CHAPTER 4

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

ABSTRACT

In this chapter is investigated the combined effect of natural organic matter (NOM) and water background ionic strength (IS) on microcystins adsorption rate onto fresh and preloaded carbon (PAC Norit SA-UF). Results with NOM surrogates and preozonated clarified water demonstrated the important role of both the adsorbate's size similarity and the water IS on NOM competition. Adsorption kinetics showed no effect of humic and salicylic acids onto microcystins adsorption rate, and a severe impact of tannic acid (TA), which, due to its closest size to microcystins, participated in pore constriction/blockage and probably direct size competition. IS induced AHA competition, by reducing its size and causing pore blockage. PAC preloading with AHA further hindered the microcystins adsorption. In opposition, IS slightly attenuated TA-microcystins competition, probably converting pore blockage into pore constriction. A same positive effect was observed by PAC preloading with TA, caused by TA displacement by microcystins. Kinetic models were consistent with these competition mechanisms. The data were best fitted by the pseudo-second order model, and the stronger the NOM competition, the lower its q_e and h parameters. Intraparticle diffusion controlled the microcystins adsorption from NOM model solutions, whereas the external diffusion was the rate-limiting step for microcystins uptake from surface water.

4.1 INTRODUCTION

Cyanotoxins may cause significant problems to water suppliers for their recognized human and animal potential health risk. Microcystins (hepatotoxins) are the most commonly occurring cyanotoxins in drinking water reservoirs. The World Health Organisation (WHO) has established a drinking water guideline value of 1.0 µg/L for microcystin-LR, one of the most toxic and commonly occurring microcystins.

Microcystins are extremely stable and resistant to conventional chemical oxidation, requiring more advanced treatment in water treatment plants (WTP). The hybrid process of powdered activated carbon adsorption and ultrafiltration (PAC/UF) is one of the most promising treatment technologies for cyanotoxin removal and its success depends of an efficient PAC adsorption.

Microcystins are moderately hydrophobic compounds and the MC-LR, -LY, -LW and -LF variants are easily adsorbed by mesoporous carbon in the absence of competing compounds (Campinas and Rosa, 2006). However, in natural waters where natural organic matter (NOM) is one thousand times more concentrated than microcystins, the competition effect of NOM onto microcystins adsorption may be critical. Previous studies have demonstrated that NOM may adversely impact the adsorption kinetics (Cook *et al.*, 2001; Newcombe *et al.*, 2002; Li *et al.*, 2003 a; Matsui *et al.*, 2003) and/or the adsorption capacity (Newcombe *et al.*, 1997, 2002; Kilduff *et al.*, 1998 a, b; Pelekani and Snoeyink, 1999; Cook *et al.*, 2001; Ebie *et al.*, 2001; Matsui *et al.*, 2003; Quinlivan *et al.*, 2005) of the target compounds.

Pore blockage and direct site competition are considered the two main mechanisms affecting the activated carbon adsorption in the presence of NOM. Newcombe *et al.* (1997) results

showed that the low molecular weight NOM compounds (500-3000 Da) exerted a higher competitive effect on 2-methylisoborneol (MIB) adsorption and attributed that effect to direct site competition. Nevertheless, recent studies have showed that the small NOM compounds may also participate in pore constriction/blockage (Pelekani and Snoeyink, 1999, 2001; Ebie *et al.*, 2001; Newcombe *et al.*, 2002), and accordingly, Li *et al.* (2003 a) concluded that NOM with MW between 200 and 700 Da was the most likely responsible for the pore blockage mechanism in atrazine adsorption.

Pore size distribution of carbon, as well as the relative sizes of the target and the competing compounds are key properties that determine the extension of competitive adsorption and the dominant mechanism of competition (Pelekani and Snoeyink, 1999, 2000, 2001; Ebie *et al.*, 2001; Newcombe *et al.*, 2002; Li *et al.*, 2003 a, b). Actually, the adsorption capacity of small micropollutants (*e.g.* MIB, atrazine and trichloroethylene (TCE)) is mostly determined by micropore volume, and several authors concluded that a broadening of PAC pore size distribution may reduce, and even avoid, pore blockage by NOM (Newcombe *et al.*, 1997; Pelekani and Snoeyink, 1999, 2001; Ebie *et al.*, 2001; Li *et al.*, 2003 a, b; Quinlivan *et al.*, 2005; Ding *et al.*, 2008).

Most competitive adsorption approaches developed to date have focused primarily the NOM impact on the equilibrium adsorption of small organics (below 300 Da, *e.g.*, TCE, atrazine, MIB) (Newcombe *et al.*, 1997; Kilduff *et al.*, 1998 a, b; Pelekani and Snoeyink, 1999) that adsorb preferentially in primary micropores, where it is believed that NOM cannot access. Microcystins are larger (~1000 Da) than those target-compounds and of similar size of the small NOM, both preferentially adsorbing in secondary micropores and mesopores (Donati *et al.*, 1994; Pendleton *et al.*, 2001). Although competition studies are important, attention has

until now been focused on carbon properties (porosity and surface chemistry) that maximize the microcystins removal (Donati *et al.*, 1994; Mohamed *et al.*, 1999; Pendleton *et al.*, 2001; Lee and Walker, 2006; Huang *et al.*, 2007) and studies on competitive adsorption kinetics are rather scarce. However, adsorption equilibrium is rarely achieved in PAC/membrane reactors and the impact of competition on kinetics is extremely important, as it controls the PAC dose required for cyanotoxins removal. PAC preloading studies are also important given that in PAC/membrane systems, PAC is kept in the system, while water passes through, exposing it to NOM and causing a similar effect to PAC preload in batch systems (Li *et al.*, 2003 a).

Furthermore, organic and inorganic matrices coexist in natural waters and there is general acceptance that the aqueous ionic strength interferes with the adsorption of NOM compounds, particularly the high molecular weight fraction (Randtke and Snoeyink, 1983; Kilduff *et al.*, 1996; Li *et al.*, 2002; Campinas and Rosa, 2006). In spite of this, the research addressing the impact of ionic strength on competitive adsorption is, as far as my knowledge go, limited to Kilduff and Karanfil (2002) study. These authors concluded that the preload of an activated carbon with humic acid in the presence of ionic strength further reduced TCE adsorption as a result of increased uptake of organic matter.

Given the previous background, it is intended to study the impact of NOM onto microcystins adsorption kinetics in the presence of controlled aqueous ionic strength and using fresh (simultaneous adsorption condition) and preloaded PAC. Besides assessing the NOM responsible for the greatest competitive effect and the probable competitive adsorption mechanisms, this paper aims to investigate the ionic strength contribution to the competitive effect of NOM onto the microcystins adsorption kinetics. The combined effect of NOM and

water background ionics onto the microcystins adsorption isotherms will be addressed in part II of this paper (chapter 5 of this thesis).

Even though the effect of NOM molecular weight has been studied by using NOM fractions (Newcombe *et al.*, 1997, 2002), it is complex to quantify the contribution of each NOM fraction to direct site competition and pore blockage as NOM molecules present in any fraction may cause both effects. To simplify the NOM system, some authors have used model compounds in competition studies (Pelekani and Snoeyink, 2000, 2001; Li *et al.*, 2003 b). In this study NOM surrogates as well as natural surface water were used.

4.2 MATERIALS AND METHODS

4.2.1 Adsorbates

Microcystins were used as the target adsorbate. Microcystins were produced and extracted from *Microcystis aeruginosa* laboratory grown culture (Pasteur Culture Collection Cyanobacteria). The procedure for microcystins extraction is described elsewhere (Campinas and Rosa, 2006). Four microcystins variants were detected by high performance liquid chromatography (HPLC), *i.e.*, MC-LR, -LY, -LW and -LF. The dominant microcystin variant was MC-LR, accounting for *ca.* 75% of total microcystins. Molecular weights of these four microcystins vary between 985 and 1024 Da (Sivonen and Jones, 1999). All variants were quantified as MC-LR equivalent and the overall concentration is therefore given in μg/L MC-LR_{eq}.

Salicylic acid (SA, reagent grade Merck), tannic acid (TA, Sigma) and humic acid (AHA, Aldrich) were used as model compounds to simulate small hydrophilic, moderate size relatively hydrophilic and large hydrophobic NOM molecules, respectively. SA has a molar

mass of 138 Da and TA is approximately 1700 Da. Molecular weight of humic acids is difficult to advance for they are mixed molecular compounds. However, values of 4100, 3070, 14500 and 3000 – 11000 Da have been reported for AHA (Chin *et al.*, 1994; Yamada *et al.*, 2000). AHA was purified through a repeated precipitation with HCl to remove bound iron and decrease the ash content, using Hong and Elimelech (1997) method. Prior to model solution preparation, AHA stock solution was filtered through GF-C (1.2 μm) and GF-F (0.7 μm) filters.

4.2.2 Model Solutions

Organic-free ultrapure water was obtained from a Milli-Q water purification system (resistance ≥ 18 MΩ/cm). Potassium chloride (1 mM IS) and calcium chloride (1.5 mM IS) were used to prepare the electrolyte solutions with 2.5 mM of overall ionic strength, which corresponded to an electric conductivity of 280-300 μS/cm. Model solutions of microcystins were prepared with controlled organic and inorganic matrices, *i.e.*, MC variants were dissolved in solutions of AHA plus SA or in TA in ultrapure water or in 2.5 mM IS background electrolyte. For comparison purposes, model solutions of each adsorbate (microcystins or NOM surrogates in ultrapure water and in electrolyte solution) were studied, corresponding to a non-competition scenario. The concentrations studied ranged from 32 to 137 μg/L MC-LR_{eq}, 1.7-2.7 mg/L of AHA, 1.6-1.9 mg/L of SA and 2-3.2 mg/L of TA corresponding to 1.5 to 3.2 mgC/L.

4.2.3 Natural Surface Water

The natural water used was Beliche reservoir water, sampled at Tavira WTP, after ozonation, and clarification by coagulation/sedimentation (TCW) (Table 4.1). Upon arrival the water was stored at 4ºC and used within two days.

Table 4.1 - Characteristics of the natural surface water (TCW) used in adsorption kinetic experiments, after spiking with microcystins.

pH	EC (µS/cm)	TOC (mg C/L)	DOC (mg C/L)	UV_{254nm} (cm^{-1})	SUVA (L/(mg.m))	Turbidity (NTU)	Ca (mg/L)	Mg (mg/L)	$MC\text{-}LR_{eq}$ (µg/L)
7.3	177	1.4	1.3	0.015	1.2	0.38	17	7.7	28

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

As expected, this preozonated clarified natural water is a very low turbidity, low organic carbon (USEPA, 1999) and moderately hard (Sawyer *et al.*, 1994) water. The background 2.5 mM ionic strength used in model solutions was in fact chosen to represent the inorganic matrix of the natural waters used to produce drinking water in Algarve region (Portugal) both in terms of conductivity and hardness cations. In addition, the low SUVA values of TCW suggest a non-humic water, with hydrophilic low molar mass NOM (Edzwald and Van Benschoten (1990) experience with numerous surface waters has shown that a SUVA of 2 L/(mg.m) indicates a non-humic water, while a SUVA greater than 6 indicates a humic rich water). This feature is easily understood, since TCW was preoxidized with ozone which breaks down NOM molecules into smaller ones. In addition, there is a clarification step before TCW samples collection, which preferentially removes the remaining hydrophobic and high molar mass NOM molecules.

4.2.4 Adsorbent

PAC Norit SA-UF was used in this research. This PAC has a low particle mean diameter (6 μm) and a wide-opened structure, which is important to adsorb microcystins in the presence of NOM. It presents a high specific surface area coupled with a large pore size distribution (38% of primary micropore volume (0,343 cm^3/g); 22% of secondary micropore volume (0,194 cm^3/g) and 40% of mesopore volume (0,357 cm^3/g) (Campos *et al.*, 2000; Li *et al.*, 2002; Li *et al.*, 2003 b). Such characteristics are important since it was found that MC-LR adsorption correlated with secondary micropores plus mesopore volumes (Donati *et al.*, 1994; Pendleton *et al.*, 2001). From previously published data on PAC surface charge measurement (Campinas and Rosa, 2006), the PAC Norit SA-UF has its point of zero charge at pH 9.6, and therefore displays a positive charge at the pH values studied in this research. Carbon was oven dried at 105ºC overnight to remove excess water and stored in a desiccator until use.

4.2.5 Analytical Methods

Filtered samples (through 0.7 μm glass-fiber filters) from the adsorption kinetic studies were analysed for conductivity, pH, microcystin variants (as MC-LR equivalents) and/or NOM surrogates. Electrical conductivity (at 25ºC) and pH (at 20ºC) were analysed electrometrically using a Crison GLP 32 conductimeter and a WTW pH 340 meter, respectively. Microcystin samples were analysed by HPLC with a photo-diode array detector, using the sampling and the analytical procedures of Meriluoto and Spoof (2005 a, b) and described in chapter 3. NOM model compounds were measured by UV absorbance with a UV/VIS spectrophotometer (Beckman DU 640B) at 254 nm for AHA, 215 nm for TA and 210 nm for SA. Calibration curves between UV absorbance and AHA, TA and SA concentrations were established with good correlations.

4.2.6 Adsorption Kinetics

Several adsorption kinetic tests using 5 mg/L of fresh PAC were performed: i) adsorption kinetics of microcystins, TA or AHA plus SA in ultrapure water and in 2.5 mM IS electrolyte solution; ii) competitive adsorption kinetics of microcystins in the presence of TA or AHA plus SA (in ultrapure water and in 2.5 mM IS electrolyte); iii) competitive adsorption kinetics of microcystins in Tavira's WTP clarified water (TCW).

The device used for the simultaneous competition kinetics was a jar-test *apparatus* with four positions (Flocumatic, Selecta). Prior to its application, PAC was soaked overnight in ultrapure water to allow for complete wetting of the pores. Mixing was maintained (125 rpm; 5 minutes) before PAC addition and samples were taken at predetermined time intervals over a 4 h period after PAC addition. Identical mixing (200 rpm), volume of water (500 mL) and temperature conditions (21-23ºC) were applied to all batch reactors.

Microcystins adsorption kinetics were also conducted using PAC preloaded with TA, AHA plus SA in ultrapure water and with a 2.5 mM IS background electrolyte. A 5 mg/L dose of PAC was first preloaded with 2-3 mg/L of NOM surrogates, in a 2.5 L glass bottle during 65 h. Samples were taken before and after the preloading to calculate the solid phase concentration of the competing compound. Mixing was maintained while taking the sample so that the carbon concentration remained the same after sampling. Microcystin solution was then spiked into the bottle to obtain the desired initial concentration, and samples were taken at predetermined time intervals over a 4 h period.

4.3 RESULTS AND DISCUSSION

4.3.1 Kinetic Studies with Model Solutions and Fresh PAC

Batch kinetic competition tests were conducted with 34 µg/L of MC-LR$_{eq}$ and with a solution containing a mixture of high and low molecular weight NOM surrogate (*ca.* 2 mg/L of AHA plus 2 mg/L SA). Several adsorption kinetics were also performed with a solution containing 2-3.2 mg/L of TA and 33-137 µg/L MC-LR$_{eq}$. To investigate the ionic strength effect, in some experiments NOM model solutions were supplemented with potassium and calcium salts to accomplish a background aqueous ionic strength of 2.5 mM.

Figure 4.1 presents microcystins adsorption kinetics, when microcystins and NOM model compounds were simultaneously contacted. For comparison purpose, single-solute kinetics of MC-LReq, SA, TA and AHA were also depicted (no competition situation). The kinetic curves presented in Figure 4.1 (right) for microcystins are the average data of four independent trials (error bars represents the standard deviation).

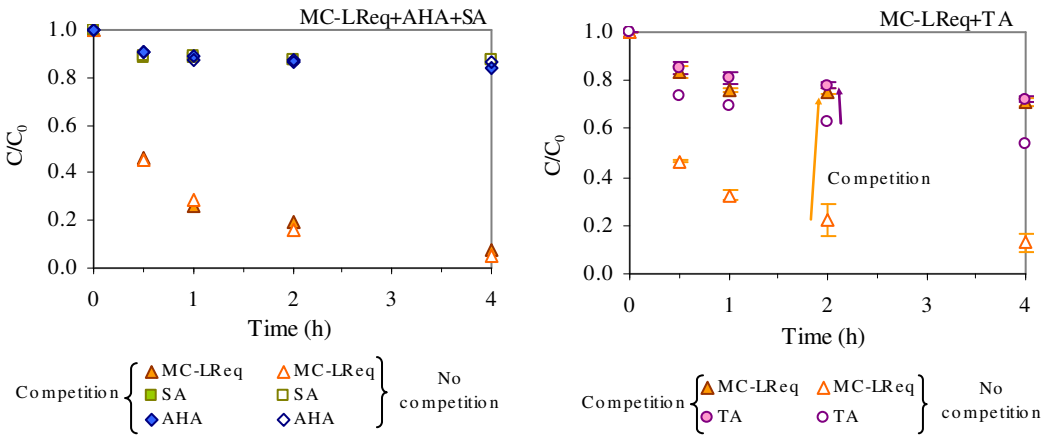

Figure 4.1 – Adsorption kinetics in the absence (open symbols) of competition and under competition (full symbols) between microcystins and AHA+SA (left) or microcystins and TA (right) (5 mg/L PAC; left: 34 µg MC-LR$_{eq}$/L, 1.6 mg SA/L, 2 mg AHA/L; right: 33-137 µg MC-LR$_{eq}$/L, 2-3.2 mg TA/L).

The kinetic curve for microcystins adsorption onto fresh PAC SA-UF in the presence of AHA and SA is close to that of microcystins in organic-free water (Figure 4.1, left), showing no effect of large (AHA) and very small (SA) molecules in microcystins adsorption rate. The absence of AHA effect may be explained by two main reasons, both related to the high molecular weight of AHA molecules compared to microcystins. First of all, these larger molecules preferentially adsorb in wider mesopores than those preferred by microcystins. Secondly, the larger AHA molecules have a slower diffusion rate through the narrow pores of PAC SA-UF and are not then able to block or constrict the pores before the microcystins adsorb to the PAC surface. On the other hand, hydrophilic SA molecules mostly adsorb in primary micropores, not disturbing microcystins adsorption.

However, the adsorption kinetic of microcystins in the presence of tannic acid (TA) is severely affected (the normalised aqueous concentration (C/C_0) increased from 0.13 to 0.70 after 4 h of contact time with 5 mg PAC/L (Figure 4.1, right), consistent with the occurrence of pore blockage/constriction mechanisms. TA molecules are probably able to access the mesopores and the large secondary micropores pores where microcystins preferentially adsorb. However, TA is bigger than microcystins (1700 Da *vs.* 994-1024 Da) and may therefore reduce the pore size (constriction), delaying the microcystins diffusion. Pore blockage of the smaller secondary micropores is also possible, restricting the direct access of microcystins, and resulting in a more tortuous diffusion path for the target contaminant. These results confirm that the competition between a microcontaminant and small NOM compounds does not necessarily imply a direct site competition mechanism. As referred by other authors, small NOM compounds may also participate in pore constriction/blockage (Pelekani and Snoeyink, 1999, 2001; Ebie *et al.*, 2001; Newcombe *et al.*, 2002; Li *et al.*, 2003 a).

Figure 4.2 presents the competitive adsorption kinetics onto fresh PAC of microcystins and NOM model compounds in the absence and in the presence of aqueous background electrolyte. The data series with error bars (standard deviations) represent three (left) or four (right) replicates.

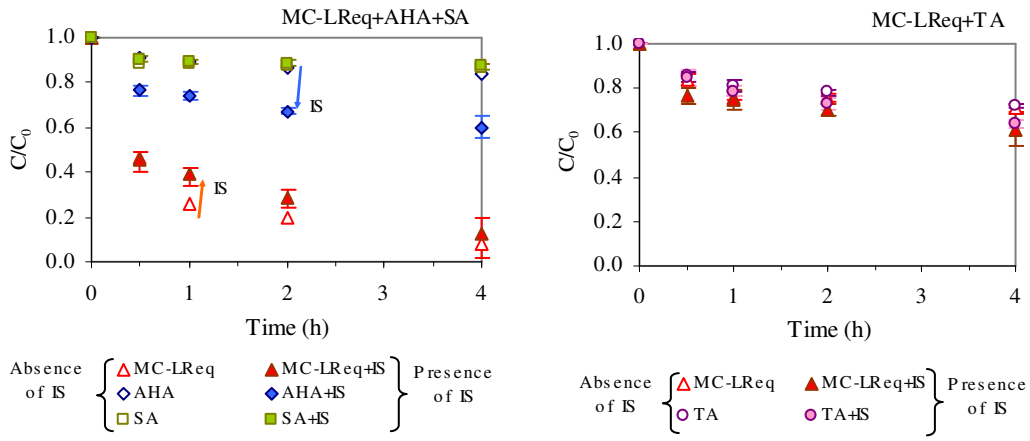

Figure 4.2 – Competitive adsorption kinetics of microcystins with AHA+SA (left) or TA (right) in the absence (open symbols) and in the presence (full symbols) of 2.5 mM background ionic strength (left: 32-46 µg MC-LR_{eq}/L, 1.7-2 mg AHA/L, 1.6-1.9 mg SA/L; right: 33-137 µg MC-LR_{eq}/L, 2-3.2 mg TA/L).

While Figure 4.1 (left) showed no effect of AHA and SA on microcystins adsorption rate in ultrapure water, Figure 4.2 (left) shows that the ionic strength addition enhanced AHA adsorption, which is apparently related with the decline observed on microcystins rate of diffusion. As previously concluded by Campinas and Rosa (2006) and by other authors (Randtke and Snoeyink, 1983; Kilduff and Karanfil, 2002; Li *et al.*, 2002), the ionic strength effect depends on the adsorbate molecular size. Campinas and Rosa (2006) (chapter 3 of this thesis) verified that potassium plus calcium addition induced negligible changes on salicylic acid adsorption, while an enhancing effect was found on the rate of adsorption of microcystins (mainly observed for the more charged variants and higher IS such as 10 and 100 mM), tannic

acid and, particularly, of humic acid. A reasonable explanation was that the ionic strength decreases the adsorbate molecular size (by reducing the intramolecular charge repulsion) and that change is more significant for larger molecules, facilitating their transport through the narrow pores of carbon and enabling them to access additional surface area, which is usually not available. These conclusions are consistent with the kinetic results presented in Figure 4.2. Probably, the above mentioned reduction of humic acids molecular size increases their adsorption diffusion and their access to smaller mesopores and thus increases transport pores tortuosity and/or blocks pore entrance for microcystins.

The rate of adsorption of microcystins in the presence of TA (Figure 4.2-rigth), on other hand, is somewhat improved by the ionic strength addition. The explanation seems to be the same as for AHA, but for TA a constriction/blockage mechanism was already observed in the ultrapure water. Therefore, the slight solute shrinkage and its better packing into pores driven by the backgrounds inorganic means that, eventually, pore blockage could have changed to pore constriction, attenuating the pore size reductions.

Since microcystins and NOM compounds may compete for the same pores, it is also interesting to analyse if microcystins also affect the rate of adsorption of AHA or TA (Figure 4.3).

Figure 4.3 (left) reveals that microcystins have a negligible effect on AHA rate of adsorption in the presence of background electrolyte and no effect at all in ultrapure water. This is in agreement with the adsorption in different pores and/or AHA constriction/blockage of pores, without the smaller microcystins molecules being able to disturb the higher AHA molecules. By other hand, microcystins and TA (Figure 4.3-right) are mutually disturbed (although TA

concentration is 15-100 times higher than the microcystins concentration), indicating an identical adsorption path.

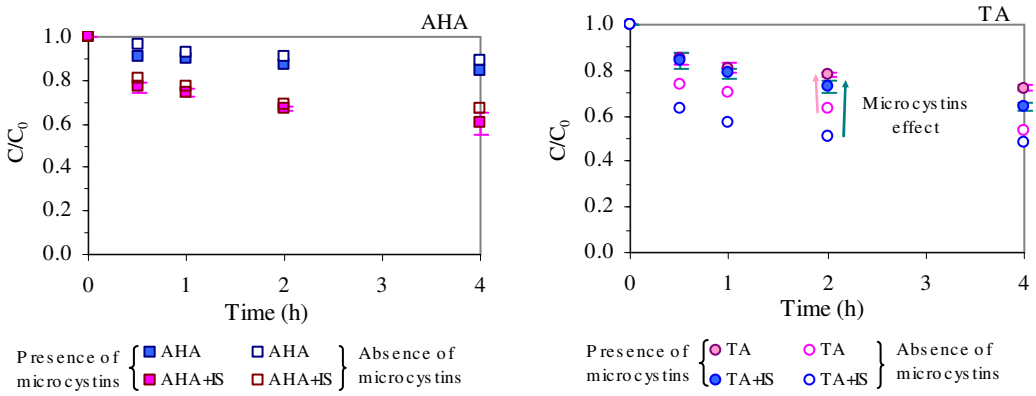

Figure 4.3 – AHA (left) and TA adsorption kinetics in the absence (open symbols) and in the presence (full symbols) of microcystins (left: 32-46 µg MC-LR_{eq}/L, 1.7-2.7 mg AHA/L; right: 31-137 µg MC-LR_{eq}/L; 2-3.2 mg TA/L).

4.3.2 Kinetic Studies with Model Solutions and Preloaded PAC

Two sets of adsorption kinetics were performed with preloaded PAC. In the first set, 5 mg/L of fresh PAC was contacted with 2 mg/L of each NOM model compound (AHA+SA or TA) during 65 h prior to the adsorption kinetic runs. A second set of preloads were performed with 3 mg/L of TA or with 3 mg/L of AHA supplemented with salts, in order to confirm the TA results and to evaluate the ionic strength contribution. After preloading the carbon, microcystins were then spiked into the isotherms bottles to obtain an initial concentration of 32-43 µg/L MC-LR_{eq}. Preloaded NOM displacement was only measured in the second set of adsorption kinetics and was evaluated through the variation of the aqueous concentration (since constant volumes were used). The results obtained are presented in Figure 4.4, as well as the comparison with the respective kinetics of simultaneous microcystins and NOM addition.

Although the PAC preloading with AHA plus SA yield a surface concentration of NOM much higher than the simultaneous adsorption (144 mg AHA/g *vs.* 36-62 mg AHA/g and 293 mg SA/g *vs.* 36-40 mg SA/g), the kinetic curves match (Figure 4.4-left), confirming that AHA, SA and microcystins adsorb on different sites.

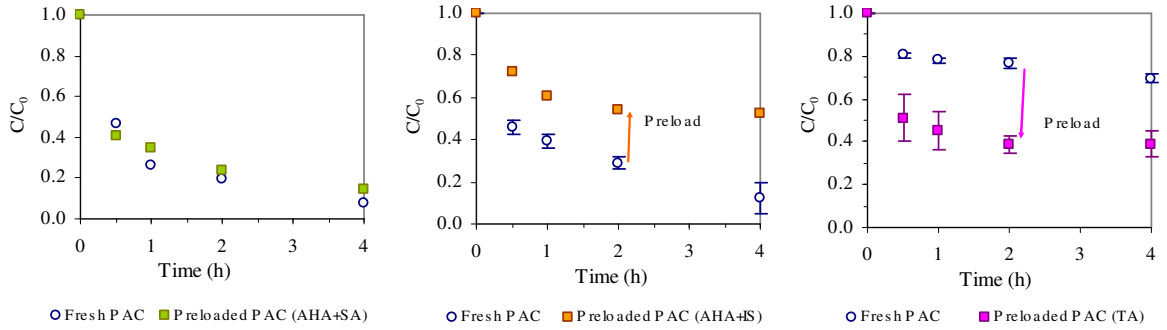

Figure 4.4 – Competitive adsorption kinetics of microcystins onto fresh and NOM preloaded PAC (32-46 µg MC-LR_{eq}/L in Milli-Q water (left and right) and in 2.5 mM IS solution (center)).

However in the presence of salts, preloading PAC with AHA has a more negative effect than the simultaneous adsorption (Figure 4.4-center), which is consistent with a pore blockage mechanism. The explanation is that preloading allowed a surface concentration of 333 mg AHA/g, while the simultaneous adsorption achieved 67-154 mg AHA/g, and therefore more pores are blocked. Adding ionic strength to NOM model solutions during the PAC preloading causes a reduction in the molecular size (and size distribution) of the humic substances, making them more adsorbable and exhibiting a greater impact on microcystins uptake. These results are in agreement with those of Kilduff and Karanfil (2002), who suggested that the increase in ionic strength does not change the way the humic acids compete with trichloroethylene, only increases the amount of humic acids adsorption. In the presence of aqueous background inorganics, AHA and microcystins must share a small range of pores, since microcystins addition caused the displacement of 8% of AHA (Figure 4.5, left).

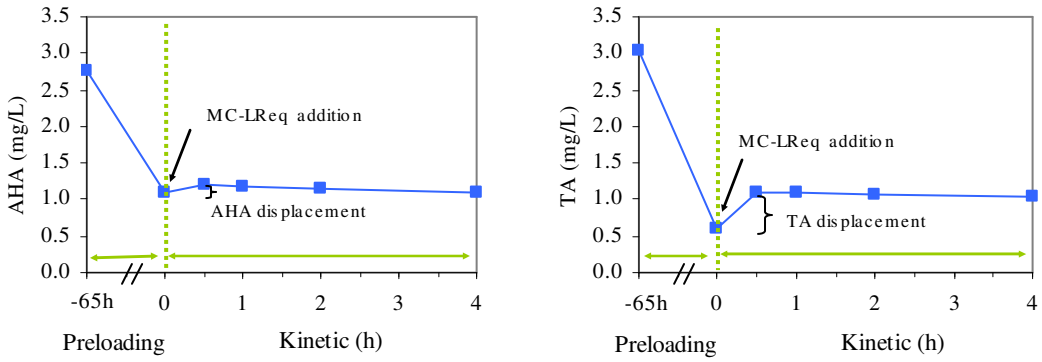

Figure 4.5 – Displaced desorption of AHA (left) and TA (right) by microcystins addition (32-37 µg MC-LR_{eq}/L; 5 mg PAC/L).

As far as TA is concerned, surprisingly, the competitive kinetic curve of microcystins beneficiated from PAC preloading with TA, even though the surface concentration has increased from 101-288 mg TA/g (simultaneous competition) to 337-484 mg TA/g (PAC preloading with TA). The results of TA concentration in the liquid phase after the microcystins addition indicate a displacement of 20 % of TA (Figure 4.5, right) and reveal the TA adsorption reversibility at high concentrations. This is, TA can be easily displaced by the competing microcystins, given their stronger affinity for PAC Norit SA-UF. To *et al.* (2008 a, b) concluded that strongly competing compounds displace adsorbed contaminants and accelerate their diffusion, while pore-blocking compounds reduce the rate of release of adsorbed contaminants. The kinetic results with both fresh and TA preloaded carbon seem to indicate a combination of two competitive mechanisms, pore constriction/blockage (evidenced in the simultaneous adsorption trials) but also direct competition (suggested by data from preloaded PAC).

4.3.3 Kinetic Studies with Natural Surface Water and Fresh PAC

Competitive adsorption trials using NOM model compounds with different characteristics were followed by experiments with natural surface water and fresh PAC. Data are shown in Figure 4.6, which, for comparison purposes, also includes data from the analogous studies performed with model solutions.

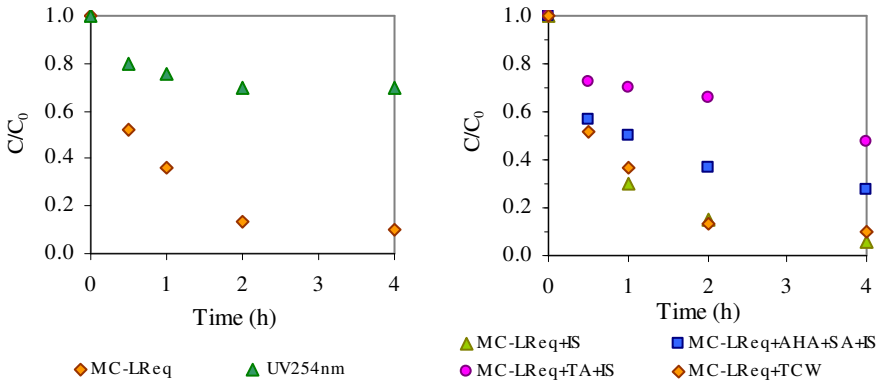

Figure 4.6 – Adsorption kinetics of microcystins onto fresh PAC in the presence of natural surface water (TCW) (left) and comparison with NOM model compounds effect (right) (28-39 µg MC-LR_{eq}/L).

Figure 4.6 (left) indicates a rapid rate of microcystins uptake from TCW, with residuals (C/Co) ranging from 0.5-0.1 after 0.5-4 hours of contact with 5 mg/L of PAC. By opposition, there is a slow rate of NOM adsorption. As found by other authors, these results must be related to the small size and the hydrophilic nature of NOM's TCW and the high mesoporous volume of PAC Norit SA-UF. Kilduff *et al.* (1996), Newcombe *et al.* (1997) and Ebie *et al.* (2001) presented data showing that small NOM is preferentially adsorbed onto microporous carbon, while Li *et al.* (2003 b) concluded that larger NOM is better adsorbed by mesoporous carbon. These authors found that 16.4% of the total DOC of a groundwater was non-adsorbable for PAC Norit SA-UF, because of their small size (200-500 Da) and probable hydrophilic nature, having poor affinity for the carbon surface.

The kinetic curve of microcystins in TCW is close to the single-solute adsorption kinetic (Figure 4.6, right), revealing that NOM's TCW has little effect on the rate of microcystins adsorption onto this PAC. This behaviour indicates that NOM molecules have similar sizes or are predominantly smaller than microcystins, not being able to block or constrict the small mesopores and secondary micropores entrance. The few larger molecules must adsorb in different pores and do not disturb the microcystins adsorption given the high volume of mesoporosity of PAC Norit SA-UF. Several studies confirm the positive effect of broadening the pore size distribution to attenuate the pore blocking effect (Newcombe *et al.*, 1997; Pelekani and Snoeyink, 1999, 2001; Ebie *et al.*, 2001; Li *et al.*, 2003 a, b; Quinlivan *et al.*, 2005).

4.3.4 Kinetic Models Analysis

For adsorption to take place, a series of four steps must occur (Snoeyink and Summers, 1999, Newcombe and Cook, 2004):

1) Bulk diffusion to PAC boundary layer;
2) Diffusion through the boundary layer to the external carbon surface (external mass transfer or film diffusion);
3) Diffusion through the pore structure to the most favourable adsorption site (intraparticle diffusion);
4) Adsorption.

Three kinetic models were used to study these processes and to investigate the mechanisms and potential rate-controlling step(s) of microcystins adsorption, such as mass transport (intraparticle diffusion model) and chemical reaction (pseudo-first and second order models) (Table 4.2) (Reichenberg, 1953; Özacar and Sengil, 2004; Yalçin *et al.*, 2004; Aksu and

Kabasakal, 2005; Eren and Acar, 2006; Önal, 2006; Ozmihci and Kargi, 2006; Janos *et al.*, 2007; Wang and Li, 2007).

Table 4.2 – Kinetic models investigated

Model	Equation	Parameters
Pseudo-first order adsorption model	$\ln (q_e - q_t) = \ln q_e - K_1 t$	q_e= equilibrium surface concentration (μg/mg) q_t=surface concentration at time t (μg/mg) K_1= equilibrium rate constant (min^{-1})
Pseudo-second order adsorption model	$t/q_t = 1/h + 1/q_e t$	h= initial adsorption rate (μg/mg.min) ($h= K_2 q_e^2$) K_2 = equilibrium rate constant (mg/μg.min)
Intraparticle diffusion model	$q_t = K_i t^{0.5} + C$	K_i = intraparticle diffusion rate constant ($\mu g/mg.min^{0.5}$) C= constant (proportional to the extent of boundary layer thickness)
Boyd *et al.* kinetic expression	$Bt = -2.30258 \log_{10} (1 - F) - 0.49770$ $Bt = 6.28318 - 3.2899F - 6.28318 (1 - 1.0470F)^{1/2}$	For $F > 0.85$ For $F \leq 0.85$ Bt= Boyd values; $F = q_t/q_e$

A straight line of $\ln (q_e - q_t)$ *vs.* t (min) suggests the applicability of pseudo-first order adsorption kinetic model, and the adsorption rate K_1 is obtained from the slope of the linear plot. If the pseudo-second-order model is applicable, the plot of t/q_t against t should give a linear relationship, from which the constants q_e, h and K_2 may be determined. In intraparticle diffusion model, K_i may be obtained from the slope of the straight-line portions of the q_t *vs.* $t^{0.5}$ plots, and C is the y-axis intercept. The linearity of the plot of Bt values against time provides useful information to distinguish between external-transport (non-linear plot) and intraparticle-transport-controlled rates of adsorption (linear plot passing through the origin) (Reichenberg, 1952; Wang and Li, 2007).

Although kinetic models are usually applied to single-solute experiments, in this study, they are also applied to competition kinetics in order to investigate if the competitive mechanisms may be reflected by the kinetic models parameters. Table 4.3 and Figures 4.7 and 4.8 present the results of the application of the pseudo-first order and pseudo-second order adsorption kinetic models.

Table 4.3 – Kinetic parameters calculated for pseudo-first order and pseudo-second order adsorption kinetic models.

MC-LR$_{eq}$ Kinetics	Pseudo-first order model			Pseudo-second order model			
	K_1 (min^{-1})	q_e (µg/mg)	R^2	K_2 (mg/(µg min))	h (µg/(mg min))	q_e (µg/mg)	R^2
Milli-Q	0.0073	3.8	0.9816	0.0058	0.263	7.2	0.9995
AHA+SA	0.0071	2.4	0.9567	0.0056	0.255	6.7	0.9984
AHA+SA+IS	0.0069	3.5	0.9954	0.0050	0.199	6.3	0.9959
TA	0.0063	1.2	0.9791	0.0157	0.079	2.3	0.9962
TA+IS	0.0067	2.0	0.9798	0.0079	0.076	3.1	0.9917
TCW	0.0068	3.1	0.8449	0.0053	0.175	5.7	0.9949

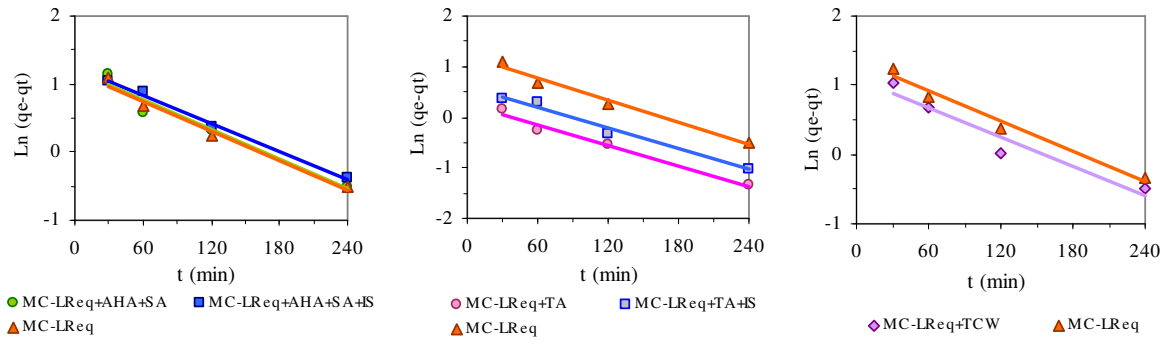

Figure 4.7 – Pseudo-first order plots for microcystins adsorption from organic free-water and NOM model solutions.

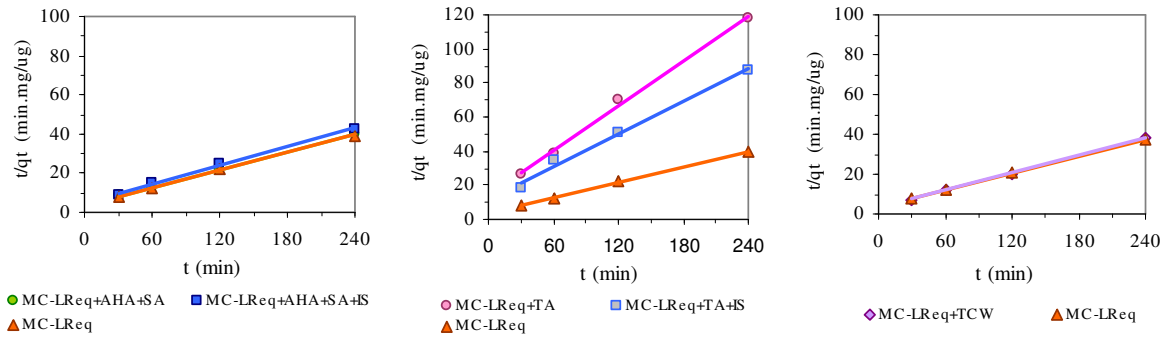

Figure 4.8 – Pseudo-second order plots for microcystins adsorption from organic free-water and NOM model solutions.

The kinetic data show an excellent compliance with the pseudo-second order equation (R^2> 0.992). Considering the pseudo-first order model, the correlation coefficient is low for TCW kinetics and as for NOM model solutions kinetics, although the correlation coefficients are high (0.957-0.995), they are lower than those of pseudo-second order model. Therefore, the microcystins adsorption kinetic data are best fitted by the pseudo-second order model, which indicates the chemisorption as the adsorption mechanism.

Figures 4.7 and 4.8 and Table 4.3 evidence the higher competitive effect of TA and that the ionic strength addition to the water enhances the AHA competitive effect, while reduces the TA competition. The equilibrium adsorption of microcystins (q_e) and the initial sorption rate (h) parameters (Table 4.3) are a function of the competitive effect, but no distinct relationship could be established for the rate constant values, K_2.

The weak AHA+SA competitive behaviour in the absence of backgrounds inorganics kept the h parameter almost constant and slightly lowered the q_e, but the addition of aqueous ionic strength induced AHA competition and therefore further reduced q_e and reduced the initial

sorption rate. The strong competition between TA and microcystins results in a huge reduction of both h and q_e parameters, especially in the absence of background ionic strength (71% h reduction and 68% q_e reduction). The attenuating effect of IS on the TA competition is evidenced by the partial recovery of q_e. The intermediate competitive behaviour exhibited by TCW is expressed by intermediate values of h and q_e. This is, the stronger the competition, the lower the q_e and the h values. In agreement with the competition mechanisms discussed in the previous sections (mostly pore blockage/constriction), this trend could be attributed to the decrease of the PAC surface area available for microcystin adsorption, which slows down the microcystins uptake.

Figure 4.9 shows the intraparticle diffusion plots for microcystins adsorption kinetics in ultrapure water and NOM model solution. In order to determine the rate-controlling step of mass transport, the kinetic data were further analysed using the Boyd kinetic expression (Figure 4.10). Table 4.4 presents the kinetic parameters obtained for both models.

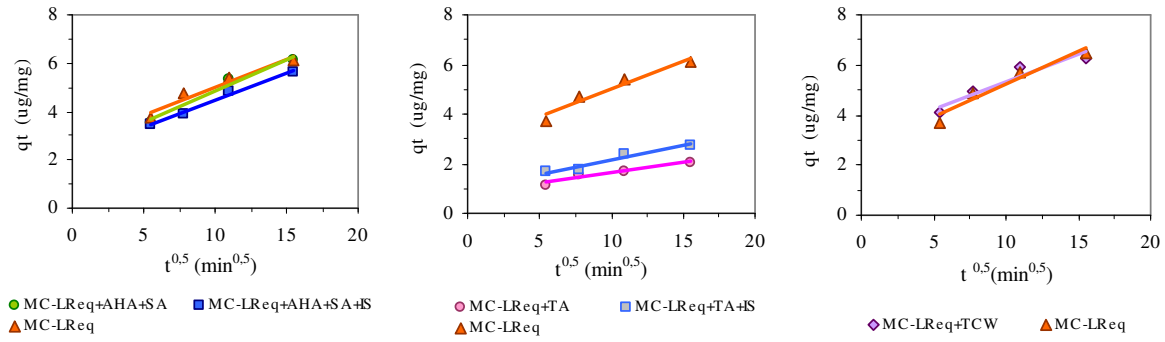

Figure 4.9 - Intraparticle diffusion kinetics for microcystins adsorption in organic free-water and NOM model solutions.

The q_t *vs.* $t^{0.5}$ plots (intraparticle diffusion model) may present a single straight line or multilinearity, indicating that two or more steps are taking place. The first, sharper portion is

the external surface adsorption, the second is the intraparticle diffusion adsorption, and the third portion is the final equilibrium stage (Yalçin *et al.*, 2004; Özacar and Sengil, 2004; Önal, 2006). Figure 4.9 shows that only one linear portion is present for all kinetics, corresponding to the second sorption stage. The external surface sorption (stage 1) is absent which reveals its completion before 30 minutes.

The linearity of the plots indicates that intraparticle diffusion model fitted well the experimental data. However, to be a rate-controlling step, the plots should be linear and pass through the origin (Aksu and Kabasakal, 2005). As the linear plots did not pass through origin the intraparticle diffusion was not the only rate-controlling step. The values of C intercept are proportional to the boundary layer thickness, *i.e.*, the greater the intercept the greater the boundary layer effect and therefore, the stronger is the role of the external film. Figure 4.9 and Table 4.4 show that the higher C values are obtained for microcystins adsorption from ultrapure water and as NOM competition increases, the C values decrease. These results point towards a decreasing importance of the intraparticle diffusion on the microcystins adsorption kinetics, in the following order: TA> TA+IS > AHA+SA+IS ~ AHA+SA > Milli-Q.

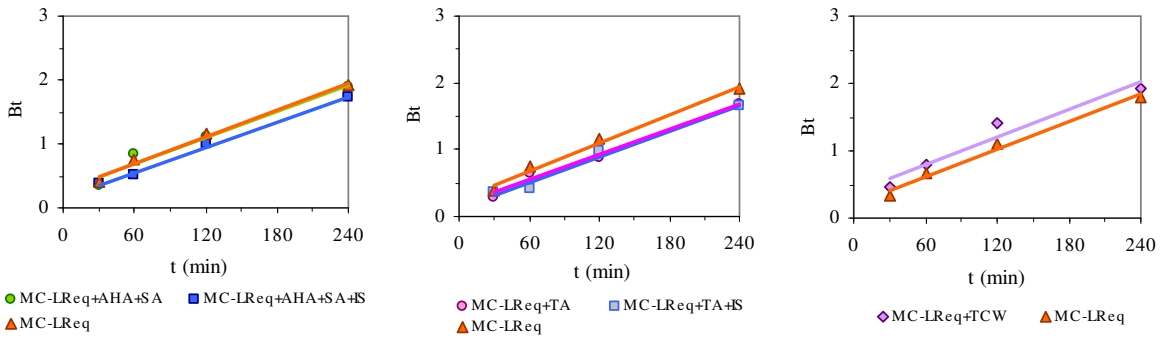

Figure 4.10 - Boyd *et al.* plots for microcystins adsorption of in organic free-water and NOM model solutions.

Table 4.4 – Kinetic parameters obtained from intraparticle diffusion model and Boyd *et al.*. expression

MC-LR_{eq} Kinetics	Intraparticle Diffusion Model			Boyd *et al.* expression Bt=a t + b		
	K_i (μg/(mg $min^{0.5}$))	C	R^2	a	b	R^2
Milli-Q	0.26	2.6	0.9349	0.0068	0.21	0.9854
AHA+SA	0.26	2.2	0.9691	0.0069	0.27	0.9681
AHA+SA+IS	0.22	2.2	0.9850	0.0066	0.16	0.9965
TA	0.08	0.8	0.9459	0.0063	0.16	0.9850
TA+IS	0.11	1.0	0.9543	0.0064	0.13	0.9832
TCW	0.23	1.7	0.8575	0.0063	0.22	0.8328

The linearity of the plot of Bt values against time (Figure 4.10 and Table 4.4) and the quite low values of b intercept also suggest that the intraparticle diffusion is mainly the rate-limiting step of microcystins adsorption kinetics from AHA+SA+IS, TA and TA+IS model solutions (even though external mass transport may not be neglected as plots do not pass through the origin). However, the kinetic data for microcystins adsorption from TCW show a poor correlation with the intraparticle diffusion model and the Boyd plots and the C values (proportional to the boundary layer thickness) are relatively high, which is consistent with external mass transport as the rate-limiting process.

The values of K_i in Table 4.4, indicate that the intraparticle diffusion rate for microcystins are equivalent in ultrapure water and in AHA+SA solution, higher than in AHA+SA+IS solution and especially higher than with TA competition. As pore dimensions decrease due to the adsorption of the competing NOM, the free path for molecules to travel within the transport pores becomes smaller (with possible pore blockage occurring) and hence their diffusion decreases. The addition of ionic strength during TA competition slightly beneficiated the intraparticle diffusion rate of microcystins. All the previous observations are in agreement with pore constriction/blockage effect of TA, AHA and TA with IS addition; with the absence

of pore constriction/blockage mechanisms for AHA and TCW and with a positive effect of ionic strength onto microcystins adsorption during TA competition.

4.4 SUMMARY AND CONCLUSIONS

NOM affected the microcystins adsorption kinetics onto the mesoporous PAC NORIT SA-UF differently, according to the NOM molecular size and the aqueous background ionic strength. The hydrophobic large AHA molecules had no effect on microcystins adsorption kinetics, probably due to their adsorption onto mesopores larger than those preferred by microcystins. However, the aqueous ionic strength induced the competitive effect of AHA, by reducing its size, and therefore enabling them to access smaller mesopores and causing pore constriction or blockage.

The small hydrophilic SA molecules did not disturb microcystins kinetics given their slower rate of adsorption and probable adsorption in small primary micropores.

TA, the compound with the closest size to microcystins, was responsible for the stronger competition, severely affecting the microcystins adsorption kinetics (microcystins residuals increased 5 times). Pore constriction/blockage mechanism seems to be the major responsible for TA effect, although the microcystins interference with the rate of TA adsorption and TA displacement from preloaded PAC due to microcystins also indicated some effect of direct site competition. Background ionic strength attenuated the TA-microcystins competition, *i.e.*, it enhanced the rate of microcystins adsorption. Due to the slight reduction in TA size driven by the water IS, some pore blockage could have changed to pore constriction, and pore size reductions were not so severe.

TCW background organic and inorganic matrices did not impact the microcystins adsorption kinetics, which is consistent with the small size and the hydrophilic character of the NOM present in this preozonated clarified surface water.

The application of kinetic models to microcystins adsorption from NOM solutions corroborated the proposed competitive mechanisms. Adsorption data were best fitted by the pseudo-second order kinetic model and the stronger the NOM-microcystin competition the lower the equilibrium surface concentration and the initial adsorption rate. The rate-limiting steps were identified: the intraparticle diffusion mainly controlled the microcystins adsorption from NOM model solutions, while the external diffusion was the limiting step for microcystins uptake from surface water.

4.5 REFERENCES

Aksu Z., Kabasakal E. (2005). Adsorption characteristics of 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution on powdered activated carbon. *Journal of Environmental Science and Health- Part B*, 40(4), 545-570.

Campinas M., Rosa M.J. (2006). The ionic strength effect on microcystin and natural organic matter surrogate adsorption onto PAC. *Journal of Colloid and Interface Science*, 299(2), 520-529.

Campos C., Schimmoller L., Mariñas B., Snoeyink V., Baudin I., Laîné J. (2000). Adding PAC to remove DOC. *Journal of American Water Works Association*, 92(8), 69-83.

Chin Y., Alken G., O´Loughlin E. (1994) Molecular weight, polydispersity and spectroscopic properties of aquatic humic substances. *Environmental Science and Technology*, 28(11), 1853-1858.

Cook D., Newcombe G., Sztajnbok P. (2001). The application of powdered activated carbon for MIB and geosmin removal: predicting PAC doses in four raw waters. *Water Research*, 35(5), 1325-1333.

Ding L., Snoeyink V., Mariñas B., Yue Z., Economy J. (2008). Effects of powdered activated carbon pore size distribution on the competitive adsorption of aqueous atrazine and natural organic matter. *Environmental Science and Technology*, 42(4), 1227-1231.

Donati C., Drikas M., Hayes R., Newcombe G. (1994). Microcystin-LR adsorption by powdered activated carbon. *Water Research*, 28(8), 1735-1742.

Ebie K., Li F., Azuma Y., Yuasa A., Hagishita T. (2001). Pore distribution effect of activated carbon in adsorbing organic micropollutants from natural water. *Water Research*, 35(1), 167-179.

Edzwald J., Van Benschoten J. (1990). Aluminium coagulation of natural organic material. *In*: *Chemical Water and Wastewater Treatment*. Hahn H.H. and Klute K. (eds). Berlin: Springer-Verlag, 341-359.

Eren Z., Acar F. (2006). Adsorption of Reactive Black 5 from an aqueous solution: equilibrium and kinetic studies. Desalination, 194, 1-10.

Hong S., Elimelech M. (1997). Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Journal of Membrane Science*, 132, 159-181.

Huang W.-J., Cheng B.-L., Cheng Y.-L. (2007). Adsorption of microcystin-LR by three types of activated carbon. *Journal of Hazardous Materials*, 141(1), 115-122.

Janos P., Michál P., Turek L. (2007). Sorption of ionic dyes onto untreated low-rank coal-oxihumolite: a kinetic study. *Dyes and Pigments*, 74(2), 363-370.

Kilduff J., Karanfil T., Chin Y.-P., Weber Jr. W. (1996) Adsorption of natural organic polyelectrolytes by activated carbon: a size-exclusion chromatography study. *Environmental Science and Technology*, 30(4), 1336-1343.

Kilduff J., Karanfil T., Weber Jr, W. (1998 a). Competitive effects of displaceable organic compounds on trichloroethylene uptake by activated carbon. I. Thermodynamic predictions and model sensitivity analyses. *Journal of Colloid and Interface Science*, 205(2), 271-279.

Kilduff J., Karanfil T., Weber Jr, W. (1998 b). Competitive effects of displaceable organic compounds on trichloroethylene uptake by activated carbon. II. Model verification and applicability to natural organic matter. *Journal of Colloid and Interface Science*, 205(2), 280-289.

Kilduff J., Karanfil T. (2002). Trichloroethylene adsorption by activated carbon preloaded with humic subtances :effects of solution chemistry. *Water Research*, 36(7), 1685-1698.

Lee J., Walker H. (2006). Effect of process variables and natural organic matter on removal of microcystin-LR by PAC-UF. *Environmental Science and Technology*, 40(23), 7336-7342.

Li F., Yuasa A., Ebie K., Azuma Y., Hagishita T., Matsui Y. (2002) Factors affecting the adsorption capacity of dissolved organic matter onto activated carbon : modified isotherm analysis. *Water Research*, 36(18), 4592-4604.

Li Q., Snoeyink V., Mariñas B., Campos C. (2003 a). Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. *Water Research*, 37(20), 4863-4872.

Li Q., Snoeyink V.,Mariña B., Campos C. (2003 b). Elucidating competitive adsorption mechanism of atrazine and NOM using model compounds. *Water Research*, 37(4), 773-784.

Matsui Y., Fukuda Y., Inoue T., Matsushita T. (2003). Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: characteristics and mechanism of competitive adsorption. *Water Research*, 37(18), 4413-4424.

Meriluoto J., Spoof L. (2005 a). SOP: Solid phase extraction of microcystin in water samples *In:* Toxic Cyanobacterial Monitoring and Cyanotoxin Analysis. J. Meriluoto and G. Codd (Ed.), Abo Akademi University Press, Finland.

Meriluoto J., Spoof L. (2005 b). SOP: Analysis of microcystins by high-performance liquid chromatography with photodiode-array detection *In:* Toxic Cyanobacterial Monitoring and Cyanotoxin Analysis. J. Meriluoto and G. Codd (Ed.), Abo Akademi University Press, Finland.

Mohamed Z., Carmichael W., An J., El-Sharouny H. (1999). Activated carbon removal efficiency of microcystins in an aqueous cell extract of *Microcystis aeruginosa* and *Oscillatoria tenuis* strains isolated from Egyptian freshwaters. *Environmental Toxicology*, 14(1), 197-201.

Newcombe G., Drikas M., Hayes R. (1997). Influence of characterised natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption of 2-methylisoborneol. *Water Research*, 31(5), 1065-1073.

Newcombe G., Morrison J., Hepplewhite C., Knappe D. (2002). Simultaneous adsorption of MIB and NOM onto activated carbon: II. Competitive effects. *Carbon*, 40(12), 2147-2156.

Newcombe G., Cook D. (2004). Removal of natural microcontaminants from drinking water using activated carbon. *In Encyclopedia of Surface and Colloid Science*. 1st Edition, P. Somasundaran (Ed.), Taylor & Francis, London.

Önal Y. (2006). Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot. *Journal of Hazardous Materials*, B137, 1719-1728.

Özacar M., Sengil A. (2004). Application of kinetic models to the sorption of disperse dyes onto alunite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 242(1-3), 105-113.

Ozmihci S., Kargi F. (2006). Utilization of powdered waste sludge (PWS) for removal of textile dyestuffs from wastewater by adsorption. *Journal of Environmental Management*, 81(3), 307-314.

Pelekani C., Snoeyink V. (1999). Competitive adsorption in natural water: role of activated carbon pore size. *Water Research*, 33(5), 1209-1219.

Pelekani C., Snoeyink V. (2000). Competitive adsorption between atrazine and methylene blue on activated carbon: the importance of pore size distribution. *Carbon*, 38(10), 1423-1436.

Pelekani C., Snoeyink V. (2001). A kinetic and equilibrium study of competitive adsorption between atrazine and Congo red dye on activated carbon : the importance of pore size distribution. *Carbon*, 39(1), 25-37.

Pendleton P., Schumann R., Wong S. (2001). Microcystin-LR adsorption by activated carbon. *Journal of Colloid and Interface Science*, 240(1), 1-8.

Quinlivan P., Li L., Knappe D. (2005). Effects of activated carbon characteristics on the simultaneous adsorption of aqueous organic micropollutants and natural organic matter. *Water Research*, 39(8), 1663-1673.

Randtke S., Snoeyink V. (1983). Evaluating GAC adsorptive capacity. *Journal of American Water Works Association*, 75(8), 406-413.

Reichenberg D. (1953). Properties of ion-exchange resins in relation to their structure. III. Kinetics of exchange. *Journal of American Chemical Society*, 75, 589-597.

Sawyer C., McCarty P., Parkin G. (1994). Chemistry for Environmental Engineering. McGraw-Hill International Editions, fourth edition.

Sivonen K., Jones G. (1999) Cyanobacterial toxins. *In*: *Toxic Cyanobacteria in Water: a Guide to Their Public Health, Consequences, Monitoring and Management*. Chorus I. and Bartram J. (Eds.), WHO.

Snoeyink V., Summers S. (1999). Adsorption of organic compounds. *In Water Quality & Treatment*. 5th Edition, AWWA, McGraw-Hill, Lisbon.

To P., Mariñas B., Snoeyink V., NG W. (2008 a). Effect of strongly competing background compounds on the kinetics of trace organic contaminant desorption from activated carbon. *Environmental Science and Technology*, 42(7), 2606-2611.

To P., Mariñas B., Snoeyink V., NG W. (2008 b). Effect of pore-blocking background compounbds on the kinetics of trace organic contaminant desorption from activated carbon. *Environmental Science and Technology*, 42(13), 4825-4830.

USEPA (1999). Enhanced coagulation and enhanced precipitative softening guidance manual. United States Environmental Protection Agency, Office of Water, EPA 815-R-99-012, May.

Wang S., Li H. (2007). Kinetic modelling and mechanism of dye adsorption on unburbed carbon. *Dye and Pigments*, 72(3), 308-314.

Yalçin M., Gürses A., Dogar Ç., Sözbilir M. (2004). The adsorption kinetics of Cethyltrimethylammonium Bromide (CTAB) onto powdered activated carbon. *Adsorption*, 10(4), 339-348.

Yamada E., Doi K., Okano K., Fuse Y. (2000) Simultaneous determinations of the concentration and molecular weight of humic substances in environmental water by gel chromatography with a fluorescence detector. *Analytical Sciences*, 16(2),125.