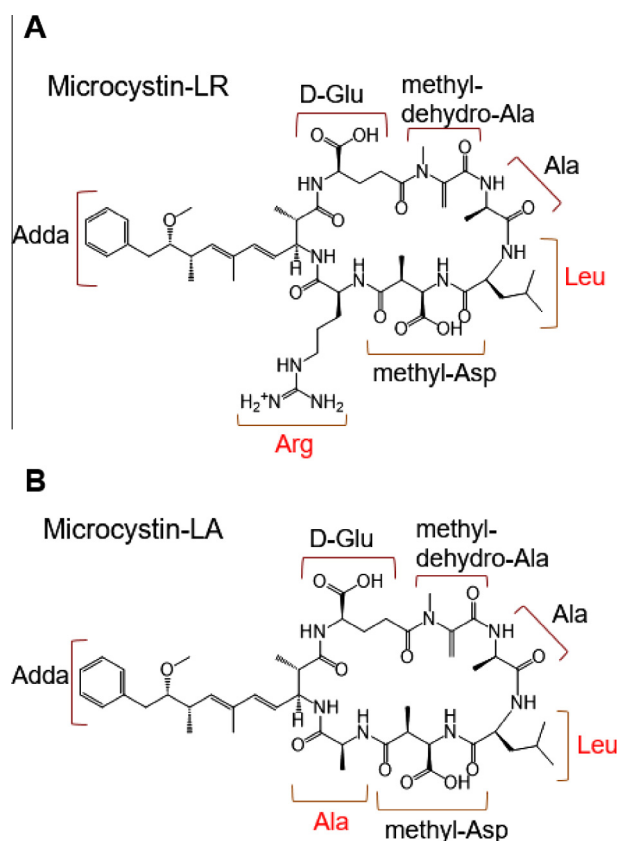


Fig. 1. Chemical structure of (A) MC-LR and (B) MC-LA. Abbreviations: D-Glu (D-glutamate); methyl-dehydro-Ala (N-methyl-dehydro-alanine); Ala (alanine); Leu (leucine); methyl-Asp (methyl-aspartate); Arg (arginine); Adda (3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid).

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