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Mechanisms and Factors Affecting Sorption of Microcystins onto Natural Sediments

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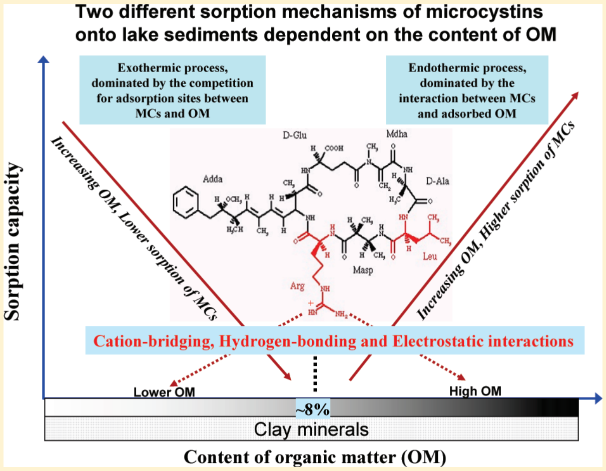
S *Supporting Information*



ABSTRACT: The sorption of microcystins (MCs) to fifteen lake sediments and four clay minerals was studied as a function of sediment/clay properties, temperature, and pH through well−controlled batch sorption experiments. All sorption data for both sediments and clays are well described by a nonlinear Freundlich model (n_f varies between 0.49 and 1.03). The sorption process for MCs exhibited different adsorptive mechanisms in different lake sediments mainly dependent on the sediment organic matter (OM). For sediments with lower OM (i.e., less than 8%), the sorption of MCs decreases with increasing OM and is dominated by the competition for adsorption sites between MCs and OM. In contrast, MC sorption to organic-rich (i.e., more than 8%) sediments increases with increasing OM and is dominated by the interaction between MCs and adsorbed OM. The sorption thermodynamics of MCs onto sediments showed that MC sorption is a spontaneous physisorption process with two different mechanisms. One mechanism is an exothermic process for sediment with lower OM, and the other is an endothermic process for sediment with higher OM. Furthermore, the sorption of MCs onto sediments is pH dependent (sorption decreased with increasing pH). These results provide valuable informations for a better understanding of the natural abiotic attenuation mechanisms for MCs in aquatic ecosystems.

■ INTRODUCTION

Microcystins (MCs) are a group of heptaptide hepatoxins produced by cyanobacteria (blue−green algae) in eutrophic lakes, ponds, and rivers which are often used as drinking water sources.[1] They are potent and specific inhibitors of the serine threonine family of protein phosphatases (PP), especially PP1 and PP2A,[2] and are responsible for liver failure in wild animals, livestock, aquatic life, and humans.[3] Their presence in water bodies has the potential to cause both acute and chronic toxicity and thus has been a public health topic of increasing attention.

MCs are normally considered to be confined within cyanobacterial cells and enter the surrounding water after lysis and cell death[4] or via an active release process.[5] However, cyanobacterial cells and/or their toxins can also enter into sediments through a variety of pathways, including chemical coagulation and flocculation,[6] coprecipitation with clays or particulate matter,[7] overwintering on the sediment surface directly coupled to the annual life cycle of the meroplanktonic cyanobacteria,[8] and precipitation with excreted particles from aquatic organisms after they have consumed cyanobacteria. Current best knowledge suggests that sediment, which often serves as one of the most important sources and sinks of environment pollutants, might also play an important role in the fate of MCs because of the strong adsorption affinity.[9,10] In addition, the sorption of MCs to sediments may also favor the biotic elimination of MCs since anoxic and aerobic biodegradation of MCs as effective removal pathways in sediments have been documented.[11] Therefore, investigations into the sorption behavior of MCs on natural sediments are of great significance for understanding the importance of abiotic elimination pathways for MCs and their transport and transformation in aquatic ecosystems. Furthermore, given that sediment/water distribution is a central process affecting contaminant fate, studies on sorption mechanisms of MCs in sediment are beneficial to (1) elucidate the role of sediments and clay minerals in the sorption behavior of different MC variants; (2) provide theoretical guidance for their risk assessment; and (3) select an appropriate remediation strategy for the removal of MCs via adsorption onto natural sediments.

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The mechanisms and factors affecting MC sorption onto lake sediments have been unclear until now. Only a few studies have investigated MC sorption onto natural sediments,[9,10] and these mainly focused on the seasonal variation of MC concentrations in sediments and sorption capacity of MCs to natural sediments. Several authors[12,13] have identified nonlinear sorption isotherms for individual MCs on agricultural soils and proposed that the clay content in sediments would have a greater contribution to MC sorption than the organic matter (OM) content, which is often considered to be the main influencing factor for pollutant sorption. Since OM and clay fractions are related in sediments, it is not yet clear which of these two components control MC sorption. Moreover, the variations in structures of MCs represent different ionizable characteristics,[14] thus different interactions and adsorption affinities may occur when different MCs adsorb onto natural sediments and clay minerals. Therefore, a more detailed study of MC sorption onto lake sediments is urgently needed to advance the knowledge of the natural elimination pathways of MCs via adsorption onto lake sediments.

The present study is primarily focused on the factors (such as sediment properties, temperature, and pH) that affect the sorption of MCs onto natural sediments. To better understand the various sorption mechanisms of MCs in different lake sediments, the experiments were designed to examine the sorption thermodynamics and relationships between the sorption coefficient and properties of both natural sediments and pure clay minerals. It is expected that the results of the present study will provide insights into the role of abiotic elimination pathways on the fate of MCs and increase understanding of the natural adsorptive mechanisms of MCs in different natural sediments.

■ EXPERIMENTAL SECTION

Materials and Chemicals. The MC-LR and MC-RR used in the experiment were isolated and purified in the laboratory (details are provided in page S1 in the Supporting Information (SI)). MC-LR and MC-RR standards were purchased from Sigma−Aldrich (St. Louis, MO, USA). Other chemicals except for HPLC grade methanol were of analytical reagent grade and deionized water was prepared by a Milli−Q filtration system (Millipore, Bedford, MA, USA).

Kaolinite was purchased from Sinopharm Chemical Reagent Company (China), and attapulgite, montmorillonite, and bentonite were obtained from the Institute of Soil Science, Chinese Academy of Sciences. The surface sediment samples (0−10 cm) used in the experiments were collected from different eutrophic lakes in China using a Petersen grab sampler, and their properties are listed in Table S1 in the SI. All sediment samples were transported to laboratory as soon as possible. After homogenizing, the samples were freeze-dried, crushed, passed through a 1−mm sieve, and then stored at 4 °C prior to analysis.

Batch Sorption Experiments. Two quite different natural sediments (Fubao Bay sediments from Lake Dianchi and Meiliang Bay sediments from Lake Taihu) and kaolinite clay (400 mesh) were used for the batch sorption experiments. Sorption isotherms were constructed according to the standard batch equilibration method.[15] All batch sorption experiments were carried out in triplicate. Fixed amounts of sorbents (1 g sediment or clay, dry weight) were immersed in 2 mL of deionized water in a 30 mL polypropylene centrifuge tube and shaken on an orbital shaker at 110 rpm for 30 min. Next, 8 mL of the MC solutions with 0.05% sodium azide as a microbial inhibitor were added to give final doses of MC-LR at 6.30, 4.73, 3.15, 1.58, 0.79 μg mL^{-1} and MC-RR at 6.24, 4.68, 3.12, 1.56, 0.78 μg mL^{-1}. Based on measurements from a previous experiment, losses due to biodegradation or sorption to the plastic wall were considered negligible. MC containing sediments and clays were maintained at 25 °C on an orbital shaker at 110 rpm for 24 h (equilibration time, also see details for the sorption kinetic and equilibrium studies shown in page S2 in the SI). After equilibrium was achieved, the tubes were centrifuged at 8000 × g for 10 min, and the clear supernatants from each were transferred to glass autosampler vials for MC analysis (ref 16, see page S2 in the SI).

To examine the influence of different components (organic materials, clays) of the sorbents on the MC sorption process, MC sorption onto sorbents with different treatment conditions (sediments without OM, original sediments, kaolinite, and kaolinite with 5% HA) was studied. Two natural sediments from Lake Dianchi and Lake Taihu were treated to remove the organic fraction, according to an adapted method using sodium hypochlorite.[17] The temperature-dependence of adsorption was used to examine the adsorption thermodynamics of MCs onto those two natural sediments, with experiments carried out at 5 ± 1, 15 ± 1, 25 ± 1, and 35 ± 1 °C. The influence of pH on MC-LR sorption to sediments is less clear when only considering the initial pH value of the solutions, thus the test solutions used to examine the influence of pH on MC-LR sorption were adjusted to final pHs of 2.5, 7.2, and 9.7 after 24 h incubation using 10 M H_2SO_4 or 1 M K_2CO_3. All other parameters and equipments were held the same as described previously for the batch tests.

Data Analysis. The amount of MCs adsorbed onto the sorbents (C_s, mg kg^{-1}) was calculated as the difference between the initial aqueous phase concentration and the equilibrium concentration (C_e, mg L^{-1}). The sorption data determined during the sorption tests under various concentrations were subjected to regression analysis and fitness of data to the three different types of sorption isotherms, as follows.

The linear adsorption isotherm

$$C_s = K_d \cdot C_e \tag{1}$$

The Freundlich isotherm

$$\log C_s = \log K_f + n_f \cdot \log C_e \tag{2}$$

The Langmuir isotherm

$$1/C_s = 1/(K_L \cdot Q_{max}) \cdot 1/C_e + 1/Q_{max} \tag{3}$$

where K_d (L kg^{-1}) is the distribution coefficient, K_f ((mg kg^{-1})(mg L^{-1})$^{-n_f}$) is the Freundlich distribution coefficient which relates to the amount of MCs absorbed at an equilibrium concentration of 1 mg L^{-1}, n_f is a Freundlich constant parameter describing the degree of nonlinearity, Q_{max} (mg kg^{-1}) is the maximum sorption capacity of an adsorption phase in the sediment, and K_L (L kg^{-1}) is a constant related to the adsorption affinity. At infinitely low C_e in eq 3, the Langmuir model assumes a constant sorption coefficient of $K_L Q_{max}$.

All data were plotted for both linear and nonlinear regressions, and the regression coefficients were calculated. A one way repeated measure ANOVA and a Pearson bivariate correlation analysis were undertaken with SPSS 16.0 (SPSS Inc., Chicago, IL, USA) for statistical analysis.

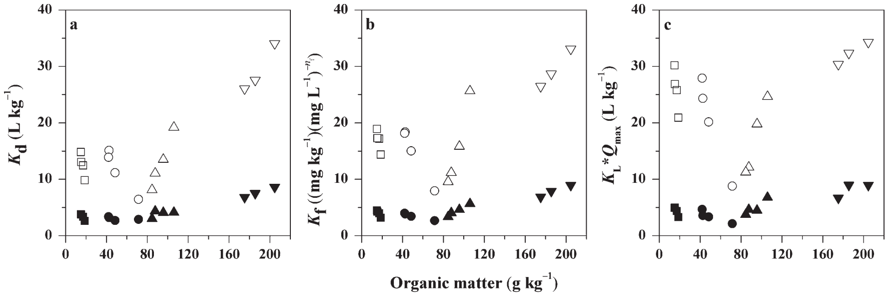

Figure 1. Correlation between the sorption parameters of (a) the linear sorption coefficient (K_d), (b) Freundlich distribution coefficient (K_f), and (c) Langmuir sorption coefficient (K_L*Q_{max}) of MCs calculated from the sorption isotherms on all tested natural sediments at pH = 7 and 25 °C and the corresponding organic matter contents at different levels: -□- and -■- 1% to 2%, -○- and -●- 4% to 8%, -△- and -▲- 8% to 11%, -▽- and -▼- 17% to 21%; Solid symbols represent MC-LR and open symbols represent MC-RR.

RESULTS AND DISCUSSION

Equilibrium Time and Effects of Toxin Structure. The sorption kinetics of MC-LR and MC-RR were measured at initial concentrations of 4.64 mg L^{-1} for MC-LR and 4.68 mg L^{-1} for MC-RR using Fubao Bay sediments from Lake Dianchi as a sorbent (Figure S1 in the SI). The results demonstrated that removal of MCs from the aqueous phase was largely associated with a rapid initial loss of MCs from the aqueous phase, as indicated by the 33% and 69.5% losses of MC-LR and MC-RR, respectively, from the aqueous phase, which occurred at 0.5 h. The implication of this finding is that sediments could act as a potential sink for MCs after a harmful algal bloom has passed. As there was no further significant change in concentrations of MCs after the initial loss, 24 h was selected as sufficient equilibration time for MCs in batch adsorption experiments, which was also consistent with the reported results of other investigations.[12,13]

The sorption of MC-RR to natural sediments was more pronounced than the sorption of MC-LR, which was consistent with the results previously reported by Chen et al.[13] and Babica et al.,[18] in which they proposed that the chemical structure of MCs are an important factor affecting the sorption of MCs onto soils and sediments. MC-RR and MC-LR have similar molecule structure and they differ only in the variable amino acid located at the second position, that is, MC-RR has one more guanidinium group of arginine residue than MC-LR. This specific property of MC-RR cause it to (1) increase propensity to form cation bridging (resulting from the additional positive protonated arginine cation) and enhance its sorption affinity to cation-exchange sites present on both OM and clay and (2) provide additional binding sites and tend to form more hydrogen bonds with sediment components (OM and/or clay). Grützmacher et al.[19] also attributed the higher sorption capacity of MC-RR in sediments to the higher acidity constant of arginine (pK_a value 12.5) for MC-RR, compared with leucine for MC-LR (pK_a value 9.7). Furthermore, the logK_{ow} values of MC-LR (−0.37) and MC-RR (−1.09) under neutral condition, which were measured in our laboratory according to De Maadg et al.,[20] indicate that both MCs are hydrophilic and thus hydrophobic interactions are unlikely to play a major role in MCs sorption onto sediment considering so much lower logK_{ow} values. For the reasons discussed above, it was likely that different types of interactions (e.g., cation-bridging, hydrogen-bonding, and surface electrostatic interactions) may occur when different MCs adsorb onto natural sediments and clay minerals.

Effect of Sediment Properties. In order to better understand the effects of sediment properties on the sorption of MCs to natural sediments, sorption isotherms were studied for both MC variants in fifteen different natural sediments and four pure clay minerals and the sorption parameters, calculated from the three proposed models, are provided in Tables S2 and S3 in the SI. The results showed that these three models matched the experimental data quite well, and the Freundlich constant parameter n_f ranging between 0.68 and 1.03 for MC-LR and 0.49−0.98 for MC-RR suggested that the nonlinearity was neither consistent nor very strong. MC-RR had lower n_f values than MC-LR for all sediments and clays, indicating a greater nonlinear sorption tendency for MC-RR than MC-LR. Moreover, all values of K_d, K_f, and K_LQ_{max} for MC-RR are much higher than those values for MC-LR, again suggesting that one more guanidinium group than MC-LR may play a key role in the sorption of MC-RR onto sediments.

As the distribution coefficients (K_d and K_f) and sorption coefficients (K_LQ_{max}) are distinctly different for the different natural sediments and clay minerals, correlations between the individual characteristics and the sorption parameters (K_d, K_f, and K_LQ_{max}) for MCs on all sediments and clay minerals were presented in Table S4 in the SI.

For clay minerals, the only significant correlation observed was between the specific surface area and K_f or K_LQ_{max} for MC-LR sorption to clay minerals ($R^2 > 0.962$), indicating that surface aera of clays has a greater influence on the sorption process of MC-LR. For the fifteen different natural sediments, the correlation coefficients (R^2) between the sorption parameters of both MC variants and characteristics of natural sediment with higher OM contents represent a good linear relationships for TN, OM, but did not show significantly linear relationships to sediments with low OM contents. The complex relationship may be mainly because the coexistence of clay minerals (the mineral compositions of the sediments tested were shown in Table S5 in the SI) and OM in these sediments complicates the interpretation of correlations between sorption parameters and sediment properties. It indicated that OM content may play a more important role in the sorption of MCs onto natural sediments (especially to the organic-rich sediments).

A systematic analysis of the relationship between sorption parameters (K_d, K_f, and K_LQ_{max}) of both MC variants and OM contents in sediments revealed that better linear correlations existed at different levels of OM (Figure 1, the fits of the equations at different OM levels were shown in Table S6 in

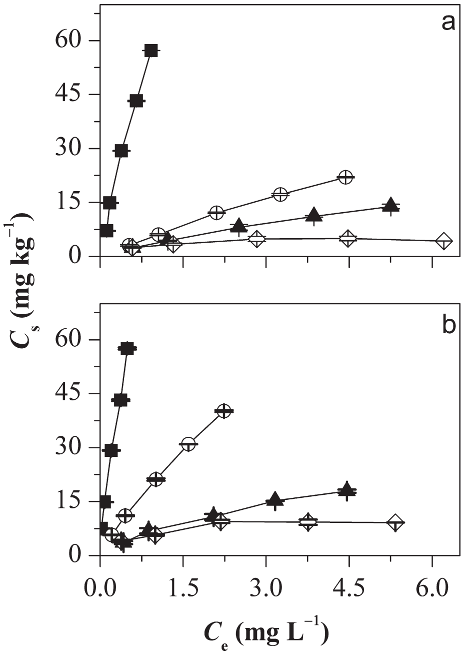

Figure 2. Sorption isotherms for (a) MC-LR and (b) MC-RR onto four different treated sorbents (-■- sediments without organic matter. -○- original sediments, -▲- kaolinite, -◇- kaolinite with 5% HA) at pH = 7 and 25 °C.

the SI). For the sediments contained higher levels of OM (i.e., more than 8%), better correlations were observed for sediments from Lake Dianchi (R^2 > 0.85 except for 0.239 in Linear adsorption of MC-LR) and Lake Caohai (R^2 > 0.97 except for 0.578 in Langmiur adsorption of MC-LR), and the sorption coefficients tended to increase with increasing OM content. Meanwhile, a good correlation but an opposite tendency was observed for the sediments contained lower levels of OM (i.e., less than 8%), as indicated by R^2 > 0.85 for Lake Taihu and R^2 > 0.80 (except for 0.261 in linear adsorption of MC-LR) for lakes group (Lake Fuxian, Xingyun, and Erhai, located at Yunnan Plateau in China), suggesting that the varied sorption phenomena may primarily relate to the heterogeneity of sediment OM, as observed for the sorption of some organic chemicals to soils and sediments.[21] These results indicate that the sorption of MCs to different natural sediments exhibited different adsorptive mechanisms which depend largely on the content of OM.

To further elucidate the significance of the components of OM and clay minerals in the MC sorption process, the sorption isotherms for each MC variant in sediments and clay minerals with different treatments (sediments without OM, original sediments, kaolinite, and kaolinite with 5% HA) were examined. As shown in Figure 2, the sorption of each MC variant to the different treatments decreased in the following order: sediments without OM > original sediments > kaolinite > kaolinite with 5% HA. These findings may be explained by different mechanisms of MC sorption to sediments, which depend on both the OM content and the types of clay minerals. It is clear that OM could lead to a reduction in the sorption capacity of kaolinite and sediments for MCs due to the competition between OM and MCs for sorption sites on kaolinite and sediment and/or the presorption of dissolved macromolecular substances (e.g., HA), which can block the microporous surfaces of sediments and clays and lower the sorption sites for MCs. In this case, the clay minerals in the sediments were the main factors influencing the sorption of MCs onto sediments. This result is similar to previous results where the sorption coefficients (K_d, K_f, and K_LQ_{max}) tended to be lower when the organic content increases and agreed with the results of Miller's and Chen's investigations,[12,13] in which they proposed that high clay contents would have a higher sorption of toxins, such as MC-RR, MC-LR, [Dha^7]MC-LR, or nodularin. However, these conclusions did not consider sediments with higher OM contents. As shown in Figure 1, when the OM content in sediments was higher than 8%, the sorption capacity of sediments for MCs increased with increasing OM, which may occur because the excess of OM could lead to an enhancement in the sorption capacity of sediments for MCs. The highest sorption coefficients were observed for the sediments in Lake Caohai, which contained the highest OM content. To summarize, the OM content in sediments is the main factor influencing the sorption of MCs to sediments if saturation of OM sorption to sediments and clay minerals has occurred. In the case of sediments with OM removed to a certain low level, the clay minerals in the sediment are the dominant factor controlling the MC sorption, so a higher sorption capacity than the original sediments (with OM) was observed. To elucidate the complex sorption phenomena, further study of the impacts of the heterogeneity of sediment OM and clay fractions on sorption of MCs in soils and sediments is undoubtedly needed.

Adsorption Thermodynamics. Sorption of MCs to sediments may occur by both reversible physical processes and irreversible chemical processes. To elucidate the significance of these sorption pathways, the sorption thermodynamics of MC-LR and MC-RR onto two quite different natural sediments under different temperatures were investigated (Figure S2 in the SI). The amount of sorption of MC-LR and MC-RR onto Fubao Bay sediments increased as temperature increased but decreased with increasing temperature for the Meiliang Bay sediments.

The thermodynamic parameters (ΔG, ΔH, ΔS) are related by the following equations and the calculated values are shown in Table 1

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

where ΔG is the change in standard Gibbs free energy (kJ mol^{-1}), ΔH is the change in enthalpy (kJ mol^{-1}), ΔS is the change in entropy (kJ mol^{-1} K^{-1}), and T is the absolute temperature (K).

At equilibrium, K is related to the standard Gibbs free energy change by

$$\Delta G = -RT\mathrm{Ln}K \tag{5}$$

where K is the equilibrium constant obtained by applying the Freundlich distribution coefficient (K_f) from eq 2, and R is the molar gas constant (8.314 J mol^{-1} k^{-1}).

The enthalpy change (ΔH) for MCs in those two types of lake sediments were analyzed using the van't Hoff isochore obtained from the variation of K with temperature, i.e., by combining eqs 4 and 5, to form eq 6

$$\mathrm{Ln}K = -\Delta H/RT + \Delta S/R \tag{6}$$

The thermodynamic quantities give an insight into the sorption processes involved. All free energies for MC sorption onto lake sediments are negative (Table 1), indicating that a net and spontaneous sorption process occurs between MCs and

Table 1. Sorption and Thermodynamic Parameters for Microcystins onto Fubao Bay and Meiliang Bay Sediments at Different Temperatures

	sediments	temperature	Freundlich equations	n_f[a]	K_f[b]	R^2 [c]	ΔG[d] kJ mol^{-1}	ΔH[e] kJ mol^{-1}	ΔS[f] J mol^{-1} K^{-1}
MC-LR	Fubao Bay	5 °C	$y = 0.95x + 0.64$	0.95	4.40	0.999	−3.42	12.30	56.56
		15 °C	$y = 0.90x + 0.70$	0.90	5.00	0.998	−3.85		56.09
		25 °C	$y = 0.82x + 0.77$	0.82	5.91	0.998	−4.40		56.04
		35 °C	$y = 0.72x + 0.87$	0.72	7.42	0.997	−5.13		56.60
	Meiliang Bay	5 °C	$y = 0.63x + 0.66$	0.63	4.62	0.982	−3.53	−14.05	−37.82
		15 °C	$y = 0.74x + 0.59$	0.74	3.86	0.999	−3.24		−37.55
		25 °C	$y = 0.84x + 0.49$	0.84	3.08	0.998	−2.79		−37.78
		35 °C	$y = 0.92x + 0.41$	0.92	2.58	0.998	−2.43		−37.74
MC-RR	Fubao Bay	5 °C	$y = 0.91x + 1.22$	0.91	16.48	0.997	−6.48	3.49	35.85
		15 °C	$y = 0.83x + 1.25$	0.83	17.80	0.999	−6.89		36.06
		25 °C	$y = 0.81x + 1.27$	0.81	18.55	0.999	−7.24		35.99
		35 °C	$y = 0.83x + 1.28$	0.83	19.12	0.999	−7.56		35.86
	Meiliang Bay	5 °C	$y = 0.75x + 1.13$	0.75	13.64	0.991	−6.04	−10.56	−16.26
		15 °C	$y = 0.78x + 1.06$	0.78	11.36	0.999	−5.82		−16.46
		25 °C	$y = 0.81x + 0.99$	0.81	9.83	0.999	−5.66		−16.44
		35 °C	$y = 0.88x + 0.94$	0.88	8.73	0.998	−5.55		−16.27

[a] Freundlich constant parameter. [b] Freundlich distribution coefficient. [c] Fit to Freudlich isotherm. [d] Change in standard Gibbs free energy. [e] Change in enthalpy. [f] Change in entropy.

sediments. The ΔH values calculated from the slope of the van't Hoff plot (Figure S2) by eq 6 are 12.30 kJ mol^{-1} for MC-LR and 3.49 kJ mol^{-1} for MC-RR in Fubao Bay sediments and −14.05 kJ mol^{-1} for MC-LR and −10.56 kJ mol^{-1} for MC-RR in Meiliang Bay sediments. The variation in ΔH values indicates that the sorption of MCs onto different sediments comprises two different processes: one is an endothermic process in sediments with higher OM (e.g., Fubao Bay sediments), associated with an entropy driven process ($\Delta S > 0$), and the other is an exothermic process in sediments with lower OM (e.g., Meiliang Bay sediments), associated with an entropy retarded process ($\Delta S < 0$). The first process has a more negative ΔG^o and stronger sorption capacity with increasing temperature, while the second process has the opposite tendency (Table 1). Change in enthalpy data is useful for distinguishing the type of binding mechanism involved, i.e., physisorption and/or chemisorption, as its magnitude is closely related to the sorption energy. Physisorption is typically fast and reversible and usually involves relatively weak intermolecular forces and has small energy requirements (e.g., 4−8 kJ mol^{-1} for London dispersion forces and 8−40 kJ mol^{-1} for hydrogen bonding,[22] while chemisorption is slow and irreversible and is typically associated with much larger enthalpy (>40 kJ mol^{-1}). The current results suggest the sorption of MCs to sediments is a physisorption process.

The different thermodynamic processes and the data shown in Figure 1 strongly suggest that the sorption mechanism of MCs onto sediments involves complex reactions, in which the sediment OM plays a critical role and has a 2-fold effect on the process. At lower OM contents, the amount of available adsorption sites on the sediment may exceed the requirements for sorption of OM, which means that there are still enough surface sites available for combination with the MCs. The number of remaining sites decreases with increasing adsorbed OM, resulting in decreased sorption of MCs onto sediments with increasing OM contents due to the competition for adsorption sites between MCs and OM. Thus, when there are sufficient adsorption sites on the sediment, a spontaneous, energetically favorable exothermic interaction dominates the sorption process. At higher OM contents (e.g., >8% in this study), there may be few surface sites available for combination with the MCs because the adsorbed OM occupies almost all the adsorption sites on the sediment until a plateau stage where sites become saturated occurs. At this stage, the interaction between the MCs and the adsorbed OM is expected to be the controlling mechanism for the sorption process and thus, the sorption of MCs to organic-rich sediments (actually to the adsorbed OM) increases with increasing OM. In this case, a spontaneous, entropy driven endothermic interaction dominates the sorption process. These findings expand our understanding of differing sorption behaviors for MCs on different eutrophic lake sediments. Similar different thermodynamic processes are also observed for sorption of other chemicals. For example, pentachlorophenol sorption to a clay soil with a lower OM content (1.7%) was shown to be a spontaneous exothermic process for the ionized species,[22] whereas sorption to allophanic soil with a higher OM content (7.9%) was an entropy driven endothermic process.[23]

Effect of pH. Solution pH has been shown to affect the adsorption of MC-LR.[12] In the present study, the influence of pH on the sorption of MC-LR to Fubao Bay sediments from Lake Dianchi and kaolinite were investigated, and the sorption isotherms are shown in Figure 3. It is clear that the maximum sorption of MC-LR onto all types of sorbents investigated occurred at pH 2.5, and the sorption decreased as pH increased. These results agreed with those of Miller et al.[12] who reported that soil suspensions in an acetate buffer (pH 4.8) generally produced significantly higher adsorption coefficients, when compared with other buffer systems.

It appears that MC-LR sorption onto sediments and clays is highly pH-dependent, which may be mainly attributed to the influence of pH on the surface charge heterogeneity of the sorbate (MC-LR) and sorbents (sediment and clay).

For the sorbents, kaolinite belongs to the class of 1:1 sheet silicates with a layer of tetrahedral silica connected to a layer of octahedral aluminate. Its pH-dependent charges develop on the

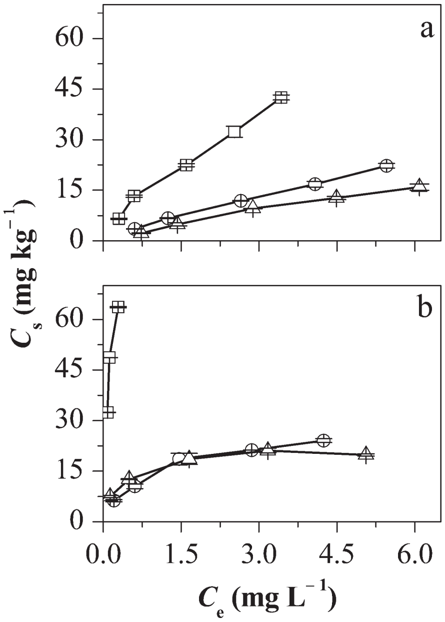

Figure 3. Sorption isotherms for MC-LR onto different sorbents (a: Fubao Bay sediment from Lake Dianchi, b: kaolinite) at different pH values. (-□- pH = 2.5, -○- pH = 7.2, -Δ- pH = 9.7).

surface hydroxyls mainly at edge and terminal Al—OH sites. The surface charges on kaolinite are positive at pHs below 6−6.5 and increase with decreasing pH, while the surface charges are negative at pHs over 6−6.5 and increase with increasing pH.[24] The pH also changes the protonation−deprotonation of sediment humic substances. It is well-known that humic substances, with HAs and fulvic acids (FAs) as the major fractions, are the dominant organic components in soils and sediments. These HAs and FAs possess various chemically reactive functional groups such as carboxyls, phenolic and alcoholic hydroxyls, and are commonly regarded as macromolecular acids or oligoelectrolytes and are capable of protonation−deprotonation on changes in solution pH. The negative charges on HAs and FAs as well as solid bonding HAs and FAs show a clear and consistent increase in charge as a function of increasing pH.[25,26]

For the sorbate, MC-LR possesses two freely ionizable carboxylic acid groups and one freely ionizable amino group. These functional groups alter their ionization states and net charges with changes in pH.[20,27] For example, the net charge of MC-LR decreases from 0 at pH = 2.1 to −1 at pH = 4 and then remains stable at −1 within the range of pH = 4−10. Based on these results, we can therefore interpret the interactions between MC-LR and sediment and clay under different pH conditions: (1) at lower pH (2.5), the net charge on MC-LR is slightly negative, while the charges on kaolinite and sediment humic substances are positive and slightly negative respectively, causing electrostatic attraction between MC-LR and kaolinite and electrostatic repulsion between MC-LR and sediment, thus leading to a higher sorption of MC-LR to kaolinite than to sediment (Figure 3); (2) at neutral (pH = 7) or slightly alkaline conditions (pH = 9.7), the net charge on MC-LR is negative and those on kaolinite and sediment humic substances are also negative, becoming more negative as pH increases and causing an increase in electrostatic repulsion between MC-LR and kaolinite or sediment. As a function of increasing pH, sorption of MC-LR to kaolinite and sediment under weak alkaline conditions was slightly lower than that under neutral conditions (the difference of MC-LR sorption to sediments was more pronounced than sorption to kaolinite) but considerably lower than that under acidic conditions (Figure 3).

The pH-dependent property of electrostatic interaction between MC-LR and clays can also partly explain the distribution coefficients presented in Table S2. For instance, under neutral condition, the surface charge density of attapulgite is approximately zero,[28] while those of montmorillonite and bentonite are positive.[29] Thus the sorption of MC-LR to kaolinite is slightly weaker than attapulgite but much weaker than montmorillonite and bentonite (see sorption coefficients in Table S2). In the case of MC-RR, however, the electrostatic interaction between the toxin and clays is unlikely the main factor affecting the sorption of MC-RR to clays because one more arginine residue than MC-LR can lead to form cation bridges and more hydrogen bonds with clay minerals. These differences in electrostatic interaction between different MC variants and clays also seem to partially explain the observation that good correlations between toxins and the specific surface area of clay minerals is observed for MC-LR but not for MC-RR (Table S4 in the SI). It is likely that other processes, such as cation bridging and hydrogen bonding interactions between mineral surface hydroxyl groups (Si—OH and Al—OH) and MC-RR, may play a relatively major role, but further studies are required to reveal this.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental section, Figures S1 and S2, and Tables S1-S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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