CHAPTER 5

RELATING THE COMPETITIVE ADSORPTION OF MICROCYSTINS WITH THE WATER BACKGROUND ORGANIC AND INORGANIC MATRICES: II. EQUILIBRIUM STUDY

ABSTRACT

Microcystins–NOM competition and the effect of the water ionic strength (IS) on the competition mechanisms were investigated. Isotherm data obtained with NOM surrogates and surface water were consistent with the adsorption kinetics conclusions from Part I, and allowed an integrated analysis. This is, NOM molecules larger than microcystins (humic acids) were responsible for pore blocking only in the presence of background IS (responsible for NOM shrinkage), whereas the direct site competition of smaller hydrophilic NOM molecules was only observed at low dosages of the mesoporous PAC. Microcystins adsorption was mostly affected by NOM of closer size (tannic acid, TA), and a slight improvement in the adsorption capacity was observed with IS addition. Pore constriction seems to lead the TA competition mechanism, and direct competition for microcystins adsorption sites would only govern at higher carbon loadings. Microcystins adsorption capacity was strongly affected by moderately hard water with hydrophilic, small organics, which is consistent with direct site competition mechanism. Microcystins residuals are not affected by its initial concentration, except when in the presence of the strong competitor TA. To overcome TA competition and achieve negligible residuals, PAC should be increased 50% in the presence of IS and doubled in its absence.

5.1 INTRODUCTION

Powdered activated carbon adsorption/ultrafiltration (PAC/UF) is one of the promising hybrid processes for cyanotoxin removal but its performance depends of an efficient PAC adsorption. PAC adsorbs most of the organic compounds in water, including natural organic matter (NOM). Although NOM is generally not adsorbed as effectively as the target contaminants, its concentration one to three order-of-magnitude higher than that of the target-contaminant makes them effective competitors. The presence of NOM may reduce the equilibrium capacity of activated carbon for microcystins, and may also affect its rate of adsorption, diminishing the efficacy of water treatment.

The extension of competitive adsorption depends on the initial concentration of the trace compound (C_0). As C_0 decreases, the adsorption isotherm capacity also diminishes (Najm *et al.*, 1991), although several authors have found that below a given low C_0 value the removal efficiency no longer depends of C_0 (Knappe *et al.*, 1998; Gillogly *et al.*, 1999; Graham *et al.*, 2000; Cook *et al.*, 2001; Matsui *et al.*, 2003)**.**

The investigation of NOM effect onto microcystins adsorption and the assessment of the leading competition mechanisms are key-issues to minimize microcystins-NOM competition, namely to choose the best local for PAC/UF application in a water treatment train.

Pore constriction/blockage and direct site competition are the two mechanisms by which NOM reduces PAC efficacy for a target-contaminant. Unlike the micropollutants usually studied, microcystins are relatively large compounds (900-1100 Da, 1.2-2.6 nm in diameter) and a fraction of the NOM compounds can access similar pores, which may change the competitive approaches normally presented. Some authors have examined the effect of NOM

on the removal of microcystin-LR, verifying a decrease in the adsorption capacity (Donati *et al.*, 1994; Lee and Walker, 2006; Huang *et al.*, 2007), but the competition mechanisms were not effectively analysed and/or the initial concentration of microcystins was extremely high compared to natural conditions.

Recent developments have demonstrated that an integrated analysis, combining adsorption isotherms and kinetics, is an important tool that could help to clarify the dominant competition mechanisms. Nowadays, it is believed that direct site competition and pore blockage are imposed by NOM fractions of different molecular size and affect trace compound adsorption equilibrium and kinetics differently (Li *et al.*, 2003 a). Direct site competition occurs when compounds are of similar size and compete for the same pores (Kilduff *et al.*, 1998; Pelekani and Snoeyink, 1999; Newcombe *et al.*, 2002), mainly reducing the carbon capacity for the trace compound (Pelekani and Snoeyink, 2000; Li *et al.*, 2003 a). Pore constriction/blockage takes place when the NOM molecules are larger than the target compound and cannot access the same pores, but may block or reduce the pores entrance (Kilduff *et al.*, 1998; Pelekani and Snoeyink, 1999) and therefore affect both the adsorption kinetics and the adsorption capacity of the trace compound (Pelekani and Snoeyink, 2001; Li *et al.*, 2003 a, b; Matsui *et al.*, 2003). This integrated approach was applied to the study of the microcystins-NOM competitive adsorption, including the effect of water background ionic strength and is presented in a series of two papers, part I (Chapter 4) for the adsorption kinetics and part II (Chapter 5) for the adsorption isotherms.

In Part I the effect of NOM surrogates onto microcystins rate of adsorption was assessed and the prevailing competition mechanisms were proposed. The contribution of ionic strength to the competitive effect of NOM was also analysed, an aspect rarely considered despite the

general acceptance that inorganic water matrices interfere with the adsorption of NOM and target compounds. It was found that the compound with the closest size to microcystins, tannic acid (TA), had the most severe impact onto microcystins rate of adsorption, participating in pore constriction/blockage and eventually (but to a much lower extension) in direct site competition. The humic acids (larger than microcystins) and the salicylic acid (much smaller, 138 Da) had no effect on microcystins adsorption kinetics since they adsorb on different pores. The water ionic strength changed adsorption, inducing the humic acids competition and attenuated the TA effect, by reducing their size, which caused pore constriction or blockage by humic acids or converted pore blockage into constriction by TA.

This chapter complements part I with respect to the proposed competition mechanisms and the combined effect of background NOM and ionic strength on the microcystins adsorption, and it also investigates the role of the initial concentration of microcystins as well as the competition impact on the PAC dose required to achieve the same low residuals.

5.2 MATERIALS AND METHODS

Experimental details on the adsorbates, adsorbent, model solutions, natural surface water and the analytical methods used in this study were the same as those used in the kinetic study and are therefore presented only in part I (Chapter 4).

The adsorbent used was Norit SA-UF powdered activated carbon. Model solutions of microcystins and NOM surrogates (Aldrich humic acids, AHA; tannic acid, TA; and salicylic acid, SA) with and without a background ionic strength of 2.5 mM provided by KCl (1 mM IS) and $CaCl_2$ (1.5 mM IS) were studied as well as preozonated, clarified surface water collected at Tavira WTP, Algarve, Portugal.

With respect to the adsorption isotherms, two types of runs were performed: single-solute isotherms with model solutions (with and without background ionic strength) and competitive adsorption isotherms with model solutions (also in the absence and presence of IS) and surface water.

Isotherms were determined using the conventional bottle-point isotherm tests fully detailed in Campinas and Rosa (2006) (chapter 3). PAC doses ranged between 8-25 mg/L and an equilibrium time of 65 h was assumed for all the isotherm tests, with exception of AHA single-solute isotherms for which a 7 day test were performed. Initial microcystins concentration studied ranged from 64 to 246 μg/L MC-LR_{eq}.

The Freundlich equation, $q_e = KC_e^{1/n}$, was used to describe the equilibrium relationship between the aqueous concentration, C_e, and the surface concentration, q_e, where K and 1/n are the Freundlich constants. K is a unit-capacity parameter (amount adsorbed at a value of C_e equal to unity) $(\mu g/mg)(L/\mu g)^{1/n}$ and n is a dimensionless parameter related to the site-energy distribution. When and if the log-log plots of microcystins isotherms were not linear at the highest equilibrium concentrations investigated, K and 1/n were determined using only the linear part of the isotherm.

5.3 RESULTS AND DISCUSSION

5.3.1 Single-Solute Isotherms

Single-solute isotherms were conducted with microcystins and NOM model compounds (SA, TA and AHA) dissolved in organic and inorganic-free water, as well as in 2.5 mM IS electrolyte solution. SA isotherms in electrolyte solution were not performed since previous

data showed no effect of background IS on the adsorption kinetics (Campinas and Rosa, 2006; chapter 3 and 4 of this thesis). The initial concentrations were 217 µg/L MC-LR_{eq} for microcystins and 2-3 mg/L for NOM model compounds. The Freundlich adsorption parameters for each compound are presented in Table 5.1 and data are depicted in Figure 5.1.

Table 5.1 – Freundlich adsorption parameters of microcystins and NOM model compounds

	K (µg/mg)(L/µg)$^{1/n}$	1/n	R^2
AHA	0.58	0.64	0.9413
AHA+IS	8.9	0.46	0.9298
TA	10.6	0.50	0.9519
TA+IS	16.5	0.55	0.9593
Microcystins	17.2	0.32	0.9299
SA	0.25	0.84	0.9612

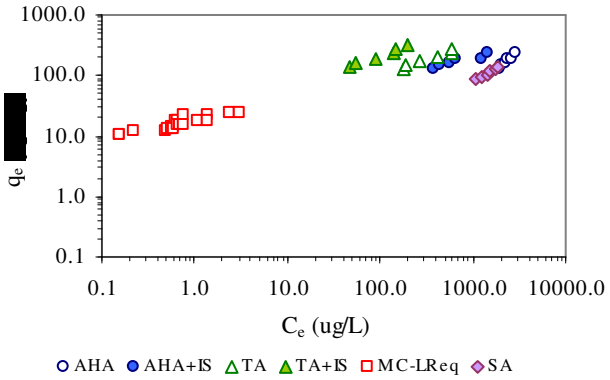

Figure 5.1 – Single-solute isotherms of microcystins and NOM surrogates in the presence and absence of background ionic strength.

Figure 5.1 and Table 5.1 demonstrate that microcystins (1.2 - 2.6 nm in diameter) have the higher adsorption capacity and adsorption intensity (smaller 1/n), which is consistent with the high volume of secondary micropores (0.8-2 nm; 22% of PAC pore volume) and mesopores (2-50 nm; 40% of PAC volume) of PAC Norit SA-UF (Donati *et al.*, 1994; Pendleton *et al.*, 2001). As it is known, compounds are more likely to adsorb in a pore of approximately its size, where there will be more contact points, and consequently stronger adsorption.

Tannic acid presented adsorption parameters comparable to those of microcystins, with a slightly lower adsorption capacity and intensity. These results provide good evidence of a similar access to a range of adsorption sites for both microcystins and TA. As TA is slightly higher than microcystins (1700 Da *vs.* 994-1024 Da), the lower adsorption capacity and the higher 1/n parameter for TA probably mean that microcystins are able to access a supplementary range of smaller secondary micropores that TA does not reach. This overall analysis agrees with Newcombe's *et al.* (1997) relation between the adsorption of 500-3000 Da NOM compounds with the volume of secondary micropores and mesopores. When in the presence of background ionic strength, there is an increase in TA adsorption capacity with no significant change in 1/n parameter, suggesting that additional pores are not available for TA, but there may be an improved packing of smaller TA molecules. In chapter 3 of this thesis, an adsorption reduced regime (decrease in adsorption with IS addition) was observed at low TA surface concentrations (6-18 mg/g). The present data, obtained at higher TA surface concentrations (131-320 mg/g), show an adsorption enhanced regime (increase in adsorption with IS). Therefore, and as predicted in chapter 3, between the two surface concentration ranges there is a crossover point corresponding to a transition regime.

The Freundlich parameters for AHA in ultrapure water indicate poor adsorption of this compound onto PAC Norit SA-UF. Although this PAC has 40% of mesoporous volume, not all mesopores are accessible to AHA molecules, which is consistent with the higher 1/n, associated with adsorption in larger pores. However, when AHA is in a 2.5 mM IS electrolyte, there is a huge improvement of its adsorption that may only be due to a reduction in AHA molecular size, enabling it to access smaller pores, and resulting in higher adsorption capacity (K) and stronger adsorption in smaller pores (lower 1/n values) (Table 5.1).

The adsorption capacity for SA and the adsorption intensity are both quite low, regardless of its small size and the high microporous volume available for adsorption (60% of PAC porous volume is on micropores). A reasonable explanation is its high hydrophilicity which renders it less adsorbable.

5.3.2 Microcystins-NOM Competition: C_0 effect

Several authors have demonstrated that in natural waters and below a given C_0 value, the percentage remaining (C/C_0) of micropollutants (simazine, simetryn, asulam, MIB, geosmin, atrazine) is not a function of C_0 for any carbon dosage (Knappe *et al.*, 1998; Gillogly *et al.*, 1999; Graham *et al.*, 2000; Cook *et al.*, 2001; Matsui *et al.*, 2003). In that case, the equilibrium adsorption may be determined by reference to one curve. However, Gillogly *et al.* (1999) referred that the relationship was specific for each type of carbon and was not valid at very high adsorbate concentrations. To investigate whether this held true for microcystins and PAC Norit SA-UF, competition isotherm data obtained at different initial microcystins concentration were represented by plotting the residual microcystins concentration (C/C_0) as a function of PAC dose (Figure 5.2).

Figure 5.2 illustrates that the residual microcystins concentration is very similar over the range of initial microcystins concentration tested (67-221µg/L MC-LR_{eq}). PAC performance, as far as microcystins residuals are concerned, is not affected by C_0, except when in the presence of a strong competitor such as TA. This behaviour is important for real PAC applications, with PAC doses being easily predicted based on the required percentage removal and on the contact time between PAC and water. Cook and Newcombe (1992) also found that the percentage remaining of MC-LR and MC-LA in natural waters was independent of C_0, with C_0 ranging between 17.3-108 µg/L for MC-LR and 20-97.2 µg/L for MC-LA.

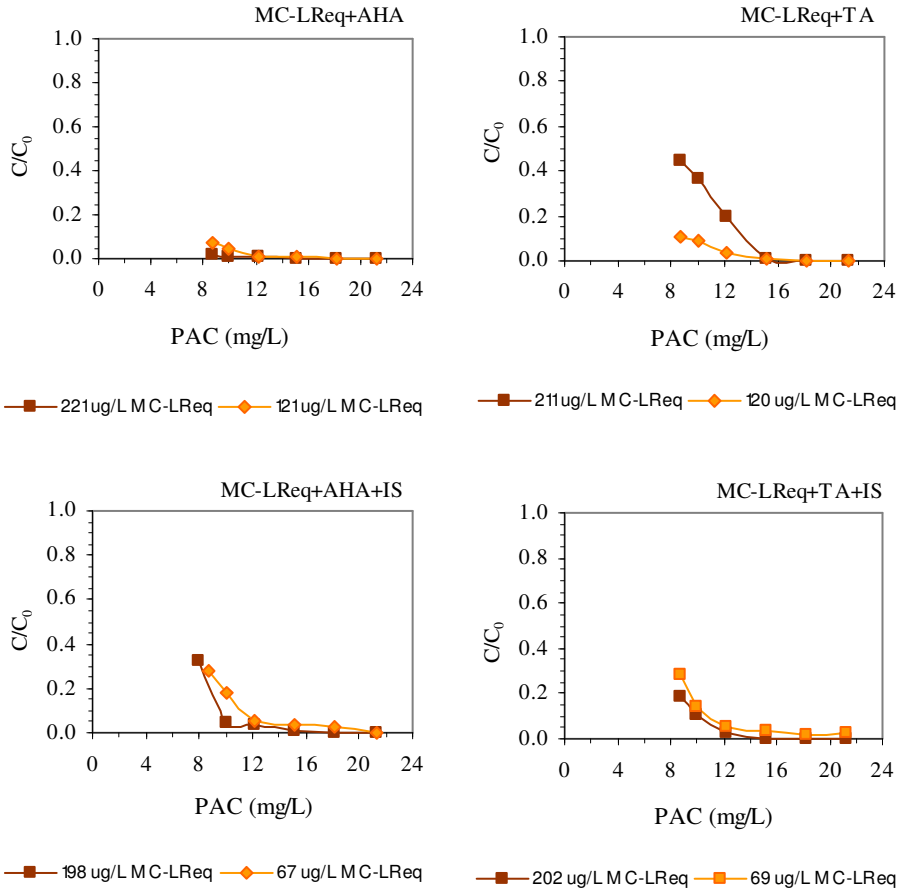

Figure 5.2 – Microcystins residuals (C/C_0) from microcystins-NOM competitive isotherms performed at different C_0, in the absence (top) and in the presence (bottom) of background 2.5 mM IS.

The C/C_0 independence relatively to C_0 results from the distinct adsorption capacity observed at different C_0, as shown in Figure 5.3. The figure shows that during competitive adsorption isotherms, the microcystins adsorption capacity was positively influenced by a C_0 increase, both in the absence and in the presence of background ionic strength. The same positive effect of C_0 on the micropollutants adsorption was already reported by Najm *et al.* (1991) for 2,4,6-trichlorophenol in the presence of background NOM. Therefore, adsorption isotherms must be carefully used for process modelling and optimisation since adsorption constants vary with C_0.

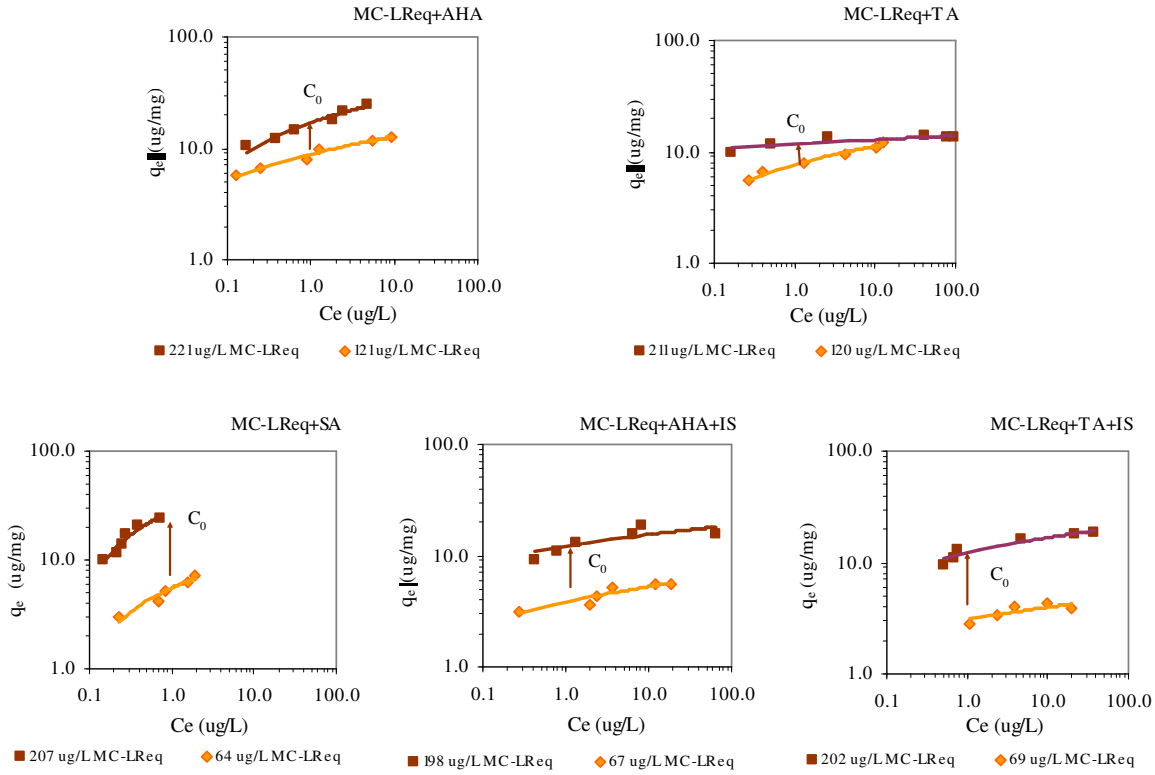

Figure 5.3 – Microcystins-NOM competitive isotherms performed at different C_0, in the absence and in the presence of background 2.5 mM IS.

5.3.3 Microcystins-NOM Competition: NOM surrogates

Several isotherm tests were performed to assess the microcystins-NOM competition at equilibrium. The initial concentrations were 207-221 µg/L MC-LR_{eq} for microcystins and 2-3 mg/L for NOM surrogates. Figure 5.4 compares the competitive adsorption isotherms of microcystins with the single-solute isotherm and Table 5.2 presents the corresponding Freundlich parameters. Figure 5.5 depicts the remaining aqueous concentration of microcystins as a function of PAC dose in competitive isotherms (*i.e.*, C/C_0 *vs.* PAC) and a comparison is made with NOM surrogate residuals.

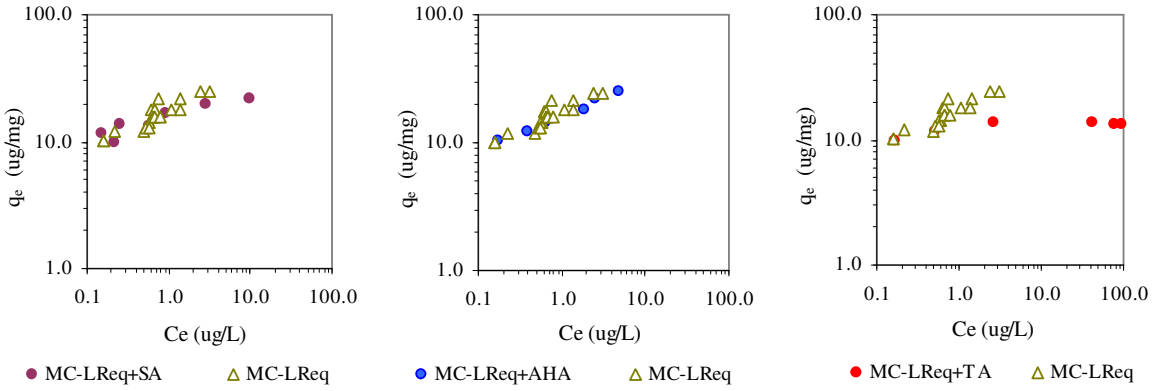

Figure 5.4 – Microcystins-NOM adsorption isotherms (left: 202 µg MC-LR_{eq}/L, 3 mg SA/L; center: 221 µg MC-LR_{eq}/L, 3 mg AHA/L; right: 211 µg MC-LR_{eq}/L, 2 mg TA/L).

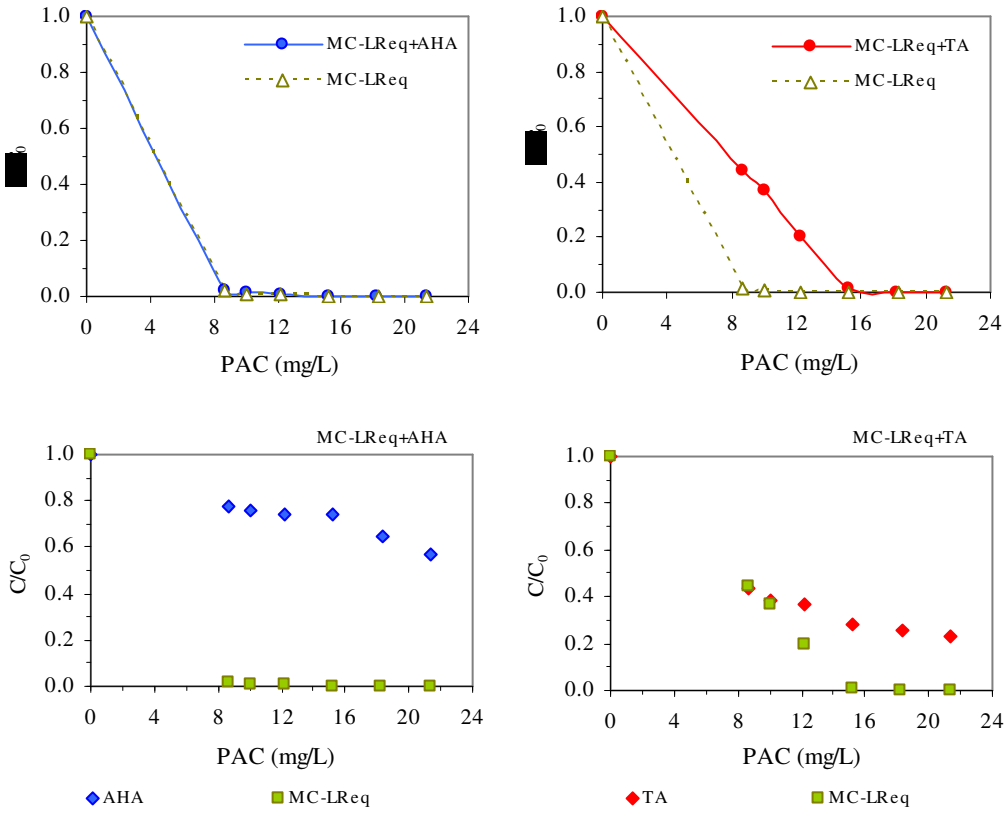

Figure 5.5 – Microcystins residuals in the presence of NOM surrogates (top) and comparison between microcystins and AHA residuals or microcystins and TA residuals (bottom) (211-221 µg MC-LR_{eq}/L, 3 mg AHA/L, 2 mg TA/L).

Table 5.2 – Freundlich adsorption parameters for microcystins in single-solute isotherms and in competitive isotherms with NOM surrogates.

	K (μg/mg)(L/μg)$^{1/n}$	1/n	R^2
Microcystins	17.2	0.32	0.9299
Microcystins + SA	15.6	0.18	0.9050
Microcystins + AHA	16.2	0.27	0.9843
Microcystins + TA	12.3	0.12	0.9963

Figure 5.4 and the Freundlich parameters in Table 5.2 reveal that, SA as previously observed in kinetic study (presented in Part I, chapter 4), has a minor effect on microcystins adsorption within the concentration and carbon dose ranges studied. A reduction in microcystins adsorption capacity was only observed at the lowest PAC dose (Figure 5.4), which is most liked caused by direct competition between SA and microcystins. At low carbon doses (yielding high equilibrium concentrations) some SA molecules must probably have to adsorb in secondary micropores and the limited number of sites results in competition with microcystins.

Concerning AHA, the competitive adsorption isotherm was also very close to the single-solute isotherm, showing a negligible competition between AHA and microcystins, as already found in the adsorption kinetics (Part I). As Figure 5.5 illustrates (bottom), AHA is much less adsorbed than microcystins (22-43% *vs.* 97.8-99.9% of the initial mass was adsorbed), and AHA molecules must adsorb in larger mesopores than those preferentially used by microcystins, which explains the low decrease of the adsorption capacity for microcystins in the presence of AHA and the very similar isotherm slope (adsorption intensity). Again, these results agree with those found in the kinetic study (Part I).

The log-log plot of microcystins isotherm in competition with TA was not linear at the highest equilibrium concentrations. K and 1/n were therefore determined using only the linear part of the isotherm. As previously observed in adsorption kinetics (Part I), TA had a more severe effect than SA and AHA, reducing both the adsorption capacity (K decreased 29%) and the slope of the single-solute isotherm. This is consistent with changes in the site-energy heterogeneity of pores used for microcystins adsorption, *i.e.*, with a direct site competition between microcystins and TA. Direct site competition also agrees with data found in Part I for the adsorption kinetics of microcystins and tannic acid: microcystins (smaller molecules) affected the rate of adsorption of TA (larger molecules) and caused TA displacement during preloaded kinetics.

However, direct site competition cannot explain the significant reduction of both the adsorption capacity and the rate of microcystins uptake (Part I), while pore constriction/blockage affects both of them (the adsorption kinetics and adsorption equilibrium) (Matsui *et al.*, 2003). Therefore and as previously proposed in Part I, direct site competition and pore constriction/blockage must both play a role in the microcystin-TA competitive adsorption. TA molecules are small enough to access small mesopores and some secondary micropores and may therefore directly compete with microcystins for the same adsorption sites. In doing so, however, TA molecules may block the access to even smaller micropores. As Kilduff *et al.* (1998) stated, pore blockage can occur on different scales, and as the scale decreases, it becomes more difficult to distinguish between pore blockage and direct site competition.

Results also demonstrate that when in competition for low carbon doses (Figure 5.4 and 5.5) the microcystins adsorption capacity was severely affected and TA and microcystins present

similar remaining concentrations (Figure 5.5, bottom), a curious aspect discussed in the next section.

5.3.4 Microcystins-NOM Competition: NOM surrogates and ionic strength

The results obtained for competitive kinetics in the presence of background aqueous ionic strength (Part I, chapter 4) revealed changes on competition for AHA and TA but not for SA. Competitive adsorption isotherms with the addition of salts were therefore studied only for AHA and TA. The initial concentrations were 198-221 μg/L MC-LR_{eq} for microcystins and 2-3 mg/L for NOM surrogate, and the background 2.5 mM IS (1 mM from K and 1.5 mM from Ca) represents moderately hard natural water. Results are presented in Figure 5.6 and Table 5.3.

As already discussed in Part I, the water ionic strength (IS) decreases the molecular size distribution of humic acid molecules initially present in solution. This solute shrinkage enables a fraction of AHA molecules to access the smaller mesopores, and perhaps the larger secondary micropores, which is in agreement with Kilduff and Karanfil (2002) results. As a consequence of this improved access to carbon pores, there is an enhancement of the AHA uptake from solution, augmenting the tortuosity of transport pores, or blocking the pores entrance against the microcystins. Isotherm results confirm the hypothesis of pore blockage, since the addition of IS is responsible for a reduction in the adsorption capacity, without changing the site-energy heterogeneity parameter, 1/n. Carter *et al.* (1992) interpreted the change in the Freundlich isotherm parameters in terms of number and heterogeneity of adsorption sites remaining. The closer the 1/n value is to unity, the more homogeneous the surface site energies. These authors suggest that a constant slope is consistent with a pore

blockage mechanism, as this would decrease the available pore sites in an even manner, thereby maintaining the overall heterogeneity of the surface.

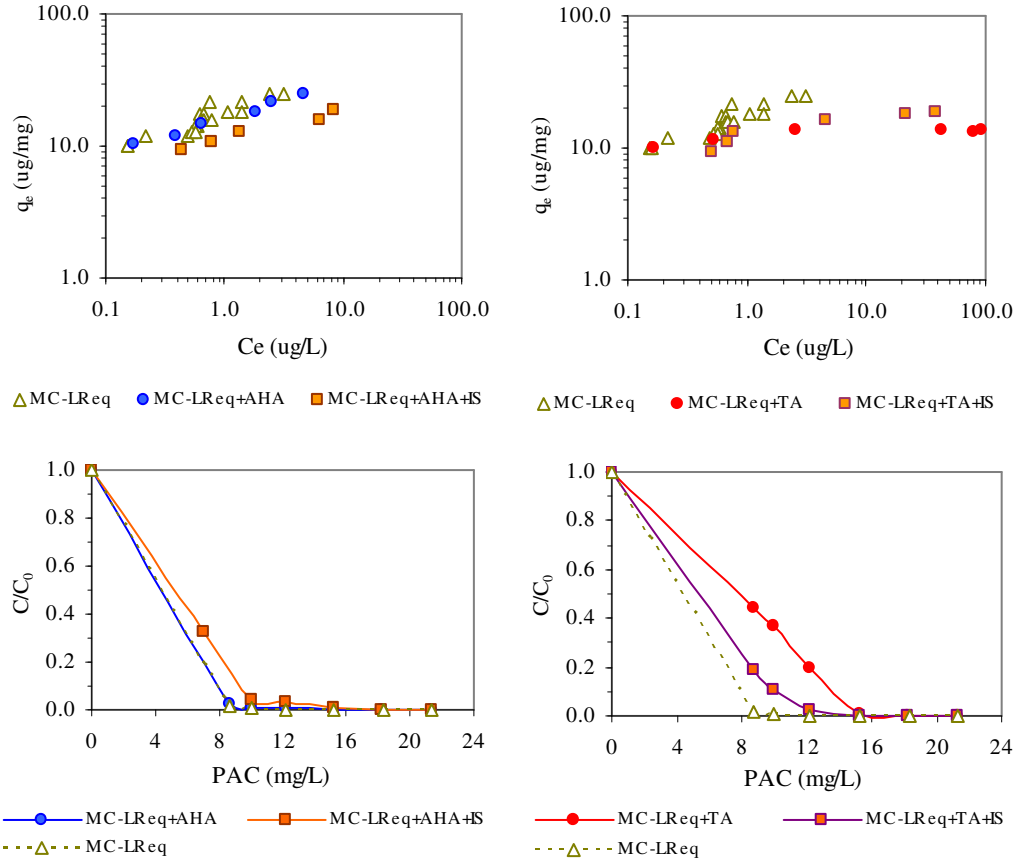

Figure 5.6 – Competitive adsorption isotherms of microcystins with AHA (left) or TA (right) in the absence and in the presence of background ionic strength (left:3 mg AHA/L, 198-221 µg MC-LR$_{eq}$/L; right: 2 mg TA/L, 202-211 µg MC-LR$_{eq}$/L).

Table 5.3 – Freundlich adsorption parameters for microcystins in competitive isotherms, in the absence and presence of ionic strength.

	K (µg/mg)(L/µg)$^{1/n}$	1/n	R^2
Microcystins + AHA	16.2	0.27	0.9843
Microcystins + AHA+IS	11.4	0.22	0.9606
Microcystins + TA	12.3	0.12	0.9963
Microcystins + TA+IS	11.9	0.14	0.8705

Regarding the microcystins-TA competition, a small enhancement of the rate of microcystins adsorption was found in the presence of background 2.5 mM IS (Part I). It was proposed that with the slight reduction in TA size, some pore blockage could have been changed to pore constriction, attenuating the negative effect of TA competition. Once again, isotherm results corroborate this hypothesis, since there is an increase in the microcystins uptake for low carbon doses (Figure 5.6). As already seen in single-solute isotherms (section 5.3.1), the water ionic strength improves TA adsorption and also enhances the microcystins adsorption during TA competition at low carbon dose. For direct competition to be the dominant mechanism, the improvement of one adsorbate adsorption should result in the reduction of the other. Since this was not the case, pore constriction must be the dominant mechanism for TA competition with microcystins.

Microcystins-TA competition may be further investigated comparing the single-solute and competitive adsorption kinetics at low PAC dose, from Part I (Figure 5.7). At low carbon doses and when individually studied, TA and microcystins have different adsorption rates, which is comprehensible given the higher affinity of microcystins to the Norit SA-UF PAC. However, when they coexist in water, they have similar adsorption rates, a curious observation found in all competitive kinetics of microcystins with TA performed with 5 mg/L PAC (Figure 5.7). The microcystins rate of adsorption is thereby strongly conditioned by TA uptake, suggesting a very similar adsorption path, where it is probable that direct competition and pore constriction/blockage coexist.

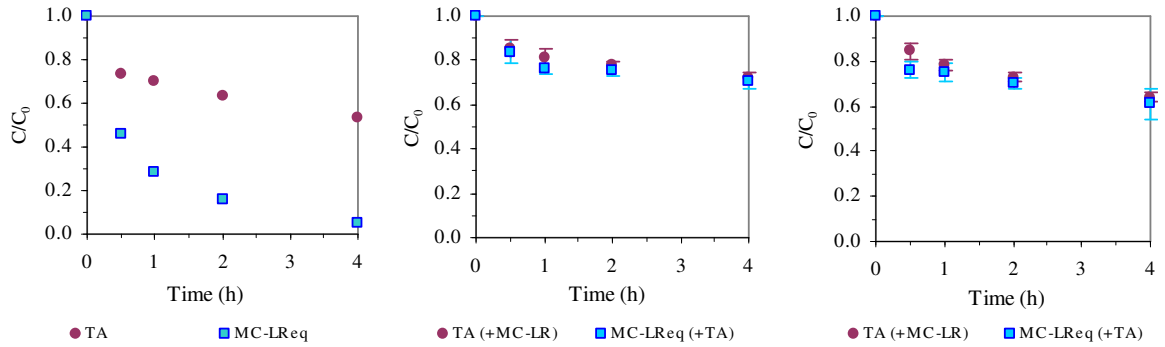

Figure 5.7 – Microcystins and TA residuals obtained during kinetics with low carbon dose (5 mg/L) (left: TA and microcystins single solute kinetics; center: MC-LR_{eq}-TA competitive kinetics; right: MC-LR_{eq}-TA competitive kinetics in the presence of 2.5 mM IS).

Concluding, the NOM model compounds studied (AHA, TA and SA) differently affected the microcystins adsorption kinetics (Part I) and equilibrium (Part II). In the presence of background 2.5 mM IS, the NOM surrogate larger than microcystins (AHA) reduced the microcystins adsorption kinetics and adsorption capacity through pore blockage, while the smaller NOM surrogate (SA) slightly reduced the microcystins adsorption capacity by direct site competition. A similar behaviour was found by Li *et al.* (2003 a) for atrazine-NOM competition. The stronger competition was verified for TA, the compound with the closest size to microcystins, a feature already obtained by other authors (Newcombe *et al.*, 1997). However, as previously observed in Part I, this does not necessarily mean that the dominant competition mechanism is direct competition as usually inferred. An integrated analysis of all TA results (Part I and II) indicate that pore constriction must be the leading mechanism, whereas direct competition for adsorption sites would only become important at higher loadings, when both adsorbate compete for large secondary micropores and small mesopores. As suggested by Kilduff *et al.* (1998), these two mechanisms become indistinguishable as the competing and target compounds become closer in size.

This strong TA competition severely impacted PAC dosage necessary to achieve the same microcystins residuals, *e.g.*, for negligible residuals PAC should be increased 50% in the presence of IS (from 8 mg/L to 12 mg/L) and doubled in its absence (from 8 mg/L to 16 mg/L).

5.3.5 Microcystins-NOM Competition: Natural surface water

Microcystins-NOM competitive adsorption isotherms were also performed with pre-ozonated clarified surface water (collected at Tavira Water Treatment Plant, in Algarve, Portugal) (Table 5.4). As discussed in Part I, this is a moderately hard water with NOM largely composed of non-humic materials, *i.e.*, with small hydrophilic NOM molecules (Edzwald and van Benschoten, 1990).

Table 5.4 − Characteristics of the natural surface water used in isotherm experiments, after spiking with microcystins

pH	EC (μS/cm)	TOC (mg C/L)	DOC (mg C/L)	UV_{254} (cm^{-1})	SUVA (L/(mg.m))	Turbidity (NTU)	Ca (mg/L)	Mg (mg/L)	$MC\text{-}LR_{eq}$ (μg/L)
7.1	213	2.7	2.1	0.012	0.6	0.36	17	8	219

EC-electric conductivity; SUVA: specific UV absorbance, defined as the UV_{254} absorbance (meter) per unit concentration of DOC in mg C/L.

Figure 5.8 compares the competitive and the single-solute adsorption isotherms, showing that, in contrast with the kinetic results (Part I), microcystins adsorption capacity is highly reduced when in the presence of the organic and inorganic matrices of the clarified water, especially at high surface concentrations. The almost vertical and negative slope observed at the lowest carbon doses studied (8-12 mg/L) points out a strongly competitive region for microcystins and water background NOM. According to Pelekani and Snoeyink (2000), this behaviour

occurs if the competing adsorbates are more strongly adsorbed than the target compound, outcompeting it for the limited number of adsorption sites available at low carbon doses.

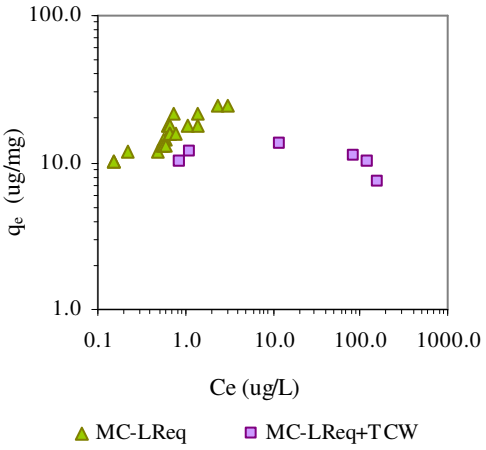

Figure 5.8 – Microcystins-NOM competitive isotherms from preozonated, clarified surface water (TCW) (219 µg MC-LR_{eq}/L).

For low Ce values, Figure 5.8 shows a reduction in the microcystins adsorption capacity and a change in the slope of the single-solute isotherm, which is in agreement with direct site competition between the water NOM and the microcystins for adsorption in small mesopores and secondary micropores. Pelekani and Snoeyink (1999) and, very recently, Ding *et al.* (2008) studies with a groundwater revealed that, indeed, the carbon capacity for NOM best correlates with the surface area in this porous range (1.5-5 nm). Based on NOM structural characterization studies, Newcombe (1994) also proposed that NOM should be able to adsorb in some secondary micropores.

These results were further supported by a latter characterisation of Tavira´s natural water NOM through size exclusion chromatography (HPSEC). The HPSEC results evidenced the small size of the filtered water, with 70% below 1 kDa and 30% between 1-3 kDa (Figure 5.9).

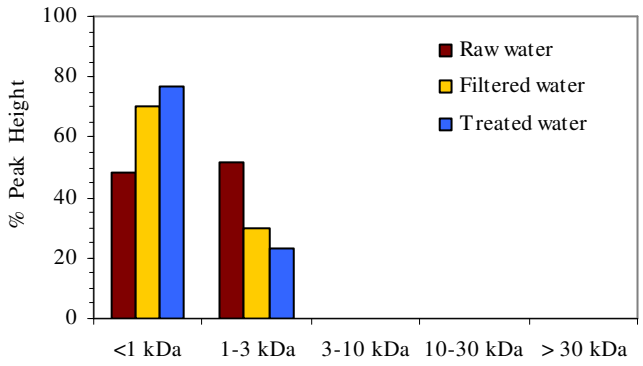

Figure 5.9 – Characterisation of Tavira´s natural water NOM by size exclusion chromatography (Dionex Summit HPLC; PDA detection at 254nm; TSK-3000SW column; phosphate buffer 20 mM, pH = 6.8; 0.5 mL/min; calibration against PSS standards).

Based on kinetic (Part I) and isotherm (Part II) results, direct site competition would rule the microcystins-NOM adsorption if a PAC/UF system was applied after the clarification step at Tavira WTP. In turn, kinetic data predict no significant negative effect of these small hydrophilic NOM competing molecules on the microcystins uptake.

5.4 CONCLUSIONS

The microcystins-NOM competition varied with the NOM molecular size and the presence of aqueous background ionic strength.

Similarly to kinetics results (Part I), AHA molecules did not affect microcystins adsorption capacity, confirming the adsorption in different pores. Also, the water background ionic strength induced AHA competition, reducing the adsorption capacity without changing the adsorption intensity. Isotherm results corroborated the pore blocking mechanism. No effect was noticed for the small, hydrophilic salicylic acid, except the direct competition observed at the lowest PAC dose.

The most severe competition was observed for tannic acid, the NOM surrogate closest in size to microcystins, a feature already observed in the adsorption kinetics (Part I), although the capacity reduction was not as extensive as the adsorption rate decrease. The water ionic strength improved the adsorption of both competing adsorbates (TA and microcystins) at low carbon doses (as well as the adsorption kinetics, Part I), which is consistent with a better arrangement of TA molecules and a change from pore blockage to pore constriction. An integrated analysis of the kinetic and equilibrium data (Part I and II) indicated that pore constriction must be the leading mechanism, whereas direct competition (for small mesopores) would only become important at higher loadings. Results confirmed that the preferential competition between compounds of similar size does not necessarily imply a direct site competition mechanism. Rather, the direct site competition and the pore blockage/constriction mechanism become indistinguishable as the target contaminants become closer in size.

PAC performance, as far as microcystins residuals are concerned, is not affected by the initial microcystins concentration, except when in the presence of the strong competitor TA. To overcome TA competition and achieve negligible residuals, PAC should be increased 50% in the presence of IS and doubled in its absence.

Kinetic (Part I) and isotherm (Part II) studies with natural surface water showed that direct site competition would rule the microcystins-NOM adsorption if a PAC/UF system is applied after the clarification step at Tavira WTP. In turn, kinetic data predict no significant negative effect of these small hydrophilic NOM competing molecules.

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