REMOVAL OF MICROCYSTIN-LR FROM DRINKING WATER USING ADSORPTION AND MEMBRANE PROCESSES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for

the Degree of Doctor of Philosophy

in the Graduate School of The Ohio State University

By

Jung Ju Lee, M.S., E.I.

*****

The Ohio State University
2009

Dissertation Committee:

Professor Harold Walker, Advisor

Professor Linda Weavers

Professor John Lenhart

Professor Yu-Ping Chin

Approved by

Advisor

Civil Engineering Graduate Program

ABSTRACT

Blooms of cyanobacteria are of emerging concern in the United States as well as other parts of the world. These cyanobacteria can make drinking water smell and taste poorly, and the cyanotoxins released from harmful cyanobacteria may cause mass mortalities of wild and domestic animals and result in human sickness. Microcystins are well known to be one of the most dangerous and most commonly occurring classes of cyanotoxins in the drinking water supplies. When consumed or in contact with skin, microcystins can lead to skin irritation or liver and kidney damage as well as may initiate liver cancer. Due to adverse health effects, the World Health Organization (WHO) set a guideline level of 1 part per billion (ppb) for microcystin. However, current water treatment facilities may not specifically treat drinking water for microcystin.

The overall goal of this research was to develop an advanced and effective process for the removal of microcystins from drinking water. To achieve this goal, powdered activated carbon (PAC), iron oxide nanoparticles, and ultrafiltration (UF) membranes were explored as promising treatment technologies. Laboratory-scale experiments were performed to examine the effectiveness of each treatment process,

determine the optimum operational conditions, and explore the mechanisms controlling toxin removal.

The use of ultrafiltration (UF) was investigated for the rejection of microcystin-LR from drinking water. Adsorption dominated rejection for most UF membranes, at least at early filtration times, while both size exclusion and adsorption were important in removing microcystin-LR by the tight thin-film (TF) membranes with a molecular weight cutoff (MWCO) of 1−4KDa. The extent of membrane adsorption was generally related to membrane hydrophobicity. The initial feed concentration had a significant influence on the adsorption capacity of TF membranes for microcystin-LR, resulting in a linear adsorption isotherm. Higher permeate flux resulting from increasing water recovery or operating pressure, led to greater adsorption of microcystin-LR on the polyethersulfone and thin-film membranes and a decrease in size exclusion.

The application of ultrafiltration coupled with powdered activated carbon (PAC-UF) was also investigated as a drinking water treatment process for microcystin-LR removal. The influence of different operating factors such as activated carbon type and dosage, membrane composition, and mixing time was examined to define optimum operational conditions for effective removal of microcystins from drinking water. Of the two different PAC materials, wood-based activated carbon was more effective at removing microcystin-LR than coconut-based carbon due to greater mesopore volume. The PAC-UF system had the highest removal efficiency among the three processes (i.e., PAC adsorption, ultrafiltration, and PAC-UF) for both hydrophobic polyethersulfone (PES) and hydrophilic cellulose acetate (CA) membranes. When PAC was coupled to UF using PES membranes, greater removal of microcystin-LR occurred compared to

when CA membranes were used, due to sorption of the toxin to the PES membrane surface.

In further studies, Suwannee River Fulvic Acid (SRFA) was used to examine the effect of natural organic matter (NOM) on the removal of microcystin-LR during ultrafiltration, either as a stand-alone process or in combination with PAC. When PES membranes were previously fouled by SRFA, increased size exclusion and reduced adsorption of microcystin-LR were observed, probably due to pore blockage and fewer available adsorption sites as a result of SRFA sorption. However, simultaneous addition of both microcystin and SRFA resulted in no change in microcystin-LR adsorption since microcystin molecules are apparently able to adsorb before significant amounts of SRFA associated with the PES membrane. The presence of SRFA reduced microcystin-LR removal by PAC-UF, primarily due to competition between SRFA and microcystin-LR for adsorption sites on the PAC surface.

Finally, an adsorption study was performed on microcystin-LR using iron oxide (maghemite) nanoparticles. Factors influencing the sorption behavior examined included microcystin-LR and maghemite concentration, pH, ionic strength, and the presence of SRFA. The results indicated that adsorption was primarily attributed to electrostatic interactions, although hydrophobic interactions may also play a role. The adsorption of microcystin-LR decreased with increasing pH, primarily due to a decrease in surface charges of maghemite and subsequently, reduced electrostatic attraction. The ionic strength (i.e. NaCl concentration) affected microcystin adsorption by screening the electrostatic interactions. The presence of SRFA strongly influenced microcystin adsorption; the extent of microcystin-LR adsorption decreased with increasing SRFA

concentration (above 2.5 mg/L) due to the preferential adsorption of SRFA over microcystin-LR.

This laboratory-scale work is an initial step in developing an advanced treatment system that could be easily incorporated into drinking water treatment facilities. It is expected that this research can provide both practical and fundamental information for more efficient process design, leading to effective removal of harmful cyanotoxins and improved water quality and safety.

Dedicated to my parents

ACKNOWLEDGMENTS

I would like to express my deepest appreciation to my adviser, Dr. Harold Walker. Without his support and encouragement, this would have been an impossible task. I would like to thank the additional members of my PhD committee, Dr. Linda Weavers, Dr. John Lenhart, and Dr. Yo Chin, for their fantastic guidance and important discussions regarding this work. I greatly acknowledge the sponsors of this research: the Ohio Sea Grant College Program, the Ohio State University Graduate Fellowship program, and the Ohio Water Development Authority (OWDA).

For technical support I thank Shengnian Wang (zeta potential analyses) and Xuejin Wen (contact angle measurements) of Chemical Engineering, and Ziqi He and Jason Cheng (BET measurements) of Environmental Engineering. I also thank Chris Taylor and Brenda Snyder in Toledo Water Treatment Plant, Ohio, for their help with collecting Lake Erie water.

It has been a pleasure working with my colleges in the Environmental Engineering Research Laboratory during my time at Ohio State. I deeply appreciate their kindness, friendship, and collaboration. Most especially, many thanks to Yu-Sik Hwang, and Maggie Pee for their valuable help and friendship. I will always remember the

wonderful time we had together at Ohio State. You are missed. JiYi Lee, HyunHee Cho, and HaeJin Kim: thank you for answering the phone over the past five years.

I would like to thank my wonderful two sisters, Jenny Lee and Jungwon Lee, brother-in-law, Samuel Lee, and my lovely nephew and nieces, Samuel, Janet, and Julia. Special thanks to my fiancé, Brian Song, for his love and understanding. I love each of you dearly.

Most importantly, I would like to dedicate this work to my parents, Soo-Choon Lee and Seung-Sook Seo, for their unconditional love and support. Their pray and belief in my ability always made me moving forward. I love you and thank you.

VITA

July 26, 1976 …….....	Born−Seoul, South Korea
1999 …….	B.S., Environmental Engineering, Ewha Womans University, South Korea
2001 …….....	M.S., Environmental Engineering, Ewha Womans University, South Korea
2001-2002 ……...	Researcher, National Research Lab, Ewha Womans University, South Korea
2003-present ……	Graduate Research Associate, The Ohio State University
2007-present ……	Graduate Administrative Assistant, The Ohio State University

PUBLICATIONS

Research Publication

1. Lee, Jungju and Walker, Harold W. "Mechanisms and Factors Influencing the Removal of Microcystin-LR by Ultrafiltration Membranes", *Journal of Membrane Science*. 2008, 320(1-2), 240-247.

2. Lee, Jungju and Walker, Harold W. "Effect of Process Variables and Natural Organic Matter on Removal of Microcystin-LR by PAC-UF", *Environmental Science and Technology*. 2006, 40(23), 7336-7342.

FIELDS OF STUDY

Major Field: Civil Engineering

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Problem Statement

The presence of cyanobacteria (blue-green algae) in surface water is of increasing concern in the United States as well as other parts of the world. Cyanobacteria naturally produce deleterious compounds, called cyanotoxins, due to cell lysis during cyanobacterial blooms. These toxins may cause mass mortalities of wild and domestic animals and farmed fish and shellfish, as well as human sickness such as nervous system damage or liver injury, and in extreme cases, death [1].

Microcystins are the most frequently occurring class of cyanotoxins, of which microcystin-LR is known to be one of the most toxic cyanotoxins in water resources [2]. When in contact with skin or consumed, microcystin-LR can lead to skin irritation or liver damage and may initiate liver tumor-promoting activity [3]. Due to these adverse health effects, the World Health Organization (WHO) established a provisional guideline of 1 part per billion (μg/L) for microcystin-LR in drinking water [4], and the United

States Environmental Protection Agency (USEPA) has placed microcystins on the Drinking Water Contaminants Candidate List [5].

A number of technologies such as coagulation, chlorination, activated carbon adsorption, and ozonation have been investigated for the removal of microcystins from drinking water, but typically, these processes are not effective to meet the WHO guideline [6] or result in other treatment challenges (e.g., disinfection by-products). Therefore, other effective approaches for the removal of microcystins during drinking water treatment are needed.

1.2 Research Objectives

The overall objective of this research was to develop an effective technology for the removal of microcystins from drinking water. To achieve this goal, powdered activated carbon (PAC), iron oxide nanoparticles, and ultrafiltration (UF) membranes were used. Activated carbon effectively adsorbs microcystins on their surfaces [7], and ultrafiltration membranes can separate PACs from the water due to the small pores of the membranes [8]. Membrane processes are being used increasingly for the production of drinking water. In combination, it was expected that PAC-UF can eliminate microcystins from drinking water. It was also hypothesized that iron oxide nanoparticles can adsorb microcystin-LR because metal oxides have a great ability to interact with dissolved organic compounds in water, especially negatively charged species. Since iron oxides (Fe_2O_3) are naturally occurring minerals, and ubiquitous in soils and sediments [9,10], the adsorption of microcystins onto iron oxide particles may also play an important role in the fate and transport of microcystins in natural environments.

The specific tasks of this research can be summarized as follow:

1. Investigate the application of ultrafiltration for the rejection of microcystin-LR and elucidate the rejection mechanisms.
2. Determine the optimum operational condition of a PAC-UF system for the effective removal of microcystin-LR from drinking water.
3. Investigate how natural organic matter (NOM) influences the removal of microcystin-LR by ultrafiltration, either as a stand-alone process or in combination with powdered activated carbon.
4. Examine the interaction between microcystin-LR and iron oxide nanoparticles in water in order to determine the applicability of metal oxide adsorption as an efficient removal technology.

1.3 Dissertation Organization

The dissertation is composed of six chapters including an introduction (Chapter 1), literature review (Chapter 2), three main chapters (Chapters 3, 4, and 5), and conclusions and future work (Chapter 6). Two of three main chapters (Chapters 3 and 4) are based on manuscripts published in peer reviewed journals and the other (Chapter 5) is a manuscript in preparation for submission.

Chapter 3: "Effect of Process Variables and Natural Organic Matter on Removal of Microcystin-LR by PAC-UF"

This chapter is largely based on a manuscript published in *Environmental Science and Technology* (2006), volume 40, 7336-7342 by Jungju Lee and Harold W. Walker. In

this chapter, ultrafiltration coupled with activated carbon adsorption (PAC-UF) was developed and tested for the removal of microcystin-LR from synthetic source water. Laboratory-scale experiments were performed for different operating conditions to evaluate the effect of activated carbon type and dosage, membrane composition, and mixing time on microcystin-LR removal. Two types of activated carbon (e.g., wood-based carbon, coconut-based carbon) in the range of 0–5 mg/L and two ultrafiltration membranes (e.g., cellulose acetate, polyethersulfone) were used.

In addition, this chapter describes how natural organic matter influences the removal of microcystin-LR by PAC-UF. Commercial Suwannee River fulvic acid (SRFA) was chosen as a representative natural organic matter (NOM). To examine the effect of NOM properties on the toxin removal by PAC-UF, additional experiments using Suwannee River humic acid (SRHA) and Lake Erie whole water were conducted.

Chapter 4: "Mechanisms and Factors Influencing the Removal of Microcystin-LR by Ultrafiltration Membranes"

This manuscript was published in *Journal of Membrane Science* (2008), volume 320, 240-247 by Jungju Lee and Harold W. Walker. This chapter describes how ultrafiltration membrane properties (e.g., material and pore size) influence the extent of adsorption, and subsequently microcystin removal. The physical and chemical interactions between microcystin and UF membranes are explored. Experiments were conducted using a cross-flow ultrafiltration system and seven different commercial UF membranes to elucidate the rejection mechanisms of microcystin-LR by ultrafiltration. Other factors governing the removal of microcystin-LR by ultrafiltration were also

examined, including system operating parameters (e.g., water recovery and operating pressure) and solution conditions (e.g., feed concentration).

Chapter 5: "Adsorption of Microcystin-LR onto Iron Oxide Nanoparticles"

This manuscript is in preparation for submission to *Water Research* by Jungju Lee and Harold W. Walker. Chapter 4 describes experimental results conducted to examine the adsorption of microcystin-LR on nano-sized iron oxide particles using batch adsorption experiments. Various factors such as iron oxide dosage, microcystin-LR concentration, solution pH and ionic strength were examined to understand microcystin-LR sorption behavior. The effect of natural organic matter (i.e., SRFA) on microcystin-LR adsorption to iron oxides was also investigated over a wide range of SRFA concentration (0–25 mg/L).

References

[1] Reynolds, K.A. 2004. *Wat. Cond. Pur*. 46(3), 78-80.

[2] Antoniou, M.G., de la Cruz, A.A., and Dionysiou, D.D. 2005. *J. Environ. Eng.* 131(9), 1239-1243.

[3] Feitz, A.J., Waite, D., Jones, G.J., Boyden, B.H., Orr, P.T. 1999. *Environ. Sci. Technol*. 33, 243-249.

[4] WHO. *Cyanobacterial toxins: Microcystin-LR. Guidelines for drinking water quality*. World Health Organization, Geneva. 1998.

[5] USEPA. *Fact sheet: The drinking water contaminant candidate list−The source of priority contaminants for the drinking water program*. EPA 815-F-05-001. Office of Water, US Environmental Protection Agency, Washington, DC. 2005.

[6] Lawton, L.A., Robertson, P.K.J. 1999. *Chem. Soc. Rev*. 28, 217-224.

[7] Falconer, I.R., Runnegar, M.T.C., Buckley, T., Huyn, V.L., Bradshaw, P. 1989. *J. Am. Water Works Assoc*. 81(2), 102-105.

[8] Campos, C., Mariñas, B.J. Snoeyink, V.L. Baudin, I., Lainé, J.M. 2000. *J. Environ. Eng*. 126(2), 97-103.

[9] Liang, L., Morgan, J. J. 1990. *Aquatic Sci*. 52(1), 32-55.

[10] Hanna, K. 2007. *J. Colloid Interf. Sci*. 309, 419-428.

CHAPTER 2

RESEARCH BACKGROUND AND LITERATURE REVIEW

This chapter provides background and a review of literature regarding the removal of microcystins from drinking water. First, the occurrence, characteristics, and fate of microcystins are identified. Next, the current technologies available for microcystin treatment are reviewed and documented. Finally, the processes used in this research such as membrane filtration, PAC-UF system, and iron oxide adsorption are described.

2.1 Blooms of cyanobacteria

Cyanobacteria, more commonly known as blue-green algae, are a type of photosynthetic bacteria living in surface water (e.g., lakes, rivers, and oceans) [1]. During warm-weather and in slow-moving and nutrient-enriched water their population can rapidly increase to form a mass large enough that is visible to the naked eye. This phenomenon is called a "cyanobacterial bloom". Recently, blooms of cyanobacteria have

more frequently occurred worldwide as a result of increasing temperature and nutrient levels [2].

Blooms of cyanobacteria are of increasing concern in the production of drinking water in the United States, as well as other parts of the world. Cyanobacterial blooms impair drinking water quality by producing tastes and odors [3]. Water affected by a bloom may be unappealing for recreational activities due to its unsightly appearance and its pungent smell. More significantly, certain species of cyanobacteria naturally produce deleterious compounds (i.e., cyanotoxins), and release these toxins into the surrounding water through cell lysis.

The concentration of cyanobacterial cells was reported up to 250,000 cells/mL during blooms, which is approximately 300 mg/L cyanobacterial biomass [4]. Cyanobacterial cells have been shown to contain an average of 0.2 pg of toxin per cell [5], ranging from 4 to 605 μg toxin/g dry weight of biomass [6]. Nicholson et al. [7] reported that total concentration of cyanotoxins in highly contaminated waters is 130−300 μg/L.

Cyanotoxins lead to serious health problems for humans such as irritation of the skin (dermatotoxins), cell damage (cytotoxins), liver damage (hepatotoxins), and damage to the nervous system (neurotoxins) [8]. The consequences of cyanobacterial blooms have been reported in the United States as well as other parts of the world. For example, exposure to cyanotoxins has been linked to increased liver cancer in China, the death of 76 dialysis patients in Brazil, and elevated kidney failure and liver injury in Australia [9,10]. Recently, harmful cyanobacterial blooms have resulted in health alerts in New York, Florida, and Nebraska [11,12]. In the Great Lakes, cyanobacterial blooms have emerged as a serious problem in the last decade [13].

2.2 Characteristics of Microcystin-LR

Microcystins, released from *Microcystis*, *Anabaena*, *Oscillatoria, and Nostoc* are the most ubiquitous class of cyanotoxins [14]. A recent study found that 82% of 181 samples of Canadian and U.S. utility waters tested were positive for the presence of microcystins [15]. More than 60 structural variants of microcystins have been identified [2], of which microcystin-LR has shown to be the most commonly occurring and one of the most toxic congeners [14,16].

The chemical structure of microcystin-LR is shown in Figure 2.1. Microcystin-LR is a monocyclic heptapeptide containing five amino acids invariant in all microcystins, and two specific amino acids, Leucine and Arginine, designated "L" and "R", respectively [17]. The size of microcystin-LR is approximately 3 nm in diameter, with a molecular weight of 995.2 [18]. Microcystin-LR is an amphiphatic molecule [18,19]. Hydrophilic functional groups include carboxyl groups on glutamic acid and methylaspartic acid and the amino group on arginine, while the ADDA residue is hydrophobic (see Figure 2.1). The net charge of microcystin-LR is negative (−1) at most pH values ($3 < pH < 12$), as the net result of the dissociation of two carboxyl groups and the single positive charge of the amino group [2].

Since microcystin-LR is the most widely distributed cyanotoxin, humans may easily come into contact with the toxin. A major route of human exposure to microcystins is the consumption of contaminated drinking water. Recreational contact via swimming in contaminated lakes and rivers can be oral and dermal. Adsorption through skin contact is unlikely since microcystin-LR is not cell permeable [20].

Recently, exposure to the toxin through the food-chain (e.g., freshwater mussels and fish) has been widely investigated [21,22].

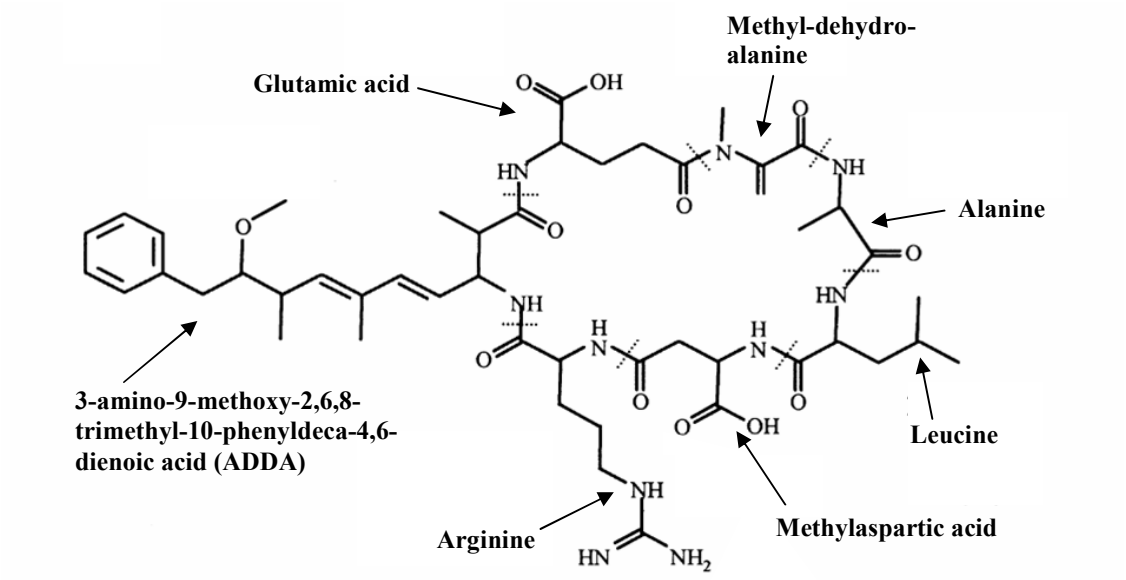

Fig. 2.1 General molecular structure of microcystin-LR (after Sielaff et al. [23])

Microcystin-LR is an extremely acute toxin. The lethal dose (LD_{50}) by the intraperitoneal route ranges from 25 to 150 μg/kg and the oral LD_{50} is 5000 μg/kg in mice [24]. The toxicity of microcystins is associated with the inhibition of protein phosphatases 1 and 2A, which are important regulatory enzymes [25,26]. Ingestion of microcystins primarily leads to severe liver damage and the promotion of liver tumors [27,28], as well as attacks other organs such as the kidney and lungs [29]. High doses of microcystin-LR may cause liver hemorrhage and death [30]. Due to these adverse health

effects, the World Health Organization (WHO) established a provisional guideline of 1 part per billion (μg/L) for microcystin-LR in drinking water [1]. The United States Environmental Protection Agency (USEPA) has also placed microcystins on the Drinking Water Contaminant Candidate List (CCL) which may require a national drinking water regulation in the future [31].

2.3 Fate of Microcystins in Aquatic Systems

Once released into surrounding waters, microcystins go through a variety of biochemical and geochemical processes in aqueous environments. Five pathways contribute to microcystin detoxification [32]: (1) dilution by uncontaminated water masses, (2) thermal decomposition aided by temperature and pH, (3) photolysis, (4) biological degradation, and (5) adsorption on particulate materials.

Thermal decomposition does not significantly contribute to the decomposition of microcystins in natural aquatic environments [32] since microcystins are non-volatile and relatively stable compounds due to their cyclic structure [26]. Microcystins are known to be resistant to pH extremes and temperatures up to 300^{o}C [33].

Microbial degradation has been a possible way to eliminate microcystins, but a lag period of several days to weeks was required before biodegradation is initiated [34]. The photolysis of microcystins by sunlight alone was very slow, though the presence of dissolved natural organic matter, such as cyanobacterial pigments and humic substances, enhanced the degradation due to the formation of highly oxidizing species [34,35]. At least 30 days are needed to achieve 90% degradation of microcystin-LR by indirect photolysis in lake water [4].

Recent studies document that microcystins are strongly adsorbed on soils, sediments and clay particles in natural environments [36,37,38,39,40]. Clay minerals, in particular, adsorb microcystins effectively, and are proposed as a removal technology for microcystins from drinking water and for mitigation of toxins in natural waters [37]. For example, Miller et al. [40] examined the effect of soil properties on the adsorption of hepatotoxins such as microcystin-LR and nodularin. They observed significant positive correlations between toxin adsorption and clay and silt contents of the soils. Morris et al. [37] found that clays in marine sediment, such as kaolinite and montmorillonite, played an important role in removing microcystin-LR from water. Suspended particulate matter (SPM) from lake sediment also significantly adsorbed both microcystin-LR and -LW, likely due to hydrophobic interactions [41].

2.4 Current Treatment Technologies for Microcystin-LR

Various treatment technologies have been investigated to inactivate, degrade, and remove microcystin-LR from drinking water. These include conventional technologies (e.g., coagulation, sand filtration, chlorination, and activated carbon adsorption) as well as advanced technologies (e.g. ozonation, Fenton oxidation, and UV photolysis). The removal of microcystin by various treatment processes is discussed below.

Coagulation, Flocculation, and Sedimentation

Coagulation, flocculation, and filtration are frequently used in drinking water treatment. These technologies are effective in removing particulate cyanobacterial cells, but not effective for the dissolved toxins like microcystins [17,42,43]. Rositano and

Nicholson [44] used three different coagulants, including ferric sulphate, alum, and polyaluminium chloride, to remove microcystins, but no toxin removal was observed. Shumidt et al. [45] reported that chemical treatment and mechanical agitation may cause damage to the cyanobacterial cells, and result in an additional release of the toxin. The management of the sludge containing cyanobacterial cells and toxins may be a serious concern in this process [14].

Sand Filtration

Direct rapid filtration was not effective in removing cyanobacterial cells, while slow sand filters can remove 99% of the cells [46]. In addition, slow sand filtration possibly develops a biofilm on the top of the filter, due to its lower loading rate, resulting in biodegradation of microcystins [14]. Grutzmacher et al. [47] found that more than 90% of microcystins were removed during slow sand filtration, primarily due to the biodegradation on or inside the filter bed. However, plugging of the filter and toxin release from the lysed cyanobacterial cells entrained in filter beds are significant problems [14].

Activated Carbon Adsorption

Activated carbon is produced by steam or chemical activation of carbonaceous materials such as wood, coal, peat and coconut shell [48]. Activated carbon has a high porosity and a large surface area, typically ranging from 600 to 1200 m^2/g, which enables activated carbon to adsorb contaminants from water [48]. Activated carbon consists of

pores of varying sizes, which are classified according to their diameter; micropores (< 2 nm), mesopores (2-50 nm), and macropores (> 50 nm) [49].

Activated carbon, in both granulated and powdered form, has been applied for the removal of microcystins, and has shown successful performance [14]. Pore size distribution was the most important physical property of activated carbon when considering adsorption performance [42]. Donati et al. [50] found that the capacity of powdered activated carbons (PAC) to adsorb microcystin-LR was directly related to the mesopore volume. Since molecular size of microcystin-LR is around 2 nm, it is too large to enter micropores while can easily adsorb in mesopores. Of various activated carbon types, wood-based PAC was shown to be the most effective in removing microcystins due to a higher fraction of mesopores [50,51,52].

Even though activated carbon adsorption can effectively remove microcystins, there are some drawbacks. High dose of PAC is required to meet the WHO guideline [53,54,55]. Also, competition with natural organic matter reduces PAC adsorption capacity for microcystins [14,50]. In granular activated carbon (GAC) filtration, GAC efficiency dropped from over 90% to 49−63%, probably due to saturation of the GAC with dissolved organic carbon [56].

Oxidizing Chemicals

The use of chlorine [7,17,42,43,57] has been investigated to remove microcystins from contaminated water. Microcystins were easily decomposed by chlorination, and the decomposition depended on the free chlorine dose, contact time, and pH [7,57]. Rositano et al. [58] observed over 70% of microcystin-LR (1 mg/L) was removed with 2 mg/L of

chlorine and a contact time of 10 minutes. The toxin destruction decreased with increasing pH above 8, due to decreasing concentrations of hypochlorous acid [7]. However, the use of chlorination on cellular material can lead to the release of toxins from cyanobacterial cells. The formation of chlorinated by-products can be more harmful for human health than the toxin itself [17,42,57].

With regard to other oxidizing chemicals, monochloramine, chlorine dioxide, and hydrogen peroxide were ineffective for treating microcystins. Potassium permanganate was shown to be more effective than chlorine in oxidizing microcystin-LR [42]. Fawell et al. [52] found that potassium permanganate effectively reduced microcystin concentration to below detection limit when applied to both raw and clarified water. It is reported, however, that permanganate induces some cell lysis and increases levels of cyanotoxins [45]. Also, little is known about the possibility of harmful by-products.

Advanced Oxidation Processes

Ozonation is a very efficient process for the rapid and complete destruction of microcystins from water [43,44,58]. Microcystin removal by ozonation can be attributed to the breaking of double bonds in the ADDA group in microcystins since they are very susceptible to ozonolysis [2]. Rositano et al. [58] reported that nearly 100% of microcystin and nodularin in natural water was oxidized by ozonation (0.22 mg/L ozone) within a short treatment time (15 seconds). However, the potential problem of ozonation is the generation of by-products due to incomplete oxidation [17,42,43, 59]. It is necessary to characterize the intermediates formed during oxidation. Also, most drinking water treatment plants currently do not utilize ozone.

UV photolysis is effective for the destruction of microcystins, but high UV radiation dosage (1530−20000 mJ/cm^2) is required for the successful UV photolysis of microcystins, which is impractical for full-scale water treatment [14,42].

Fenton (i.e., hydrogen peroxide with iron) [60,61] and titanium dioxide (TiO_2) photocatalysis [62] were recently studied for the degradation of microcystin-LR. These advanced oxidation processes effectively removed microcystin-LR due to the generation of extremely reactive hydroxyl radicals. Despite the high removal efficiency, these processes suffer from drawbacks that limit their applicability in municipal water treatment such as the creation of excess iron sludge from the Fenton process [14] and low mineralization efficiency (<10 %) by UV-TiO_2 [17].

2.5 Membrane Filtration

Membrane filtration is a physical separation process. For a cross-flow system, an influent water stream fed into the filtration module is divided into two fractions; (1) a permeate containing any material passing through the membrane, which is purified water, and (2) a retentate (or concentrate) containing the materials that have been separated out.

The pressure-driven membrane filtration processes most commonly used in drinking water treatment are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Low-pressure membranes such as microfiltration and ultrafiltration are alternative methods of conventional filtration. MF and UF membranes are primarily used for the removal of turbidity, pathogens, and particles from fresh waters [63]. Nanofiltration is used to soften fresh waters and to remove synthetic organic contaminants (e.g., pesticides) and disinfection by-product precursors [63]. Reverse

osmosis is mainly used for desalination. RO membranes are also very effective in removing aqueous salts and metal ions as well as synthetic organic compounds. The relative size of common contaminants and associated membrane processes are shown in Figure 2.2.

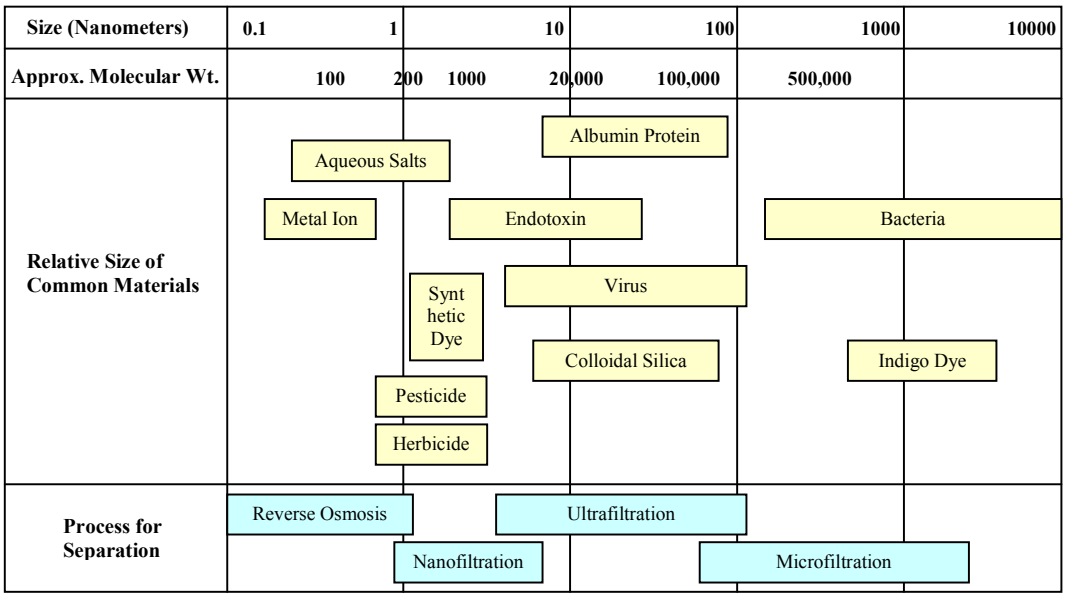

Figure 2.2 Membrane separation and filtration spectrum modified from Osmonics Inc. (http://www.osmolabstore.com/documents/spec2.pdf)

2.5.1 Rejection mechanisms for organic solutes

Possible rejection mechanisms of organic compounds during membrane filtration include size exclusion, electrostatic interaction, diffusion, and adsorption [64]. The main rejection mechanisms in membrane filtration processes are shown in Figure 2.3.

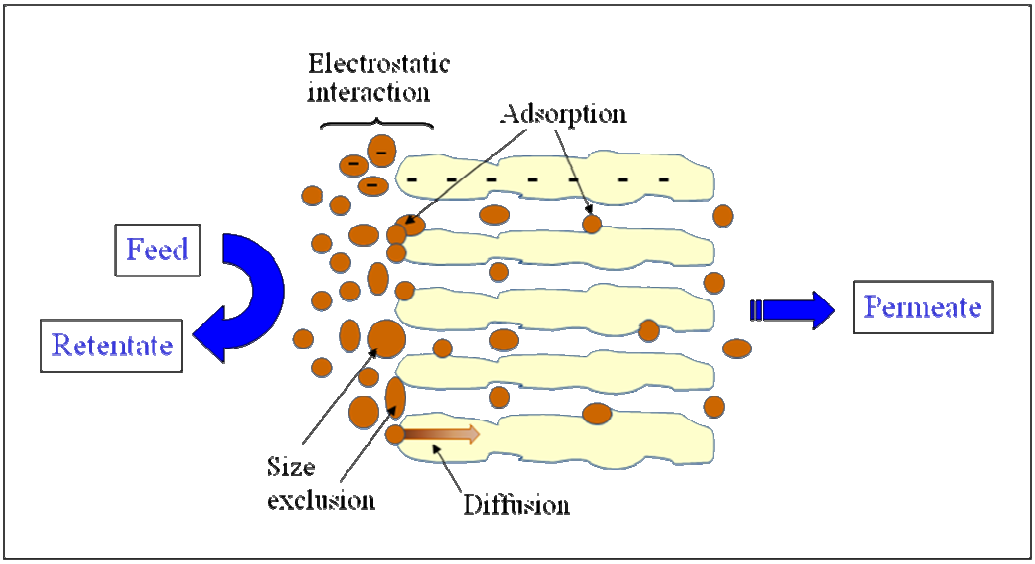

Figure 2.3 Principle mechanisms for separation in membrane filtration.

Size exclusion

The major rejection mechanism for organic compounds is size exclusion (physical sieving) [64]. The pore size of membranes and molecular size of solutes are important factors that influence the extent of size exclusion. For particles equal to or larger than the pore size of the membrane, 100% rejection is predicted. However, no significant rejection occurs for particles much smaller than the pore if size exclusion is the only

means of rejection. A molecular weight cut-off (MWCO) for a membrane is defined as the molecular weight of a certain solute which corresponds with a rejection of 90% [65]. This MWCO value can provide a rough estimate of the sieving effect for the membrane [65, 66].

Electrostatic interaction

Electrostatic interactions may affect the rejection of charged compounds by charged membrane surfaces [66, 67, 68]. Electrostatic repulsion can lead to higher rejection by decreasing the proximity of solutes to the membrane surface, while attraction can decrease rejection. The surface charge of membranes and solutes as well as solution conditions (e.g., pH and ionic strength) strongly affect rejection through electrostatic interaction. Kimura et al. [69] investigated the rejection of disinfection by-products (DBPs), endocrine disrupting compounds (EDCs), and pharmaceutically active compounds (PhACs) by negatively charged NF and RO membranes. They found that negatively charged compounds were always effectively rejected (>90%) regardless of either molecular weight of the compound or MWCO of membranes, due to electrostatic repulsion between the anionic compounds and the negatively charged membranes. For non-charged compounds, size exclusion was most likely the driving mechanism for rejection. The rejection was influenced mainly by the molecular weight of the compounds, leading to varied rejection efficiency (12−99%).

Adsorption

Previous research found that some membranes could adsorb organic molecules, subsequently resulting in an initially high retention [70,71,72,73,74]. Yoon et al. [74] studied the removal of EDCs and PhACs by NF and UF membranes. They observed that NF removed the compounds by both size exclusion and adsorption, while UF removal was mainly due to adsorption. Physico-chemical interactions between the membrane polymer and organic solutes play an important role in governing adsorption. For example, Jones and O'Melia [71] reported that bovine serum albumin (BSA) was adsorbed on UF membranes through hydrophobic interactions with the membrane polymer. Adsorption of steroid hormones to NF membranes occurred by specific interactions such as hydrogen bonding or hydrophobic interaction [72,73].

Diffusion across the membrane

Diffusion across membranes is one of the main driving forces for permeation of organic compounds [75]. Adsorption or partitioning onto membranes and the resulting diffusion through the membrane polymer matrix resulted in lower rejection [76]. RO and tight NF membranes (Na^+ rejection > 90%) only allow the diffusion of water and certain ionic solutes (monovalent ions) and restrict the transport of large organic solutes through diffusion limitations [64]. Diffusion limitations, as well as size exclusion, can play a key role in the rejection of organic compounds by these membranes.

2.5.2 Factors affecting membrane performance

Characteristics of the membranes

Intrinsic properties of membranes affecting membrane filtration performance include pore size (MWCO), membrane surface charge, hydrophobicity, morphology (e.g., surface roughness), and porosity [77,78]. Increased surface charge can lead to increased electrostatic repulsion. A more hydrophobic membrane can more strongly sorb organic compounds due to increased hydrophobic interaction between organic solutes and membranes. Membrane morphology (e.g., physical structure, porosity, roughness, tortuosity, and thickness) also influences attachment of organic molecules [78,79,80,81]. For example, membranes with greater surface roughness cause higher colloid fouling due to increased particle deposition in "valleys" on rough membranes [78].

Physicochemical Properties of the Solutes

Rejection generally increases with increasing molecular size of solutes. Larger molecules are more easily rejected by the membrane through physical sieving. Moreover, they have lower diffusion than smaller molecules, resulting in slow transport through the membrane polymer matrix [64]. Chemical structures or properties of organic molecules such as solute charge, hydrophobicity, and polarity can also significantly influence rejection. For example, an increase in the octanol-water partition coefficient (K_{ow}) of organic molecules enhanced adsorption to the membrane, resulting in higher rejection [74]. High polarity (dipole moment) of organic molecules decreased rejection by NF since electrostatic attraction between the molecular polar centers and charge groups on

the membrane surfaces can direct the molecule toward the membrane pores, leading to permeation [65,82].

Solution Chemistry

Solution conditions such as pH and ionic strength significantly influence the rejection of charged organic compounds. Solution pH changes membrane surface charge as well as molecular charge (expressed by the pK_a). For example, Hong and Elimelech [83] observed a decrease in rejection of NOM by NF membranes with decreasing pH. This can be explained by the reduced electrostatic repulsion due to the less negative membrane surface charge at lower pH. Ozaki and Li [84] reported the rejection of acetic acid increased at pH values above the pKa, likely due to the increased electrostatic repulsion by the deprotonation of acetic acid. Jones and O'Melia [71] studied the effects of solution chemistry on the adsorption of a protein (BSA) and humic acid onto a regenerated cellulose UF membrane. A decrease in solution pH resulted in higher adsorption of both compounds, probably due to the decreased electrostatic repulsion between the adsorbing compound and the membrane surface. Increased ionic strength reduced electrostatic repulsion between like-charged materials (increasing adsorption), but decreased electrostatic attraction between oppositely charged materials (decreasing adsorption).

Operating Conditions

Membrane operating conditions such as feed pressure and water recovery (i.e., ratio between the permeate and feed flow rate) may influence the rejection of organic

solutes. For example, Chellam and Taylor [75] reported that rejection of DBPs by NF membranes decreased with increasing recovery. This is because higher water recovery increased the concentration differential across the membrane, leading to greater diffusion (i.e., low rejection). Tang et al. [85] observed that an increase in initial flux and/or applied pressure enhanced accumulation of perfluorooctane sulfonate (PFOS), probably due to increased hydrodynamic permeate drag that moves PFOS molecules towards membrane surfaces.

Natural Organic Matter (NOM)

The presence of NOM in the feed water can affect the performance of membrane filtration for other target compounds through the formation of larger complexes in the bulk solution or through NOM fouling or accumulation on the membrane surfaces. NOM possibly adsorbs in the pores or deposits on the membranes surface, which causes membrane fouling. The fouling can increase or decrease the rejection of organic solutes, which depends on the type of fouling formation (pore adsorption or deposition on membranes) and the nature of the foulants [86]. Adsorption in pores and pore blocking may increase solute rejection due to increased physical sieving whereas cake-enhanced concentration polarization (i.e., accumulation of solutes at the membrane surface) may decrease rejection through increased diffusion [86,87].

A build-up of a layer of high NOM concentration at the membrane surface can increase complexation and precipitation of aggregates. This enhanced fouling causes increased pressure and/or permeate flux decline during operation [83].

2.5.3 Application to Microcystin Removal

Pressure-driven membrane filtration is a promising treatment process to effectively remove cyanobacteria and cyanotoxins [88]. However, only a few studies have examined the application of membrane filtration for the removal of cyanobacteria and cyanotoxins [53,88,89,90,91].

RO and NF membranes are effective for rejecting microcystins via size exclusion since the pore size of these membranes (MWCO ~100 Da for RO, 150−200 Da used for NF) is smaller than the molecular weight of microcystins (≈1000 Da). For example, Hart and Stott [53] found that nanofiltration reduced microcystin-LR level from 5-30 μg/L to less than 1 μg/L. Neumann and Weckesser [91] observed over 95% and 99% rejection for microcystin-LR and –RR using RO membranes, respectively. Despite high rejection for microcystins, RO and NF processes require a high level of maintenance to prevent membrane fouling by NOM and cyanobacterial cells during cyanobacterial blooms. [38,42].

Low-pressure membrane filtration, such as UF and MF, is adequate for removing cyanobacterial cells, but theoretically unable to reject dissolved toxins due to the high MWCO of these membranes [42,88]. Chow et al. [92] used flat-sheet MF and UF membranes to remove the cells and toxins of a *Microcystis aeruginosa* bloom. These membranes removed more than 98% of the cells, but not for the toxins. Gijsbertsen-Abrahamse et al. [89] observed high rejection (>99%) of *microcystis* cells by the UF membranes with MWCO of 100 KDa, but a maximum of 2% of the cell-bound microcystins was released from the cells due to the shear of the feed pump.

2.6 PAC-UF System

PAC-UF is a combination of powdered activated carbon adsorption and ultrafiltration membrane separation. Typically, PAC is added to the feed water upstream of the membranes. Activated carbon suspended in feed water adsorbs taste and odors as well as a variety of other organic chemicals, which are too small to be removed by UF alone. Ultrafiltration is then able to retain these PAC particles consistently and efficiently from the feed water since PAC is considerably larger than the UF membrane pores.

Coupling activated carbon to ultrafiltration is an emerging technology for the treatment of organic micropollutants in drinking water. Previous research showed an effective removal of turbidity and bacteria as well as dissolved organic contaminants (e.g., atrazine, phenol and dichlorobenzene) by the PAC-UF system [93,94,95,96].

The PAC-UF system provides several benefits. It is possible to maintain the desired quality of the treated water because the removal can be controlled by varying PAC dosage according to water quality [97]. PAC can be recycled to the feed water by using a cross-flow membrane filtration system or by using submerged membranes. This recirculation can increase PAC contact time with organic contaminants, lower PAC doses [98], and subsequently, reduce sludge volume [99] and cost. Moreover, membrane fouling caused by natural organic matter (NOM) may be reduced since activated carbon adsorbs at least a fraction of NOM before ultrafiltration [95,99]. This enhances the permeate flux, reduces the frequency of chemical cleanings, and prolongs the life of the membranes [99]. No studies, however, have examined the use of PAC-UF for the removal of cyanotoxins.

2.7 The Use of Nanoparticles for Water Treatment

The use of nanoparticles as an adsorbent is an innovative technology for efficient water treatment. Nanoparticles are extremely small in size (1-100 nm), which can provide higher surface area per unit mass and more available sites for chemical reaction than conventional adsorbents such as activated carbon [100]. Generally, carbonaceous nanomaterials (i.e., carbon nanotubes), metal oxide nanoparticles, zeolites, and dendrimers are four classes of nanoscale materials that are being evaluated as functional materials for water purification [101].

Iron oxides have been widely used for adsorption since they are naturally occurring minerals and chemically interactive with many organic and inorganic species dissolved in aqueous environments [102]. A number of studies addressed the adsorption of NOM, particularly humic substances, onto iron oxides [103, 104, 105, 106, 107]. Interaction between NOM and iron oxide minerals occurs through various adsorption mechanisms such as electrostatic interaction, ligand exchange, hydrophobic interactions, hydrogen bonding, and cation bridging [104]. Water chemistry strongly influenced the adsorption behavior of NOM. For the adsorption of humic acid on positively charged minerals, it was observed that adsorption increased with decreasing pH and increasing ionic strength [103].

Recently, nanoscale iron oxides have been used for separation and removal of organic and inorganic contaminants [100,108,109]. Various iron nanoparticles such as nanostructured ferric oxides, magnetite, maghemite, and mackinawite have been investigated as an adsorbent for a targeted compound [110]. For example, nanoscale

magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) showed high removal efficiency for heavy metals [111,112]. Liu [108] observed that nano-ferric oxide (Fe_2O_3) effectively removed both organic (e.g., humic acid) and inorganic compounds (e.g., molybdenum, arsenic). Peng et al. [113] examined the adsorption of protein (BSA) on nanosized magnetic particles (Fe_3O_4) for magnetic separation processes. They found that adsorption was primarily attributed to electrostatic interactions, and affected greatly by the pH due to changes in the surface charge of iron oxide and BSA. No research, however, has yet explored the use of nanoparticles for the removal of cyanotoxins.

References

[1] WHO. *Cyanobacterial toxins: Microcystin-LR. Guidelines for drinking water quality*. World Health Organization, Geneva. 1998.

[2] Antoniou, M.G., de la Cruz, A.A., Dionysiou, D.D. 2005. *J. Environ. Eng*. 131(9), 1239-1243.

[3] Falconer, I.R. 1999. *Env. Toxicol*. 14, 5-12.

[4] Lahti, K., Rapala, J., Fardig, M., Niemela, M., Sivonen, K. 1997. *Water Res*. 31, 1005-1012.

[5] Fitzgerald, D.J., Cunliffe, D.A., Burch, M.D. 1999. *Environ. Toxicol*. 14(1), 203-209.

[6] Kotak, B.G., Kenefick, S.L., Fritz, D.L., Rousseaux, C.G., Prepas, E.E., Hrudey, S.E. 1993. *Water Res*. 27(3), 495-506.

[7] Nicholson, B.C. Rositano, J. Burch, M.D. 1994. *Water Res*. 28(6), 1297-1303.

[8] Wiegand, C., Pflugmacher, S. 2005. *Toxicol. Appl. Pharmacol*. 203(3), 201-218.

[9] McElhiney, J., Lawton, L.A. 2005. *Toxicol. Appl. Pharmacol*. 203, 219-230.

[10] Meriluoto, J., Gueimonde, M., Haskard, C.A., Spoof, L. 2005. *Toxicon* 46, 111-114.

[11] Renolds, K.A. 2004. *Wat. Cond. Pur*. 46(3), 78-80.

[12] Walker, S.R. Nebraska Experience. *Proceedings of International Symposium on Cyanobacterial Harmful Algal Blooms (ISOC-HAB)*, USEPA. September 2005.

[13] NOAA. *Harmful algal blooms in the Great Lakes*. NOAA Great Lakes Environmental Research Laboratory, National Oceanic and Atmospheric Administration 2006. http://www.glerl.noaa.gov/res/Centers/HumanHealth/hab/EventResponse/

[14] Svrcek, C., Smith, D.W. 2004. *J. Environ. Eng. Sci*. 3, 155-185.

[15] AWWARF. Project No. 256. American Water Works Association Research Foundation, Denver, Colorado, 2001.

[16] Gupta, N., Pant, S.C., Vijayarghavan, R., Rao, P.V.L. 2003. *Toxicology*. 188, 285-296.

[17] Lawton L.A., Robertson, P.K.J. 1999. *Chem. Soc. Rev.* 28, 217-224.

[18] Vesterkvist, P.S.M., Meriluoto, J.A.O. 2003. *Toxicon*. 41. 349-355.

[19] Pendleton, P., Schumann, R., Wong, S.H. 2001. *J. Colloid Interf. Sci*. 240, 1-8.

[20] Eriksson J. E. Gronberg, L., Nygard, S., Slotte, J.P., Meriluoto, J.A.O. 1990. *Biochimica Biophysica Acta*. 1025, 60-66.

[21] Watanabe, M.F., Park, H.-D., Kondo, F., Harada, K.-I., Hayashi, H., Okino, T. 1997. *Nat. Toxins*. 5, 31-35.

[22] Williams, D.E., Dawe, S.C., Kent, M.L., Andersen, R.J., Craig, M., Homes, C.F.B. 1997. *Toxicon*. 35(11), 1671-1625.

[23] Sielaff, H., Dittmann, E., Tandeau de Marsac, N., Bouchier, C., Von Döhren, H., Börner, T., Schwecke, T. 2003. *Biochem. J.* 373, 909-916.

[24] Fawell, J.K., James C.P., James, H.A. *Toxins from blue-green algae: toxicological assessment of microcystin-LR and a method for its determination in water*. FWR Report No. FR0359/2/DoE 3358/2. Foundation of Water Research, Medmenham, Marlow, Bucks, UK. 1994.

[25] Mackintosh, C., Beattie, K.A., Klumpp, S., Cohen, P., Codd, G.A. 1990. *FEBS Lett*. 264, 187-192.

[26] Metcalf, J.S., Godd, G.A. *Cyanobacterial toxins in the water environment*. FWR Report No. FR/R0009. Foundation for Water Research, UK. February 2004.

[27] Yoshizawa, S., Matsushima, R., Watanabe, M.F., Harada, K.-I., Ichihara, A., Carmichael, W.W., Fujiiki, H. 1990. *J. Cancer Res. Clin. Oncol*. 116, 609-614.

[28] Nishiwaki-Matsushima, R., Ohta, T., Nishiwaki, S., Suganuma, M., Kohyama, K., Ishikawa, T., Carmichael, W.W., Fujiki, H. 1992. *J. Cancer Res. Clin. Oncol*. 118, 420-424.

[29] Hooser, S.B., Beasley, V.R., Basgall, E.J., Carmichael, W.W., Haschek, W.M. 1990. *Vet Pathol*. 27(1), 9-15.

[30] Bischoff, K. 2001. *Vet. Hum. Toxicol*. 43(5), 294-297.

[31] USEPA. *Fact sheet: The drinking water contaminant candidate list−The source of priority contaminants for the drinking water program*. EPA 815-F-05-001. Office of Water, US Environmental Protection Agency, Washington, DC. 2005.

[32] Harada, K.-I., Tsuji, K. 1998. *J. Toxicol Toxicon Rev*. 61, 385-403.

[33] Wannemacher, M.F., Harada, K.I., Matsuura, K., Watanbe M., 1989. *J. Appl. Phycol*. 1, 161-165.

[34] Welker, M., Steinberg, C. 2000. *Environ. Sci. Technol*. 34, 3415-3419.

[35] Tsuji, K., Naito, S., Kondo, F., Ishikawa, N., Watanabe, M.F., Suzuki, M., Harada, K.-I. 1994. *Environ. Sci. Technol*. 28, 173-177.

[36] Tsuji, K., Masui, H., Uemura, H., Mori, Y., Harada, K.-I. 2001. *Toxicon*. 39, 687-692.

[37] Morris, R.J., Williams, D.E., Luu, H.A., Holmes, C.F.B., Andersen, R.J., Calvert, S. E. 2000. *Toxicon*, 38, 303-308.

[38] Miller, M.J., Critchley, M.M., Hutson, J. Fallowfield, H.J. 2001. *Water Res*. 35, 1461-1468.

[39] Mohamed, Z.A., El-Sharouny, H.M., Ali, W.S. 2007. *Arch. Environ. Contam. Toxicol*. 52, 489-495.

[40] Miller, M.J., Hutson, J., Fallowfield, H.J. 2005. *J. water and health*, 3(4), 339-347.

[41] Liu, G., Qian, Y., Dai, S., Feng, N. 2008. *Water Air Soil Pollut*. 192, 67-76.

[42] Drikas, M., Newcombe, G., Nicholson, B. Water treatment options for cyanobacteria and their toxins. *Proceedings of AWWA-Water Quality Technology Conference (WQTC)*. Nashville, TN, November 2001, 2006-2033.

[43] Himberg K., Keijola A.-M., Pyysalo, H., Sivonen K. 1989. *Water Res*. 23(8), 979-984.

[44] Rositano, J., Nocholson, B.C. *Water treatment techniques for removal of cyanobacteiral toxins from water*. Australian Centre for Water Quality Research, Salisbury, South Australia, 1994.

[45] Shumidt, W., Willmitzer, H., Bornmann, K., Pietsch, J. 2002. *Environ. Toxicol*. 17(4), 375-385.

[46] Mouchet, P., Bonnelye, V. 1998. *AQUA* 47(3), 125-141.

[47] Grutzmacher, G., Bottcher, G., Chorus, I., Bartel, H. 2002. *Environ. Toxicol*. 17(4), 386-394.

[48] Schaeffer, K. 2008. *Water Technol. Magazine*. 31(1), Technical pages.

[49] Lambert, T.W., Holmes, C.F.B., Hrudey, S.E. 1996. *Water Res*. 30(6), 1411-1422.

[50] Donati, C., Drikas, M., Hayes, R., Newcombe, G. 1994. *Water Res*. 28(8), 1735-1742.

[51] Mohamed, Z.A., Chrmichael, W.W., An. J., El-Sharouny, H.M. 1999. *Env. Toxicol.* 15, 197-201.

[52] Fawell, J., Hart, J., James, H., Parr, W. 1993. *Water Supply*. 11(3-4), 109-121.

[53] Hart, J., Stott, P. *Microcystin-LR removal from water*. FWR Report No. FR0367. Marlow, Buckinghamshire, Foundation for Water Research, UK. 1993.

[54] Falconer I.R., Runnegar, M.T.C., Buckley, T., Huyn, V.L., Bradshaw P. 1989. *J. Am. Water Works Assoc*. 81(2), 102-105.

[55] Song, W., Teshiba, T., Rein, K., O'Shea, K.E. 2005. *Environ. Sci. Technol.* 39, 6300-6305.

[56] Bruchet, A., Bernazeau, F., Baudin, I., Pieronne, P. 1998. *Water Supply* 16(1-2), 619-623.

[57] Tsuji, K., Watanuki, T., Dondo, F., Watanabe, M.F., Nakazawa, H., Suzuki, M., Uchida, H., Harada, K.-I. 1997. *Toxicon* 35(7), 1033-1041.

[58] Rositano, J., Nicholson, B.C., Pieronne, P. 1998. *Ozone Sci. Eng*. 20(3), 223-238.

[59] Shawwa, A.R., Smith, D.W. 2001. *Ozone Sci. Eng*. 23 (2), 161-170.

[60] Bandala, E.R., Martinez, D., Martinez, E., Dionysiou, D.D. 2004. *Toxicon* 43(7), 829-832.

[61] Gajdek, P., Lechowski, Z., Bochnia, T., Kepczynski, M. 2001. *Toxicon* 39(10), 175-1578.

[62] Robertson, P.K.J., Lawton, L.A., Munch, B., Cornish, B. 1999. *J. Adv. Oxid. Technol*. 4(1), 20-26.

[63] AWWA (American Water Works Association). *Water Quality and Treatment: A Handbook of Community Water Supplies*. McGraw-Hill Inc. New York, 1999.

[64] Bellona, C., Drewes, J.E., Xu, P., Amy, G. 2004. *Water Res*. 38, 2795-2809.

[65] Van der Bruggen, B., Schaep, J., Wilms, D., Vandecasteele, C. 1999. *J. Membr. Sci*. 156, 29-41.

[66] Mohammad, A.W., Ali, N. 2002. *Desalination* 147, 205-212.

[67] Childress, A.E., Elimelech, M. 2000. *Environ. Sci. Technol*. 34, 3710-3716.

[68] Xu, Y., Lebrun, R.E. 1999. *J. Membr. Sci*. 158, 93-104.

[69] Kimura, K., Amy, G., Drewes, J.E., Heberer, T., Kim, T.-U., Watanabe, Y. 2003. *J. Membr. Sci*. 227, 113-121.

[70] Kimura, K., Amy, G., Drewes, J., Watanabe, Y. 2003. *J. Membr. Sci*. 221, 89-101.

[71] Jones, K.L., O'Melia, C.R. 2000. *J. Membr. Sci*. 165, 31-46.

[72] Schäfer, A.I., Nghiem, L.D., Waite, T.D. 2003. *Environ. Sci. Technol*. 37(1), 182-188.

[73] Nghiem, L.D., Schäfer, A.I. 2002. *Environ. Eng. Sci*. 19(6), 441-451.

[74] Yoon, Y., Westerhoff, P., Snyder, S.A., Wert, E.C. 2006. *J. Membr. Sci.*, 270, 88-100.

[75] Chellam, S., Taylor, J.S. 2001. *Water Res*. 35(10), 2460-2474.

[76] Nghiem, L.D., Schäfer, A.I., Elimelech, M. 2004. *Environ. Sci. Technol*. 38, 1888-1896.

[77] Zander, A.K., Curry, N.K. 2001. *Water Res*. 35, 4426-4434.

[78] Vrijenhoek, E.M., Hong, S., Elimelech, M. 2001. *J. Membr. Sci*. 188, 115-128.

[79] Howe, K.J., Clark, M.M. 2002. *Environ. Sci. Technol*. 36, 3571-3576.

[80] Ho, C.-C., Zydney, A.L. 1999. *J. Membr. Sci*. 155, 261-275.

[81] Elimelech, M., Zhu, X., Childress, A.E., Hong, S. 1997. *J. Membr. Sci*. 127, 101-109.

[82] Nghiem, L.D., Schäfer, A.I., Elimelech, M. 2005. *Environ. Sci. Technol*. 39, 7698-7705.

[83] Hong, S., Elimelech, M. 1997. *J. Membr. Sci*. 132(9), 159-181.

[84] Ozaki, H., Li, H. 2002. *Water Res*. 36(1), 123-130.

[85] Tang, C.Y., Fu, Q.S., Criddle, C.S., Leckie, J.O. 2007. *Environ. Sci. Technol*. 41, 2008-2014.

[86] Schafer, A.I., Fane, A.G., Waite, T.D. 2000. *Desalination* 131, 215-224.

[87] Hoek, E.M.V., Kim, A.S., Elimelech, M. 2003. *Environ. Sci. Technol*. 37, 5581-5588.

[88] Teixeira, M.R., Rosa, M.J. 2006. *Water Res*. 40, 2837-2846.

[89] Gijsbertsen-Abrahamse, A.J., Schmidt, W., Chorus, I., Heijman, S.G.J. 2006. *J. Membr. Sci*. 276, 252-259.

[90] Teixeira, M.R., Rosa, M.J. 2005. *Sep. Purif. Technol*. 46, 192-201.

[91] Neumann, U., Weckesser, J. 1998. *Environ. Toxicol. Water Qual*. 13, 143-148.

[92] Chow, C.W.K., Panglisch, S., House, J., Drikas, M., Burch, M.D., Gimbel, R. 1997. *AQUA* 46(6), 324-334.

[93] Kim, J.-S., Lee, S.-J., Yoon, S.-H., Lee, C.-H. 1996. *Water. Sci. Technol*. 34(9), 223-229.

[94] Tomaxzewska, M., Mozia, S. 2002. *Water Res*. 36, 4137-4143.

[95] Adham, S.S., Snoeyink, V.L., Clark, M.M., Bersillon, J.L. 1991. *J. Am. Water Works Assoc*. 83, 81-91.

[96] Adham, S.S., Snoeyink, V.L., Clark, M.M., Anselme, C. 1994. *J. Am. Water Works Assoc*. 85, 58-68.

[97] Matsui, Y., Colas, F., Yuasa, A. 2001. *Water Res*. 35(2), 464-470.

[98] Tomaszewska, M., Mozia, S. Effectiveness of organics removal in hybrid process. *Proceedings of ARS separatoria*, Zloty Potok, Poland. 190-193, 2003.

[99] Mozia, S., Tomaszewska, M., Morawski, A.W. 2005. *Water Res*. 39, 501-509.

[100] Rajagopalan, G., Leong, L.Y.C., Jain, M., Larson, L.E. Use of nanoscale adsorbents for water treatment. *Proceedings of the 40th Western Regional Meeting*. Jan. 22-25, 2006.

[101] Savage, N., Diallo, M. 2005. *J. Nanoparticle Research* 7, 331-342.

[102] Liang, L., Morgan, J.J. 1990. *Aquatic Sci*. 52(1), 32-55.

[103] Davis, J.A. 1982. *Geochim. Cosmochim. Acta* 46, 2381-2393.

[104] Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J.F. 1994. *Environ. Sci. Technol*. 28, 38-46.

[105] Vermeer, A.W.P., van Riemsdijk, W.H., Koopal, L.K. 1998. *Langmuir* 14, 2810-2819

[106] Vermeer, A.W.P., Koopal, L.K. 1998. *Langmuir* 14, 4210-4216.

[107] Weng, L., Van Riemsdijk, W.H., Koopal, L.K., Hiemstra, T. 2006. *Environ. Sci. Technol*. 40, 7494-7500.

[108] Liu, B.H. *Contaminants removal from water using nanoparticles*. MS thesis. Dept. of Environmental Science, California State University, Fullerton. 2006.

[109] Izumi, Y, Masih, D., Aika, K.-I., Seida, Y. 2005. *J. Phys. Chem. B* 109(8), 3227-3232.

[110] Bottero, J.-Y., Rose, J., Wiesner, M.R. 2006. *Integr. Environ. Assess. Manag*. 2(4), 391-395.

[111] Hu, J., Chen, G., Lo, I.M.C. 2006. *J. Environ. Eng*. 132(7), 709-715.

[112] Uheida, A., Salazar-Alvarez, G., Björkman, E., Yu, Z., Muhammed, M. 2006. *J. Colloid and Interf. Sci*. 298, 501-507.

[113] Peng, Z.G., Hidajat, K., Uddin, M.S. 2004. *J. Colloid and Interf. Sci*. 271, 277-283.

CHAPTER 3

EFFECT OF PROCESS VARIABLES AND NATURAL ORGANIC MATTER ON REMOVAL OF MICROCYSTIN-LR BY PAC-UF

Environmental Science and Technology 40 (2006) 7336-7342

3.1 Abstract

The release of cyanobacterial toxins, such as microcystin-LR, in drinking water supplies is of increasing concern. In this study, we investigated the use of ultrafiltration (UF) combined with adsorption on powdered activated carbon (PAC) for the removal of microcystin-LR from drinking water. Process variables examined included PAC type, PAC dosage, membrane characteristics (material and pore size), and the presence of natural organic matter (NOM). Due to greater mesopore volume, wood-based activated carbon was up to 4-times more effective at removing microcystin-LR than coconut-based carbon, depending on contact time. Cellulose acetate (CA) membranes with a molecular weight cutoff (MWCO) of 20,000 Da did not reject or adsorb microcystin-LR. Membranes composed of polyethersulfone (PES) of similar pore size, on the other hand, adsorbed microcystin-LR presumably through hydrophobic interactions. A PES membrane with a MWCO of 5,000 Da sorbed microcystin-LR, and also rejected 8.4% of

the toxin through a size exclusion mechanism. When PAC was coupled to UF using PES membranes, greater removal of microcystin-LR occurred compared to when CA membranes were used due to sorption of the toxin to the PES membrane surface. The presence of Suwannee River Fulvic Acid (SRFA) reduced microcystin-LR removal by PAC-UF, primarily due to competition between SRFA and microcystin-LR for sites on the PAC surface.

3.2 Introduction

The presence of cyanobacteria (e.g., *Anabaena*, *Aphanizomenon*, *Cylindrospermopsis*, *Lyngbya*, *Microcystis*, *Nodularia*, and *Planktothrix*) and associated cyanotoxins in surface water is of increasing concern [1]. Microcystins are the most frequently occurring class of cyanobacterial toxins, of which microcystin-LR is the most toxic and frequently detected congener [2,3,4]. Microcystin-LR is a cyclic heptapeptide containing five amino acids invariant in all microcystins, and two additional amino acids, Leucine and Arginine, which are designated "L" and "R", respectively [3].

Recently, blooms of *Microcystis* have resulted in health alerts in Nebraska and other parts of the Midwestern United States [5]. Ingestion of microcystins can lead to liver damage and may initiate liver tumor-promoting activity [6]. Contamination of drinking water by microcystins has been linked to cases of primary liver cancer in China and the deaths of 76 patients undergoing dialysis in Brazil [4,5,6,7]. Due to adverse health effects, the World Health Organization (WHO) established a provisional concentration limit of 1 μg/L for microcystin-LR in drinking water [8] and the United

States Environmental Protection Agency (USEPA) has placed microcystins on the Drinking Water Contaminant Candidate List [9].

A number of approaches have been investigated for the removal of microcystins from drinking water. Conventional treatment technologies such as coagulation, flocculation, and sand filtration are effective for the removal of particulate cyanobacterial cells but not the dissolved toxins [3,10,11]. Activated carbon adsorption can remove microcystins, but may require high carbon doses to meet the WHO guideline, and competition with natural organic matter reduces adsorption capacity [12,13,14]. Chlorination and ozonation are effective for removing microcystins, but the high dosage required may result in the formation of disinfection by-products [3,11,15].

Powdered activated carbon coupled to ultrafiltration (PAC-UF) is an emerging technology for the removal of organic micropollutants from drinking water. PAC-UF is effective at removing turbidity and bacteria as well as a host of dissolved organic compounds, such as atrazine, phenol and dichlorobenzene [16,17,18,19], to name a few. It can lower powdered activated carbon (PAC) dosage [20], and hence reduce sludge volume [21]. Moreover, membrane fouling caused by natural organic matter (NOM) is decreased since activated carbon adsorbs at least a fraction of NOM before ultrafiltration [18,21]. No research, however, has been carried out to examine the effectiveness of PAC-UF for the removal of microcystins from drinking water. In this study, we investigate the removal of microcystin-LR from drinking water using a bench-scale PAC-UF system. We examine the effect of PAC type and dosage, membrane characteristics, and NOM on the removal of microcystin-LR by this process.

3.3 Experimental Section

3.3.1 Materials

Microcystin-LR with a molecular weight of 995.2 Da was purchased from Spectrum (New Brunswick, NJ) and was used as received. Two different PACs obtained from PICA (Columbus, OH) were used; the properties of which are shown in Table 3.1. PAC size and surface zeta potential were measured using a Malvern Mastersizer (Southborough, MA) and a zeta potential analyzer (Brookhaven Instruments Corp., Holtsville, NY), respectively. Specific surface areas were obtained from BET measurements (Micromeritics, Norcross, GA). Prior to use, both PACs were washed with Milli-Q water (18.2 MΩ cm), filtered, and then dried overnight in an oven at 125^{o}C. Suwannee River Fulvic Acid (SRFA) and Suwannee River Humic Acid (SRHA) were purchased from the International Humic Substances Society (St. Paul, MN) and used as received. Other chemicals such as acetonitrile, ammonium acetate, and sodium bicarbonate were HPLC grade (Fisher Scientific). Polyethylene glycol (PEG) molecules of size 1000, 2000, 4000, 6000, 10000, 20000 Da were purchased from Fisher Scientific for pore size characterization using a previous developed method [22]. All solutions were prepared in Milli-Q water.

3.3.2 UF Membranes

Flat sheet ultrafiltration membranes with an effective surface area of 155 cm^2 were supplied by GE Osmonics (Minnetonka, MN); one cellulose acetate (CA) membrane and two polyethersulfone (PES) membranes were selected for use. CA and PES membranes of similar pore size, 20KDa, were used to examine the effect of

membrane composition. The two PES membranes with 20KDa and 5KDa pores were used to study the effect of membrane pore size on the rejection of microcystin-LR. The characteristics of the membranes are shown in Table 3.2. Prior to use, all membranes were soaked in Milli-Q water for 3 days to remove the glycerin preservative, washed with Milli-Q water for 2 hours, and soaked again in Milli-Q water until use. The membrane zeta potential was determined using an Electro Kinetic Analyzer (EKA) with a clamping cell (Anton Paar, Inc., Austria). The zeta potential of the clean membranes was measured in 10^{-3} M KCl solutions at pH 7.0 ± 0.2.

3.3.3 PAC Adsorption

50 μg/L of Microcystin-LR and 2 mg/L of wood-based or coconut-based activated carbon were added to a 1 L mixing tank and continuously mixed with a magnetic stirrer for four hours. Samples were filtered through 0.45 μm PVDF membrane syringe filters (Millipore, Bedford, MA). The concentration of microcystin-LR was determined at 238 nm using high performance liquid chromatography (Hewlett Packard Series 1100 HPLC) with a diode array detector and a 4.6×150 mm C18 analytical column (Agilent Technologies, Wilmington, DE). The HPLC was operated under isocratic conditions using a mobile phase consisting of 28% acetonitrile and 72% 10 mM ammonium acetate buffer adjusted to pH 7.0 at a flow rate of 0.4 ml/min, as modified from previous methods [23,24]. The pH and ionic strength of all samples were fixed at pH 7.0 ± 0.2 and 5 mM, respectively, using sodium bicarbonate buffer and HCl. Experiments were conducted at a temperature of 23 ± 1 ^{o}C.

3.3.4 Membrane System Operation

The cross-flow, flat-sheet ultrafiltration system used in this study (Sepa CF) was obtained from GE Osmonics. Prior to each experiment, membranes were run with Milli-Q water for at least 2 hours to obtain a steady permeate flux (3.87×10^{-5} m^3/m^2-sec). Once a steady permeate flux was obtained, each filtration run was operated under constant-pressure mode. Different pressures were used for each membrane in order to achieve the same initial flow rates of feed (1.2×10^{-3} L/sec) and permeate (6.0×10^{-4} L/sec), which were 25±5 psi, 20±2 psi, and 55±2 psi for the CA-20KDa, PES-20KDa, and PES-5KDa membranes, respectively.

The membrane filtration system was operated in the batch-recirculation mode in which both permeate and retentate were recycled back to the feed tank. This batch recycle membrane system has been used in numerous previous studies of membrane fouling by NOM and proteins [25,26,27,28]. Operation in the batch recirculation mode was necessary to conserve feed solution composition throughout operation and to quantify membrane adsorption and rejection by size exclusion. Nevertheless, this is quite different from the actual operation in a membrane treatment plant and hence the experimental results obtained in this study vary compared to that expected in a continuous flow treatment system.

Experiments were conducted with a feed volume of 1 L containing an initial concentration of microcystin-LR of 50 μg/L at pH 7.0 ± 0.2, 5 mM ionic strength, and a temperature of 23 ± 1 ^{o}C. SRFA (5 mg/L) or SRHA (5 mg/L) was added to the feed tank with microcystin-LR in select experiments. The amount of microcystin-LR was

measured in the feed, permeate and retentate using HPLC as described previously. Desorption experiments were conducted by switching the feed solution containing microcystin-LR with $NaHCO_3$ solution (pH 7.0 ± 0.2, 5 mM ionic strength, temperature = 23 ± 1 ^oC) free of microcystin.

To examine the effect of membrane fouling on microcystin-LR removal, SRFA or SFHA was added to microcystin-free feed water and the ultrafiltration system was run for 4 hours to allow for deposition of organic matter onto the membrane. The membrane was then rinsed with Milli-Q water and the system run with a feed solution containing 50 μg/L microcystin-LR for another 4 hours as described above.

3.3.5 PAC-UF System

To study PAC-UF, the cross-flow membrane filtration system was coupled to a PAC reactor, as shown in Figure 3.1. The initial concentration of microcystin-LR in the feed tank was 50 μg/L. Various concentrations of wood-based carbon were added directly to the PAC reactor. The feed solution in the reactor was continuously mixed with a magnetic stirrer and fed to the membrane cell with a pump. Prior to each run, the initial flow rates of feed and permeate were adjusted to 1.2×10^{-3} L/sec and 6.0×10^{-4} L/sec, respectively, using Milli-Q water in all experiments. Once a steady permeate flux (3.87×10^{-5} m^3/m^2-sec) was obtained with Milli-Q water, each filtration run was operated under constant-pressure mode. During ultrafiltration, both permeate and retentate were recycled back to the PAC reactor. The pH and temperature of the feed solution were kept constant at 7.0 ± 0.2 and 23 ± 1 ^oC, respectively, and the ionic strength was fixed at 5 mM. Samples taken from the feed, permeate and retentate at various time intervals were

filtered with 0.45 μm PVDF membrane filters and analyzed for microcystin-LR by HPLC. The percent removal was calculated from the change in feed concentration of microcystin-LR by the following equation:

$$\% \text{ Removal} = \frac{(C_{feed,0} - C_{feed,t})}{C_{feed,0}} \times 100$$

where $C_{feed,0}$ is the microcystin-LR concentration in the feed tank at time zero and $C_{feed,t}$ is the microcystin-LR concentration in the feed tank at various times. SRFA (5 mg/L) or SFHA (5 mg/L) was added to the feed tank with microcystin-LR and wood-based carbon in select experiments, and the system was operated as described above.

3.4 Results and Discussion

3.4.1 Adsorption of microcystin-LR on PAC

Initial experiments examined the adsorption of microcystin-LR on two different activated carbons. Wood-based activated carbon adsorbed approximately 80% of microcystin-LR from solution while coconut-based carbon adsorbed only about 20% after 4 hours contact. Previous research reported that the capacity of PAC to adsorb microcystin-LR is directly related to the pore volume in the mesopore region, which is dependent on the starting material [29,30,31]. Pore size distribution of the activated carbon plays an important role in microcystin-LR adsorption because the toxin, with an estimated diameter of 3 nm [2], is too large to enter micropores (diameter less than 2.0 nm) but adsorbs in mesopores (diameter between 2 and 50 nm). The wood-based carbon used here had significant mesopore volume, while the coconut-based carbon was dominated by micropores [30,31]. Total available surface area was not an important

factor given that the wood-based carbon had a slightly lower specific surface area than the coconut-based carbon (see Table 3.1). Also, Pendleton et al. demonstrated that PAC surface chemistry does not play a significant role with respect to microcystin-LR adsorption [31]. Therefore, wood-based carbon was more effective at removing microcystin-LR than coconut-based carbon primarily due to greater mesopore volume. Wood-based carbon was subsequently used in PAC-UF experiments.

3.4.2 Ultrafiltration of microcystin-LR

Figure 3.2 shows the feed, retentate, and permeate concentrations of microcystin-LR for the three different UF membranes listed in Table 3.2. The cellulose acetate membrane with a MWCO of 20,000 Da (CA-20KDa) did not reject or adsorb microcystin-LR (Figure 3.2a). The microcystin-LR concentrations in feed, permeate and retentate did not change over the duration of the experiment. For the polyethersulfone membrane with a similar pore size (PES-20KDa), the concentration of microcystin-LR initially decreased in the feed and retentate and increased in the permeate until reaching steady-state after approximately 60 minutes (Figure 3.2b). Because the retentate and permeate were recycled back to the feed tank, this loss of mass indicates that microcystin-LR adsorbed to the surface of the PES-20KDa membrane or other components of the system. Control experiments verified that microcystin-LR did not adsorb to other components (e.g., tubing and membrane housing) of the UF system. No additional decrease in feed concentration of microcystin-LR occurred after 60 minutes, presumably due to the limited adsorptive capacity of the membrane.

Microcystin-LR is composed of amino acids possessing hydrophobic properties in aqueous media, especially the highly hydrophobic ADDA residue [31,32]. Contact angle measurements [33] indicated that PES membranes are more hydrophobic than membranes made of cellulose acetate (Table 3.2). Therefore, the adsorption of microcystin-LR on PES membranes, and lack of sorption to CA membranes, can be explained by the different hydrophobicities of these two materials. Microcystin-LR is negatively charged over most of the pH range due to deprotonation of carboxylic groups [2] and both CA and PES membranes were negatively charged at the pH used in this study (Table 3.2). The negatively charged microcystin-LR adsorbed on the PES membranes despite the fact that this material was more negatively charged than the CA membrane. This further supports the idea that hydrophobic interactions were the primary driving force leading to the adsorption of microcystin-LR to the PES membranes. It should be noted, however, that the limited adsorption capacity of PES suggests that sorption of microcystin-LR to the membrane surface will not provide long-term removal of the toxin in practice. Previous studies also reported that adsorption of trace contaminants on membranes is a temporary effect that occurs in the initial stages of filtration since breakthrough is observed once membrane adsorptive sites become saturated [34,35].

The feed, retentate and permeate concentrations for the PES membrane with a MWCO of 5,000 Da (PES-5KDa) are shown in Figure 3.2c. In the first 120 minutes, the feed and retentate concentrations of microcystin-LR dropped, and the permeate concentration increased, similar to observations for the PES-20KDa membrane. This indicates that the adsorption of microcystin-LR onto the PES-5KDa membrane was again

an important removal mechanism at the early stage of the filtration run. Unlike PES 20KDa, however, PES 5KDa rejected 8.4% of microcystin-LR at the later stages of filtration, as demonstrated by the slightly lower permeate concentration compared to the feed after 120 minutes. Even though this apparent rejection rate of 8.4% may not be statistically significant, this percent rejection was quite close to the 7.7% rejection of polyethylene glycol (PEG) with a molecular size of 1000 Da, determined in a separate UF test (see Table 3.3). Microcystin-LR is only weakly charged [36] and sorbed to PES, suggesting that repulsive charge interactions between the toxin and the membrane were of secondary importance. Thus, size exclusion was the dominant rejection mechanism after 120 minutes of filtration.

We also examined whether the sorption of microcystin-LR to the PES membrane was reversible. After a 3-hour contact time with microcystin-LR, the feed was replaced with microcystin-free $NaHCO_3$ solution and the system was run for another 3 hours. In this desorption experiment, the permeate and retentate were wasted and not recycled back to the feed tank. A sharp increase in the permeate concentration of microcystin-LR occurred within 2 minutes of replacing the feed solution (Figure 3.3a), indicating that the toxin was quickly desorbed from the PES membrane surface. As the surface coverage of microcystin-LR decreased, the rate of desorption also slowed, which is in agreement with a previous study on surfactant desorption [37]. A mass balance indicated that nearly all of the microcystin-LR (83%) was released from the PES membranes by the 3-hour water rinse (Figure 3.3b). As mentioned previously, microcystin-LR was likely adsorbed on PES membranes through hydrophobic interactions. Because of the low activation energy (~15 kJ/mol) of these interactions [38], water flushing can easily disrupt the sorbed

complexes. For example, the adsorption of proteins on some hydrophobic surfaces is attributed to hydrophobic interactions and is reversible [39,40]. Balannec et al. found that the deposition of negatively charged proteins on membranes was reversibly removed by a flush with tap water under pressure [41].

3.4.3 Removal of microcystin-LR by PAC-UF

Figure 3.4 compares the removal of microcystin-LR by three processes (e.g., PAC adsorption, ultrafiltration, and the PAC-UF system). Testing of PAC adsorption was performed in the PAC-UF system without membranes installed, while UF was tested in the same system without the addition of activated carbon. The PAC-UF system had the highest removal efficiency among the three processes for both the PES and CA membranes. The removal profiles, however, differed for the two membranes. As shown in Figure 3.4a, UF using CA membranes without PAC addition did not remove microcystin-LR while the PAC-UF system resulted in 70% removal of the toxin. The removal of microcystin-LR by the PAC-UF system as a function of time followed a similar trend as PAC adsorption alone, which suggests that PAC adsorption was the dominant removal mechanism. In the case of the PES membrane (Figure 3.4b), the PAC-UF system removed microcystin-LR more effectively than membrane filtration or PAC adsorption alone, since both activated carbon and the PES membrane adsorbed microcystin-LR. At the early stage of the PAC-UF process, microcystin-LR was removed quickly by adsorption on the membrane surface. Later, wood-based carbon adsorbed microcystin-LR and ultrafiltration separated out these PAC particles.

Subsequently, microcystin-LR was removed to a greater extent than the maximum adsorption capacity of the PES membrane.

Activated carbon dose significantly affected the removal of microcystin-LR by PAC-UF (Figure 3.5). Removal of microcystin-LR increased as the dosage of wood-based activated carbon increased. When 5 ppm of activated carbon was added to the feed solution, more than 95% of microcystin-LR was removed by PAC-UF using either CA or PES membranes and less than 1 μg/L of microcystin-LR, which is the WHO guideline, was detected in feed tank and permeate channel. The use of CA membranes in the PAC-UF system was more affected by PAC dose than when the system was run with PES membranes due to lack of sorption of microcystin-LR on the CA membrane surface.

3.4.4 Effect of SRFA on microcystin-LR removal

Natural organic matter (NOM) may compete with microcystins for available PAC sites and block or narrow membrane pores, leading to a negative effect on process performance. Therefore, it is important to examine how organic matter existing in natural waters influences the removal of microcystin-LR by PAC adsorption, membrane filtration or PAC-UF. SRFA was used to examine the effect of natural organic matter on the removal of microcystin-LR. SRFA was chosen given that fulvic acid has been used as a model organic compound in numerous previous studies. Table 3.4 shows the effect of SRFA on microcystin-LR removal by three the processes. In ultrafiltration, initial experiments were carried out by running a 5 mg/L SRFA solution through the system for 4 hours, followed by a 50 μg/L microcystin-LR solution for another 4 hours. While CA membranes were not affected by SRFA (i.e., constant permeate flux was observed), flux

measurements suggested PES membranes were fouled by SRFA. SRFA associated with the membranes blocked membrane pores, which was evident in a greater rejection of 1000 Da-PEG and the 6~11% decrease in permeate flux, as shown in Table 3.3. The removal of microcystin-LR decreased by 21.3% and 13.0% for PES-20KDa and PES-5KDa, respectively, when PES membranes were previously fouled by SRFA (see the sequential adsorption data in Table 3.4). This reduction in removal was attributed to fewer available adsorption sites in the membrane pores and external surfaces for microcystin-LR as a result of the association of SRFA with the PES membranes. Jucker and Clark reported that, based on contact angle measurements, membranes coated with SRFA were more hydrophilic [42], which also may contribute to the decrease in the adsorption of microcystin-LR to the fouled PES membrane surface.

However, when SRFA and microcystin-LR were added to the feed tank simultaneously, the removal of microcystin-LR was not reduced for either the CA or PES membranes (see the simultaneous adsorption in Table 3.4). Microcystin-LR molecules are apparently able to adsorb before significant amounts of SRFA associate with the membrane and block available surface sites.

The presence of SRFA reduced the removal of microcystin-LR in the PAC-UF system using either CA or PES membranes, as shown in Table 3.4. In these experiments, microcystin-LR and SRFA were added to the feed tank simultaneously. Because microcystin-LR removal was not affected when SRFA was added simultaneously with the toxin during UF without PAC addition, the primary cause of the reduced removal in the PAC-UF experiments was a result of competitive adsorption between microcystin-LR and SRFA for available adsorption sites on the activated carbon surface. In the testing of

PAC adsorption alone using the PAC-UF system without membranes installed, the adsorption of microcystin-LR was reduced by 11.3% in the presence of SRFA (Table 3.4). Both microcystin-LR and SRFA compete for similar mesoporous sites due to the similar molecular size of the two compounds. Donati et al. reported that the maximum adsorption of microcystin-LR on activated carbon was lower for river water compared to Milli-Q water due to the presence of natural organic matter [30]. Table 3.4 also demonstrates that PAC-UF using the CA membrane was affected more significantly by SRFA compared to when PES membranes were used. The greater performance of PAC-UF with PES membranes in the presence of SRFA was likely due to the potential for sorption of microcystin-LR to the membrane surface.

3.4.5 Effect of NOM type on microcystin removal by UF or PAC-UF

To examine the effect of NOM characteristics on microcystin-LR removal by UF or PAC-UF, additional experiments using Suwannee River humic acid (SRHA) were conducted. Table 3.5 shows the characteristics of SRFA and SRHA. Based on both High-Pressure Size Exclusion Chromatography (HPSEC) and X-ray scattering, it was previously reported that the molecular weight (MW) of SRHA is larger than that of SRFA. The higher molecular size of SRHA resulted in a greater rejection by both CA and PES membranes (Figure 3.6). SRHA also showed higher aromaticity and lower density of acidic functional groups, which can make SRHA surfaces less negatively charged and more hydrophobic than SRFA. UV absorbance of SRHA was higher than that of SRFA, due to larger molecular weight and higher aromaticity [43].

As shown in Table 3.6, CA membranes were little affected by SRHA, while SRHA associated with the PES membranes likely blocked or narrowed membrane pores, causing the decrease in permeate flux and greater rejection of 1000 Da-PEG molecules as well as microcystin-LR. It can be seen that SRFA more seriously fouled PES membranes than SRHA, since SRFA-fouled membranes showed approximately twice higher increases in the rejection of both PEG molecules and microcystin-LR. It is possibly explained that SRFA may be easier to penetrate into the pore structure and deposit on the pores, due to smaller molecular weights. Subsequently, deposition of smaller SRFA molecules within the membrane pores decreased pore diameter and the effective MWCO [43]. Taniguchi et al. [44] also suggested that low MW species of NOM contributed to pore blockage and were difficult to remove, causing irreversible fouling.

Figure 3.7 shows the comparison between SRFA and SRHA for their effect on microcystin-LR adsorption to the membranes. Overall, the effect of SRHA on the removal of microcystin-LR was similar to that of SRFA. The simultaneous addition of SRHA did not influence the adsorption of microcystin-LR on the PES membranes. The association of either SRFA or SRHA with the membranes, however, reduced microcystin-LR removal due to fewer available sorption sites in the membrane surfaces. The removal of microcystin-LR decreased by 21.3% and 8.5% when PES membranes were previously fouled by SRFA and SRHA, respectively (see the sequential adsorption data in Figure 3.7). Greater reduction by SRFA-fouled membranes may be attributed to reduced available sites for microcystin-LR in external membrane surfaces as well as in the pores. Since SRFA contains more acidic functional groups (Table 3.5), more negative charged and hydrophilic surfaces of SRFA-fouled membranes may also

contribute greater decrease in the adsorption of microcystin-LR. Jucker and Clark [42] also observed, based on zeta potential analysis, the membranes coated with SRFA were more negatively charged than SRHA-coated membranes.

Figure 3.8 shows the effect of NOM type on microcystin removal by PAC adsorption alone and PAC-UF. Adsorption of microcystin-LR by PAC adsorption alone was reduced in the presence of SRFA or SRHA, due to competitive adsorption between microcystin-LR and humic substances. Since PAC adsorption was the dominant removal mechanism during the PAC-UF process, a reduction of microcystin removal by PAC-UF in the presence of NOM followed a trend similar to that by PAC adsorption alone (see Figure 3.8). Type of NOM had little effect on microcystin-LR removal by PAC-UF. Newcombe et al. [45] reported that competitive adsorption to activated carbons was strongly dependent on the relative size of the NOM and the target compounds. Both SRFA and SRHA are suitable to adsorb in mesopores (diameter between 2 and 50 nm) despite of larger molecular weight of SRHA. Thus, similar to SRFA, SRHA competed with microcystin-LR for mesoporous sites on the activated carbon, resulting in a similar reduction of microcystin removal.

In addition to humic substances (HS), whole water samples from Lake Erie were also used to examine how natural lake affects microcystin removal by PAC-UF. (Note that the Lake Erie water was prefiltered using a Watmann filter paper and 0.45 μm groundwater filter before use to remove suspended particles and minimize contributions to flux decline. The pH of all feed solutions was adjusted to pH 7 using HCl.) As shown in Figure 3.8, the removal of microcystin-LR by PAC alone or PAC-UF was lower for Lake Erie water compared to Milli-Q water (i.e. without NOM), which was probably

attributed to the presence of organic matter dissolved in the natural Lake Erie water. Organic carbon content of whole water samples (3.0 mg OC/L) was quite similar to that of 5 mg/L SRFA solution (3.3 mg OC/L) (see Table 3.5 and 3.7), which probably resulted in a removal trend similar to 5 mg/L of HS. The effect of dissolved metal ions was negligible since the total concentration of ions, shown in Table 3.7, would not be much different with feed conditions for HS tests (5.0×10^{-3} mol/L of $NaHCO_3$). Also, the ionic strength did not significantly affect the removal of microcystin-LR by PAC-UF, as shown in Figure 3.9.

Acknowledgments

The authors acknowledge the support of the Ohio Sea Grant College Program and the Ohio State University Graduate Fellowship program. Chin-Min Cheng and Shengnian Wang contributed to BET surface area measurements and zeta potential analyses, respectively. We also thank PICA USA, Inc., Columbus OH, for providing the powdered activated carbon.

References

[1] Carmichael, W.W. 1997. *Adv. Bot. Res.* 27, 211-256.

[2] Antoniou, M.G., de la Cruz, A.A., Dionysiou, D.D. 2005. *J. Environ. Eng.* 131(9), 1239-1243.

[3] Lawton, L.A., Robertson, P.K.J. 1999. *Chem. Soc. Rev.* 28, 217-224.

[4] Meriluoto, J., Gueimonde, M., Haskard, C.A., Spoof, L. 2005. *Toxicon* 46, 111-114.

[5] Walker, S.R. Nebraska Experience. *Proceedings of International Symposium on Cyanobacterial Harmful Algal Blooms (ISOC-HAB)*, USEPA, Research Triangle Park, NC, September 2005.

[6] Feitz, A.J., Waite, D., Jones, G.J., Boyden, B.H., Orr, P.T. 1999. *Environ. Sci. Technol.* 33, 243-249.

[7] McElhiney, J., Lawton, L.A. 2005. *Toxicol. Appl. Pharmacol.* 203, 219-230.

[8] WHO. *Cyanobacterial toxins: Microcystin-LR. Guidelines for drinking water quality*. World Health Organization, Geneva. 1998.

[9] USEPA. *Fact sheet: The drinking water contaminant candidate list−The source of priority contaminants for the drinking water program*. EPA 815-F-05-001. Office of Water, US Environmental Protection Agency, Washington, DC. 2005.

[10] Himberg, K., Keijola, A.-M., Pyysalo, H., Sivonen, K. 1989. *Water Res.* 23(8), 979-984.

[11] Drikas, M., Newcombe, G., Nicholson, B. Water treatment options for cyanobacteria and their toxins. *Proceedings of AWWA-Water Quality Technology Conference (WQTC)*, Nashville, TN, November 2001, 2006-2033.

[12] Hart, J., Stott, P. *Microcystin-LR removal from water.* FR 0367, Marlow, Buckinghamshire, Foundation for Water Research, UK. 1993.

[13] Falconer, I.R., Runnegar, M.T.C., Buckley, T., Huyn, V.L., Bradshaw, P. 1989. *J. Am. Water Works Assoc*. 81(2), 102-105.

[14] Song, W., Teshiba, T., Rein, K., O'Shea, K.E. 2005. *Environ. Sci. Technol.* 39, 6300-6305.

[15] Shawwa, A.R., Smith, D.W. 2001. *Ozone Sci. Eng.* 23(2), 161-170.

[16] Kim, J.-S., Lee, S.-J., Yoon, S.-H., Lee, C.-H. 1996. *Water. Sci. Technol.* 34(9), 223-229.

[17] Tomaxzewska, M., Mozia, S. 2002. *Water Res*. 36, 4137-4143.

[18] Adham, S.S., Snoeyink, V.L., Clark, M.M., Bersillon, J.L. 1991. *J. Am. Water Works Assoc*. 83, 81-91.

[19] Adham, S.S., Snoeyink, V.L., Clark, M.M., Anselme, C. 1994. *J. Am. Water Works Assoc.* 85, 58-68.

[20] Tomaszewska, M., Mozia, S. Effectiveness of organics removal in hybrid process. *Proceedings of ARS separatoria*, Zloty Potok, Poland, 2003, 190-193.

[21] Mozia, S., Tomaszewska, M., Morawski, A.W. 2005. *Water Res.* 39, 501-509.

[22] Cleveland, C.T., Seacord, T.F., Zander, A.K. 2002. *J. Environ. Eng.* 128, 399-407.

[23] Neumann, U., Weckesser, J. 1998. *Environ. Toxicol. Water Qual.* 13, 143-148.

[24] Lambert, T.W., Holmes, C.F.B., Hrudey, S.E. 1996. *Water Res.* 30(6), 1411-1422.

[25] Braghetta, A., DiGiano, F.A., Ball, W.P. 1997. *J. Environ. Eng.* 123(7), 628-641.

[26] Song, W., Ravindran, V., Koel, B.E., Pirbazari, M. 2004. *J. Membr. Sci.* 241, 143-160.

[27] Matthiasson, E. 1983. *J. Membr. Sci.* 16, 23-36.

[28] Turker, M., Hubble, J. 1987. *J. Membr. Sci.* 34, 267-281.

[29] Mohamed, Z.A., Carmichael, W.W., An, J., El-Sharouny, H.M. 1999. *Environ. Toxicol.* 14, 197-201.

[30] Donati, C., Drikas, M., Hayes, R., Newcombe, G. 1994. *Water Res*. 28(8), 1735-1742.

[31] Pendleton, P., Schumanss, R., Wong, S.H.J. 2001. *J. Colloid Interf. Sci.* 240, 1-8.

[32] Vesterkvist, P.S.M., Meriluoto, J.A.O. 2003. *Toxicon* 41, 349-355.

[33] Cho, J., Amy, G., Pellegrino, J., Yoon, Y. 1998. *Desalination* 118, 101-108.

[34] Nghiem, L.D., Schafer, A.I. 2002. *Env. Eng. Sci.* 19(6), 441-451.

[35] Nghiem, L.D., Schafer, A.I., Waite, T.D. 2002. *Desalination* 147, 269-274.

[36] Lawton, L.A., Cornish, B.J.P.A., Macdonald, A.W.R. 1998. *Water Res.* 32(3), 633.

[37] Geffroy, C., Cohen Stuart, M.A., Wong, K., Cabane, B., Bergeron, V. 2000. *Langmuir* 16, 6422-6430.

[38] Nghiem, L.D., Schafer, A.I., Elimelech, M. 2004. *Environ. Sci. Technol*. 38(6), 1888-1896.

[39] Santos, J.H., Matsuda, N., Qi, Z., Yoshida, T., Takatsu, A., Kato, K. 2003. *Surf. Interface Anal.* 35, 432-436.

[40] Krisdhasima, V., Vinaraphong, P., McGuire, J. 1993. *J. Colloid Interf. Sci.* 161, 325-334.

[41] Balannec, B., Vourch, M., Rabiller-Baudry, M., Chaufer, B. 2005. *Sep. Purif. Technol.* 42, 195-200.

[42] Jucker, C., Clark, M.M. 1994. *J. Membr. Sci.* 97, 37-52.

[43] Aoustin, E., Schafer, A.I., Fane, A.G., Waite, T.D. 2001. *Sep. Purif. Technol*. 22-23, 63-78.

[44] Taniguchi, M., Kilduff, J.E., Belfort, G. 2003. *Environ. Sci. Technol*. 37, 1676-1683.

[45] Newcombe, G., Drikas, M., Hayes, R. 1997. *Water Res*. 31(5), 1065-1073.

[46] O'Loughlin, E., Chin, Y.-P. 2001. *Water Res*. 35(1), 333-338.

[47] Thurman, E.M., Wershaw, R.L., Malcolm, R.L., Pinckney, D.J. 1982. *Org. Geochem*. 4, 27-35.

[48] International Humic Substances Society (IHSS) website (http://www.ihss.gatech.edu).

Table 3.1 Characteristics of PACs

Characteristics	**PICASORB 16**	**GX 203**
PAC Source Material	Wood	Coconut Shell
Dominant pore volume [a]	Micro/Mesoporous	Microporous
BET surface area (m^2/g)	640.0	752.8
Geometric mean size (μm)	17.0	9.6
$pH_{(zero\ zeta\ potential)}$	3.02	2.04

[a] Ref. 30, 31.

Table 3.2 Characteristics of ultrafiltration membranes

Characteristics	**CA-20KDa**	**PES-20KDa**	**PES-5KDa**
Membrane composition	Cellulose Acetate	Polyethersulfone	Polyethersulfone
MWCO (Da) [a]	20000	20000	5000
Contact angle (^{o}) [b]	17.0	49.5	49.5
Zeta potential at pH 7 (mV)	-9.3	-13.2	-13.0

[a] Nominal value reported by the manufacturer.
[b] Ref. 33.

Table 3.3 The permeate flux and PEG rejection of clean and SRFA-associated membranes

Membranes	Permeate flux (m^3/m^2-sec)		PEG rejection (%) [a]	
	clean	fouled	clean	fouled
CA-20KDa	3.87×10^{-5}	3.87×10^{-5}	-	-
PES-20KDa	3.87×10^{-5}	3.35×10^{-5}	0.4	3.6
PES-5KDa	3.87×10^{-5}	3.64×10^{-5}	7.6	9.8

[a] Rejection for 1000 Da-PEG molecules, which is the closest in molecular weight (MW) to microcystin-LR (MW=995.2 Da).

Table 3.4 The effect of SRFA on the removal of microcystin-LR by PAC adsorption, UF process, and the PAC-UF system

Processes	Removal of microcystin-LR (%)[a]		
	without SRFA	with SRFA	
		simultaneous	sequential
Ultrafiltration			
CA-20KDa	0.9	1.2	1.1
PES-20KDa	78.0	76.2	56.7
PES-5KDa	66.8	67.3	53.8
PAC adsorption	97.3	86.0	
PAC-UF system			
CA-20KDa	97.4	77.7	
PES-20KDa	95.3	88.7	
PES-5KDa	98.8	89.6	

[a] Percent removal was determined by the feed concentration of microcystin-LR after 4 hours compared to the initial feed concentration using the equation:

$$\% \text{ Removal} = \frac{(C_{feed,0} - C_{feed,4hr})}{C_{feed,0}} \times 100 .$$

Table 3.5 The characteristics of SRHA and SRFA.

Characteristics		Suwannee River Fulvic Acid	Suwannee River Humic Acid
Molecular weight	HPSEC at 280 nm [a]	2290 Da	3759 Da
	X-ray scattering [b]	1-1.5 kDa	5-10 kDa
Acidic functional groups [c]		- Carboxyl group: 11.44 meq/g carbon - Phenolic group: 2.91 meq/g carbon	- Carboxyl group: 9.59 meq/g carbon - Phenolic group: 4.24 meq/g carbon
^{13}C NMR estimates of carbon distribution [c]		Aromatic: 24 % Aliphatic: 33 %	Aromatic: 31 % Aliphatic: 29 %
UV absorbance for 5 mg/L humic substances (HS)		254 nm: 0.09 cm^{-1} 280 nm: 0.06 cm^{-1}	254 nm: 0.12 cm^{-1} 280 nm: 0.09 cm^{-1}
Concentration of dissolved organic carbon (DOC) for 5 mg/L HS [d]		3.3 mg/L	–
Specific UV Absorbance at 254 nm ($SUVA_{254}$) for 5 mg/L HS [e]		2.7 L/mg-m	

[a] Ref. 46; [b] Ref. 47; [c] Ref. 48
[d] Measured by a Total Organic Caron (TOC) analyzer
[e] Calculated by dividing the UV absorbance at 254nm by the DOC of the sample

Table 3.6 The permeate flux, PEG rejection, and microcystin-LR rejection of clean, SRFA-associated, and SRHA-associated membranes

Membranes		Permeate flux (m^3/m^2-sec)	PEG rejection (%) [a]	Microcystin rejection (%)
CA-20KDa	Clean	3.87×10^{-5}	−	1.8
	SRFA-fouled	3.87×10^{-5}	−	0.9
	SRHA-fouled	3.87×10^{-5}	−	0.6
PES-20KDa	Clean	3.87×10^{-5}	0.4	0.0
	SRFA-fouled	3.35×10^{-5}	3.6	9.1
	SRHA-fouled	3.42×10^{-5}	2.1	4.9

[a] Rejection for 1000 Da-PEG molecules, which is the closest in molecular weight (MW) to microcystin-LR (MW=995.2 Da).

Table 3.7 The characteristics of Lake Erie water composition.

pH	7.97	
Organic carbon	TOC: 3.0 mg OC/L UV_{254}: 0.026 cm^{-1} UV_{280}: 0.015 cm^{-1} $SUVA_{254}$: 0.87 L/mg-m	
Ca	26.8 mg/L	6.7×10^{-4} mol/L
Na	5.0 mg/L	2.2×10^{-4} mol/L
Mg	9.5 mg/L	3.9×10^{-4} mol/L
K	1.5 mg/L	3.8×10^{-5} mol/L

* Concentrations of cations were measured by ICP-OES.

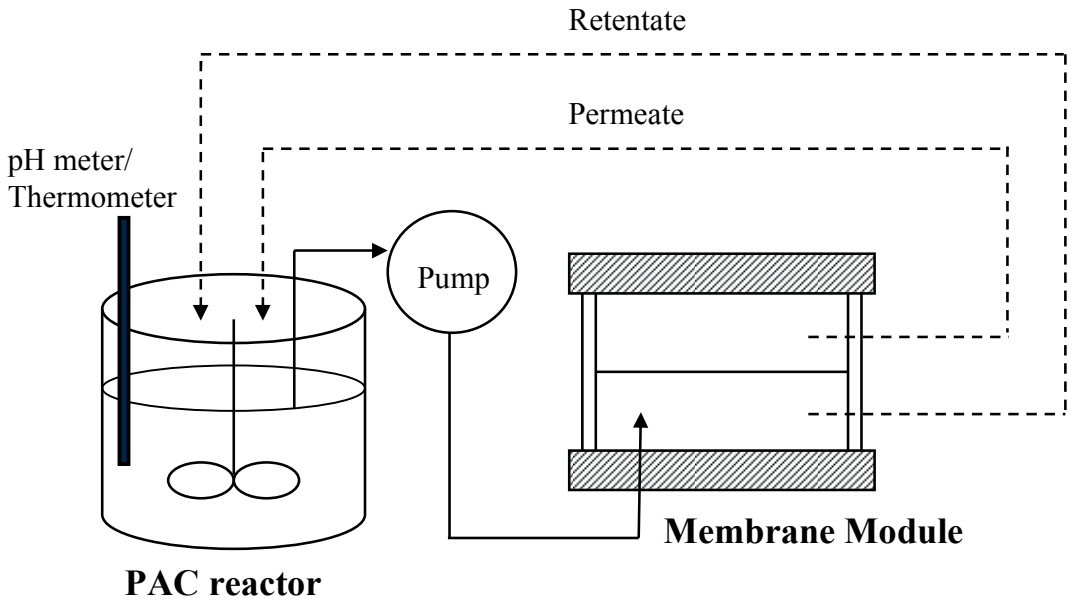

Figure 3.1 A schematic diagram of the bench-scale PAC-UF system.

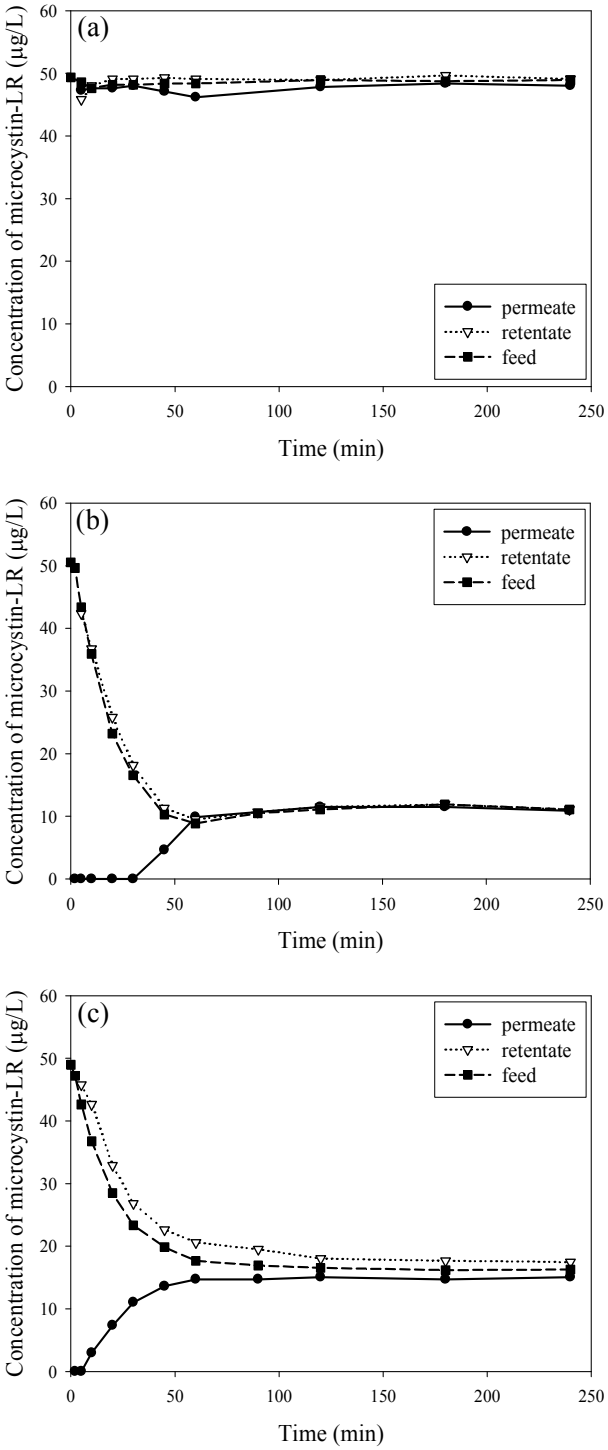

Figure 3.2 The concentrations of microcystin-LR in permeate, retentate, and feed as a function of filtration time for (a) CA-20kDa, (b) PES-20KDa, and (c) PES-5KDa membranes.

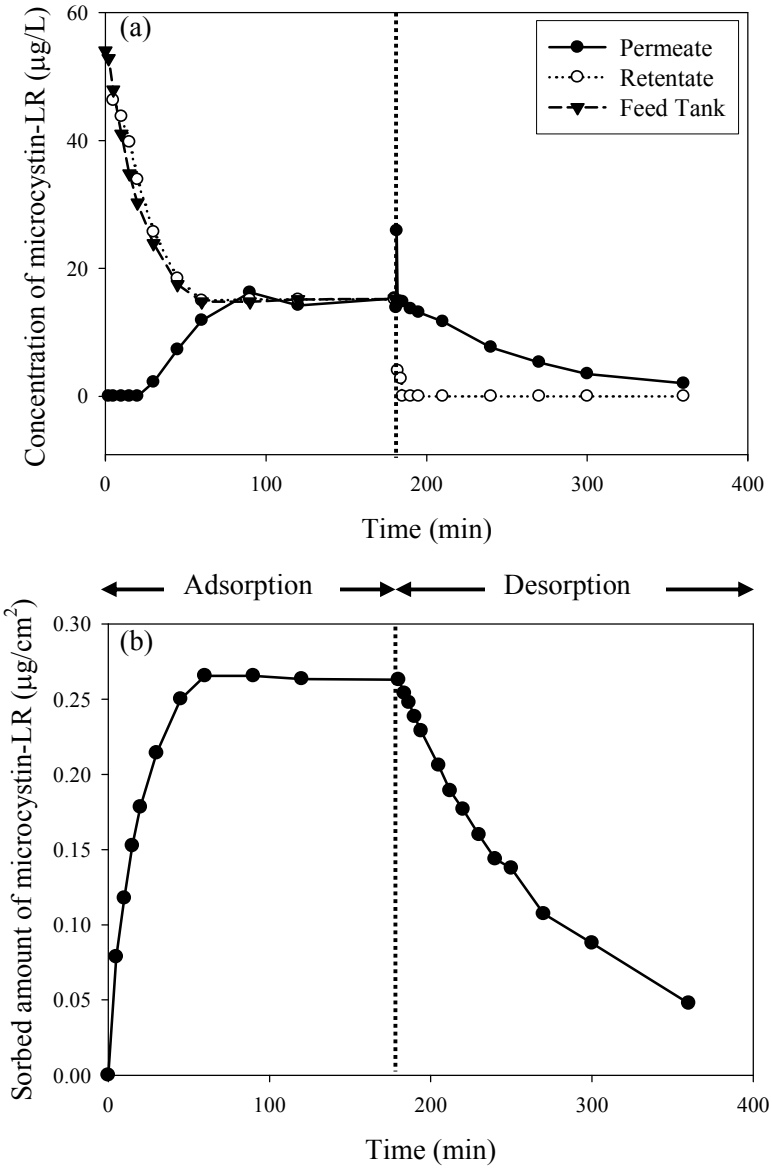

Figure 3.3 (a) The change of microcystin-LR concentrations in permeate, retentate, and feed during adsorption and desorption for the PES-20KDa membrane, (b) The amount of microcystin-LR (μg) sorbed on the PES-20KDa membrane per membrane surface area (cm^2). Feed solution contains 50 μg/L of microcystin-LR for the adsorption period (0~180 minutes) and microcystin-free $NaHCO_3$ solution for the desorption period (180~360 minutes).

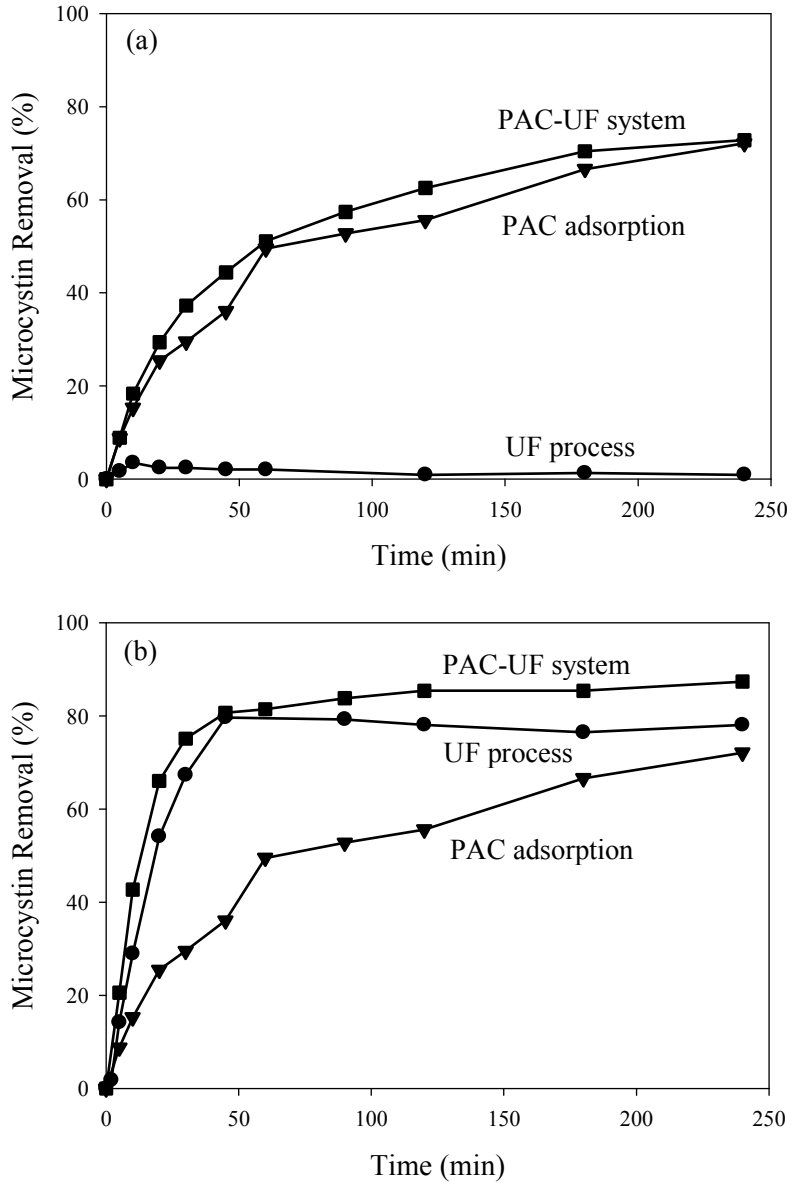

Figure 3.4 Comparison of the microcystin-LR removal by PAC adsorption, ultrafiltration, and the PAC-UF system; (a) CA-20KDa membrane, (b) PES-20KDa membrane. Experimental conditions: microcystin-LR = 50 μg/L, wood-based activated carbon = 2 mg/L, initial permeate flux = 3.87×10^{-5} m^3/m^2-sec, pH = 7.0 ± 0.2, ionic strength = 5 mM, and temperature = 23 ± 1 ^oC.

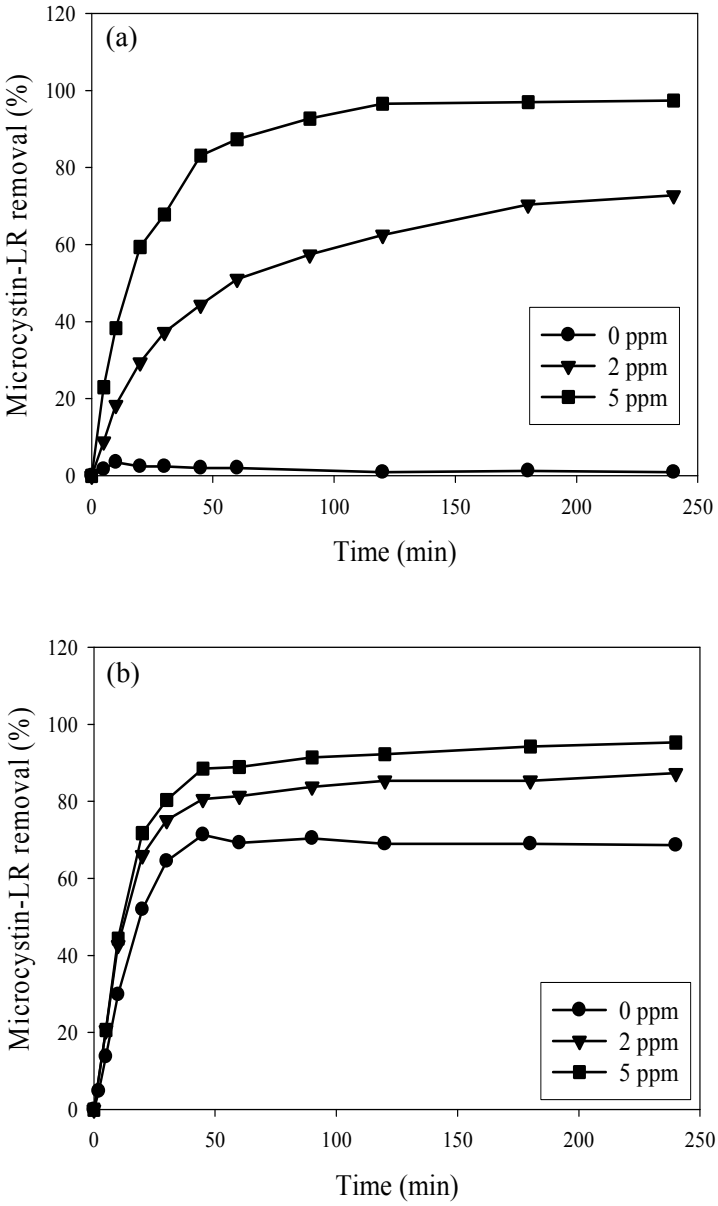

Figure 3.5 The removal of microcystin-LR using (a) CA-20KDa membrane and (b) PES-20KDa membrane with various doses of wood-based activated carbon. Experimental conditions: microcystin-LR = 50 μg/L, initial permeate flux = 3.87×10^{-5} m^3/m^2-sec, pH = 7.0 ± 0.2, ionic strength = 5 mM, and temperature = 23 ± 1 ^{o}C.

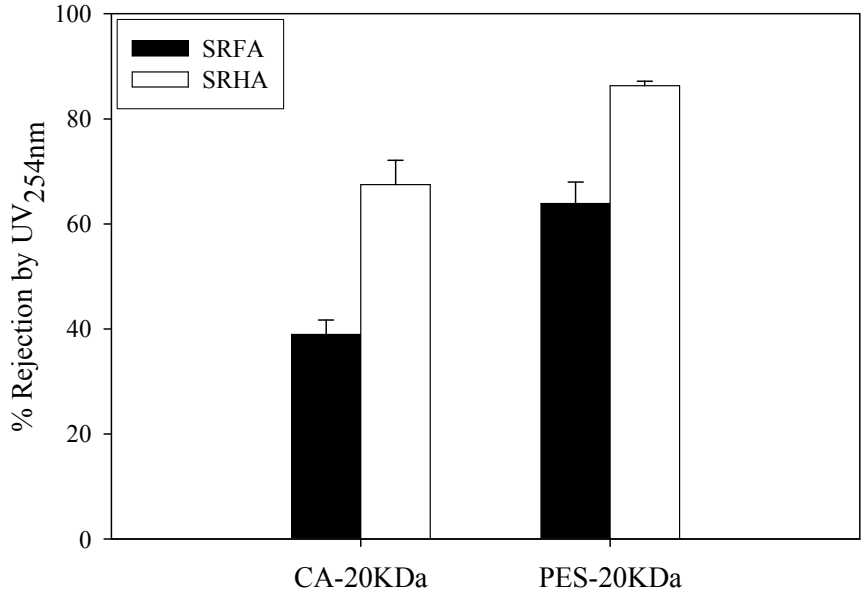

Figure 3.6 The rejection of SRFA and SRHA by CA and PES membranes.

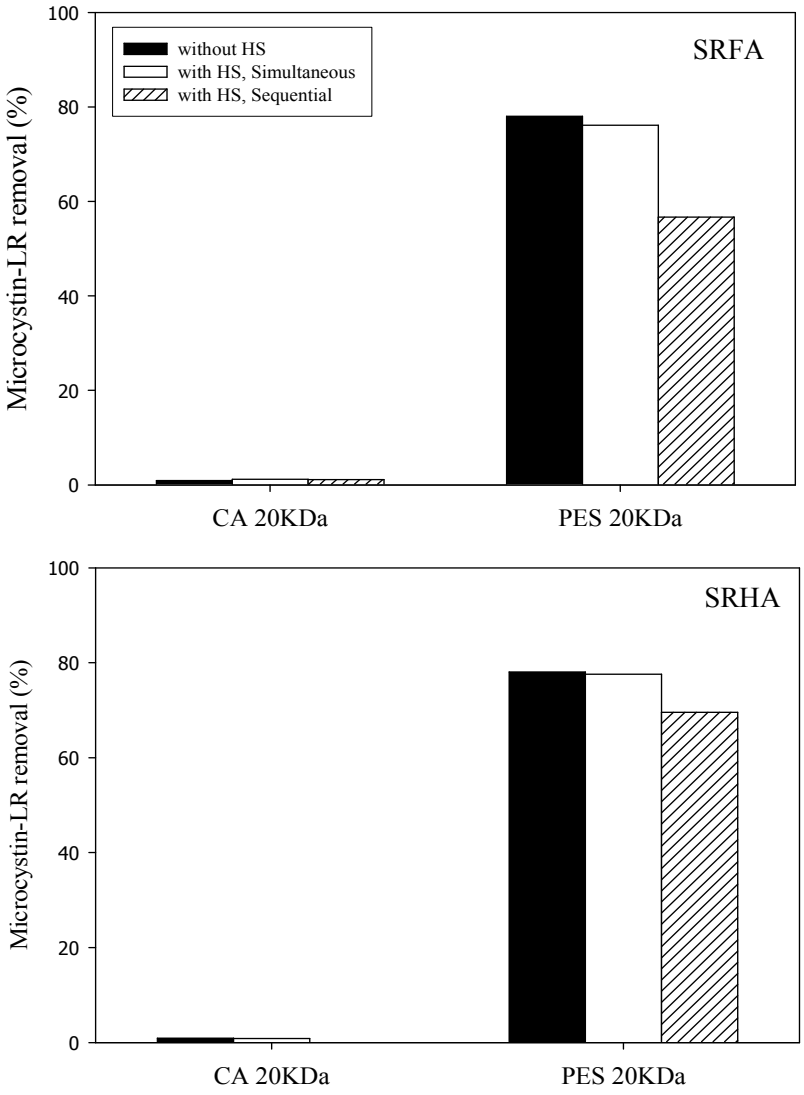

Figure 3.7 Comparison between the effects of SRFA and SRHA on the adsorption of microcystin on UF membranes. Experimental conditions: microcystin-LR = 50 μg/L, initial permeate flux = 6.0×10^{-4} L/sec, pH = 7.0 ± 0.2, ionic strength = 5 mM, and temperature = 23 ± 1 ^{o}C.

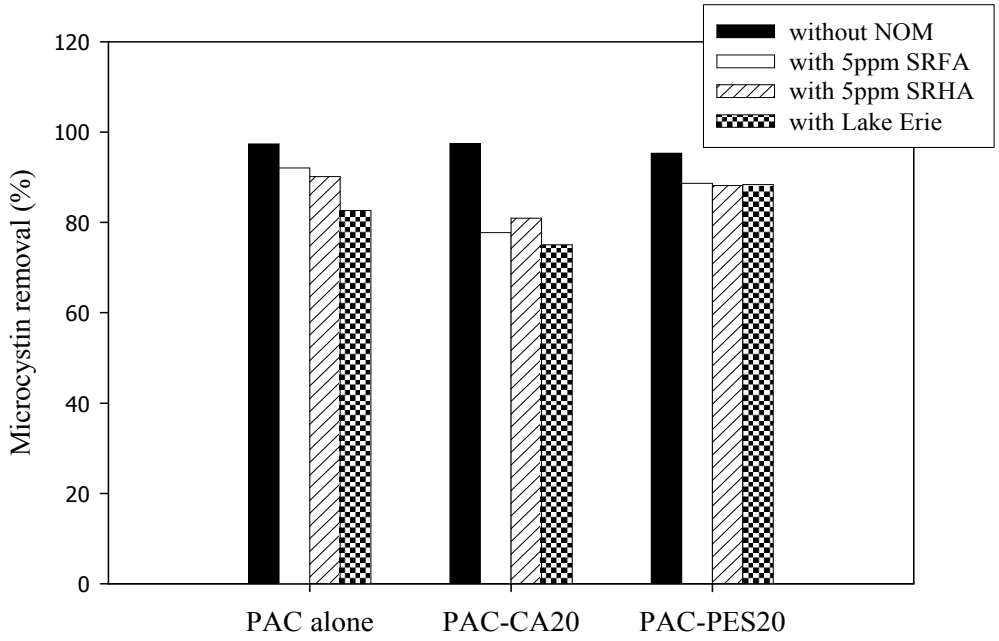

Figure 3.8 The effect of NOM type on microcystin removal by PAC adsorption alone and a PAC-UF system. Experimental conditions: microcystin-LR = 50 μg/L, PAC = 5 mg/L, initial permeate flux = 6.0×10^{-4} L/sec, pH = 7.0 ± 0.2, ionic strength = 5 mM, and temperature = 23 ± 1 ^{o}C.

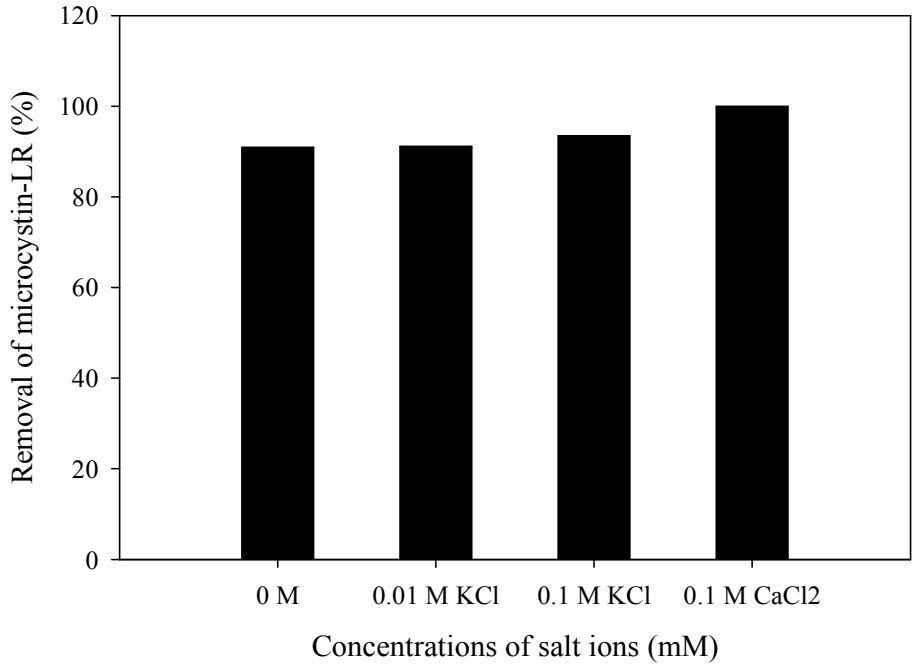

Figure 3.9 The effect of ionic strength on the removal of microcystin-LR by PAC-UF.

CHAPTER 4

MECHANISMS AND FACTORS INFLUENCING THE REMOVAL OF MICROCYSTIN-LR BY ULTRAFILTRATION MEMBRANES

Journal of Membrane Science 320 (2008) 240-247

4.1 Abstract

In this study, we investigate the application of ultrafiltration (UF) for the removal of the cyanotoxin, microcystin-LR, and determine the dominant removal mechanisms. System variables examined included membrane characteristics, feed concentration, water recovery and operating pressure. While adsorption dominated rejection for most UF membranes, at least at early filtration times, both size exclusion and adsorption were important in removing microcystin-LR by the tight thin-film (TF) membranes. Adsorption was primarily attributed to hydrophobic interactions, although hydrogen bonding and physical surface properties such as surface roughness, thickness, and porosity may also play a role. Polysulfone membranes, the most hydrophobic membrane examined, significantly adsorbed microcystin-LR (~91%), whereas the more hydrophilic cellulose acetate membranes adsorbed little or no microcystin-LR. The initial feed concentration had a significant influence on the adsorption capacity of TF membranes for

microcystin-LR, which could be described based on a linear adsorption isotherm. An increase in water recovery and/or operating pressure led to an increase in the adsorption of microcystin-LR, probably due to increased convective transport. On the other hand, microcystin-LR rejection through size exclusion was reduced for higher water recovery and/or applied pressure.

4.2 Introduction

The prevalence of harmful cyanobacterial blooms in drinking water reservoirs is of increasing concern. Cyanotoxins produced by cyanobacteria may cause serious health problems for humans, such as irritation of the skin (dermatotoxins), cell damage (cytotoxins), liver damage (hepatotoxins), and damage to the nervous system (neurotoxins) [1]. Human exposure occurs via recreational contact in surface water, or from ingestion of drinking water that uses a surface water source contaminated with cyanotoxins [2].

Microcystins are the most frequently occurring class of cyanotoxins, of which microcystin-LR is the most toxic and frequently detected congener [3]. As shown in Figure 4.1 [4], microcystin-LR is a cyclic heptapeptide containing five amino acids invariant in all microcystins, and two specific amino acids, Leucine and Arginine, designated “L” and “R”, respectively [5]. Microcystin-LR is an amphiphatic molecule [6,7]. Hydrophilic functional groups include carboxyl groups on glutamic acid and methylaspartic acid and the amino group on arginine, while the ADDA residue is hydrophobic (see Figure 4.1). The net charge of microcystin-LR is negative (−1) at most pH values ($3 < pH < 12$) as a result of the dissociation of the carboxyl groups.

Microcystins are approximately 3 nm in diameter and have a molecular weight of 900−1100 Da [15,18]. Ingestion of microcystin-LR can lead to liver damage and the promotion of liver tumors [8,9]. The World Health Organization (WHO) established a provisional concentration limit of 1 μg/L for microcystin-LR in drinking water [10] and the United States Environmental Protection Agency (USEPA) has placed microcystins on the Drinking Water Contaminant Candidate List [11].

Conventional drinking water treatment processes are either ineffective at removing dissolved cyanotoxins, or have other drawbacks. Coagulation, flocculation, and sand filtration are effective for the removal of particulate cyanobacterial cells but not the dissolved toxins [17,12]. Activated carbon adsorption can remove microcystins, but may require high carbon doses to meet the WHO guideline, and competition with natural organic matter reduces adsorption capacity [13,14,15]. Chlorination and ozonation are effective for removing microcystins, but the high dosage required may result in the formation of harmful by-products [17,16].

Recently, pressure-driven membrane filtration has emerged as a promising treatment process to effectively remove microcystins from drinking water. Nanofiltration (NF) or reverse osmosis (RO) remove microcystins via size exclusion given the molecular weight of microcystins is around 1000 Da [17,18,19]. Previous studies reported that microfiltration (MF) and ultrafiltration (UF) with a molecular weight cut-off (MWCO) of 100 KDa rejected cyanobacterial cells but not the cyanotoxins [19,20]. Our previous research, however, found that UF membranes were able to remove dissolved microcystins mainly by adsorption [21], at least at the early stages of filtration. The adsorption of microcystin-LR was not influenced by natural organic matter (NOM) when

both occurred together in feed water since microcystin molecules are apparently able to adsorb before significant amounts of NOM associated with the membrane. When membranes were previously fouled by NOM, however, a decrease in the adsorption of microcystin-LR was observed. Despite these studies, little is known regarding how ultrafiltration membrane properties (material and pore size) influence the extent of adsorption, and subsequently, microcystin removal. Membrane properties as well as system operating parameters will also influence rejection of microcystin-LR, and their effects are not well understood.

In this study, we investigated how membrane characteristics influence the rejection of microcystin-LR during ultrafiltration. Experiments were conducted using a cross-flow ultrafiltration system and seven different commercial UF membranes to elucidate the rejection mechanisms of microcystin-LR. Other factors governing the removal of microcystin-LR by ultrafiltration such as system operating conditions (e.g., water recovery and operating pressure) and solution conditions (e.g., feed concentration) were also examined.

4.3 Materials and methods

4.3.1 Chemicals and solution chemistry

Microcystin-LR with a molecular weight of 995.2 Da was purchased from Spectrum (New Brunswick, NJ) and was used as received. Other chemicals such as acetonitrile, ammonium acetate, and sodium bicarbonate were HPLC grade (Fisher Scientific). All solutions were prepared in Milli-Q water (resistivity 18.2 MΩ-cm) and

stored at < 4°C. The background electrolyte consisted of 5.0×10^{-3} M $NaHCO_3$ and solution pH was adjusted to pH 7.0 ± 0.2 with 2.0 M HCl.

4.3.2 Ultrafiltration membranes

Flat sheet ultrafiltration membranes with an effective surface area of 140 cm^2 were supplied by GE Osmonics (Minnetonka, MN). Seven ultrafiltration membranes were selected for this study, as shown in Table 4.1. Prior to use, all membranes were soaked in Milli-Q water for 3 days, washed with Milli-Q water for at least 2 hours, and soaked again in Milli-Q water until use to remove any preservatives.

Each membrane was characterized according to molecular weight cut-off (MWCO), membrane hydrophobicity (i.e., contact angle), surface charge (i.e., zeta potential), and pure water permeability (PWP). The characteristics of the membranes are shown in Table 4.1. The nominal MWCO values of membranes were provided by the manufacturer (GE Osmonics). The contact angle of the membranes was determined using the conventional sessile drop technique with Milli-Q water [22]. The membranes were washed with Milli-Q water and then dried in an oven at 70°C for 1.5 hours prior to contact angle measurements. Zeta potential was determined by a streaming potential measurement using an Electro Kinetic Analyzer (EKA, Anton Paar, Austria) equipped with an asymmetric clamping cell. The zeta potential of clean membranes was measured in a solution of 5.0×10^{-3} M $NaHCO_3$ at pH 7.0 ± 0.2. Details on the instrument and measurement procedure can be found elsewhere [23,24,25]. The pure water permeability of each membrane was measured using Milli-Q water following stabilization of water flux through the membrane.

4.3.3 Membrane filtration system

The cross-flow ultrafiltration system used in this study was the commercially-available, stainless-steel Sepa CF II membrane system from GE Osmonics (see Figure 4.2). Prior to introducing microcystin-LR, membranes were equilibrated in the ultrafiltration system with Milli-Q water for at least 2 hours until a steady permeate flux was achieved. Once a steady permeate flux was obtained, each filtration run was operated under constant-pressure mode.

Experiments were conducted with an initial feed concentration of microcystin-LR of 50 μg/L, unless otherwise stated. The pH and temperature of the feed solution were kept constant at 7.0 ± 0.2 and 23 ± 1 ^{o}C, respectively, and the ionic strength was fixed at 5 mM. The membrane filtration system was operated in the batch-recirculation mode, in which both permeate and retentate were recycled back to the feed tank, as shown in Figure 4.2. Operation in the batch recirculation mode was necessary to conserve feed solution and to quantify membrane adsorption and rejection by size exclusion.

Samples were taken from the feed, permeate and retentate at various time intervals for analysis. The concentration of microcystin-LR was determined at 238 nm using high performance liquid chromatography (Hewlett Packard Series 1100 HPLC) with a diode array detector and a 4.6×150 mm C18 analytical column (Agilent Technologies, Wilmington, DE). The HPLC was operated under isocratic conditions using a mobile phase consisting of 28% acetonitrile and 72% 10 mM ammonium acetate buffer adjusted to pH 7.0 at a flow rate of 0.4 ml/min, as modified from previous methods [26,27].

The rejection of microcystin-LR, including both size exclusion and sorption, was calculated as:

$$\% \text{ Rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad [1]$$

where C_p and C_f are microcystin-LR concentrations in the permeate and feed tank, respectively.

Microcystin removal by adsorption alone was calculated from the change in feed concentration as:

$$\% \text{ Adsorption} = \frac{C_{f,0} - C_{f,t}}{C_{f,0}} \times 100 \quad [2]$$

where $C_{f,0}$ is the microcystin-LR concentration in the feed tank at time zero and $C_{f,t}$ is the microcystin-LR concentration in the feed tank at time, t. The retentate and permeate were recycled back to the feed tank, therefore, the amount of microcystin-LR adsorbed on the membranes could be determined by mass-balance:

$$C_{f,0}V_{f,0} = AQ_m + C_{f,f}V_{f,f} + \sum C_s V_s \quad [3]$$

where A is the membrane surface area, Q_m is the adsorbed amount of microcystin-LR per surface area of membrane, $C_{f,0}$ and $C_{f,f}$ are the initial and final feed concentrations of microcystin-LR, $V_{f,0}$ and $V_{f,f}$ are the initial and final volumes of the feed tank, and C_s and V_s are concentration and volume of samples taken for the analysis, respectively. Control experiments verified that microcystin-LR did not adsorb to other components of the UF system (e.g., tubing and membrane housing).

4.4 Results and discussion

4.4.1 Adsorption of microcystin-LR on membranes

The extent of microcystin-LR adsorption was examined for a variety of membranes with varying composition. Figure 4.3 shows the concentrations of microcystin-LR in the permeate and feed tank during filtration using five different UF membranes listed in Table 4.1. For the cellulose acetate (CA) membranes, the microcystin-LR concentrations in the feed and permeate did not change over the duration of the experiment. For other membrane types, however, the microcystin-LR concentrations in the permeate increased with time while the concentration in the feed tank decreased, until reaching steady-state. This observed loss of microcystin-LR in the feed tank could be attributed to adsorption on the membrane surface since both permeate and retentate were recycled back to the feed tank. No loss of microcystin-LR to other components of the filtration system was observed, as verified in control experiments.

In our previous research, we found that microcystin-LR adsorbed to polyethersulfone (PES) membranes, presumably due to hydrophobic interactions since microcystin-LR is composed of amino acids possessing hydrophobic properties in aqueous media, especially the highly hydrophobic ADDA residue [21]. Comparing the data in Figure 4.3 and Table 4.1 suggests that greater membrane hydrophobicity results in higher adsorption of microcystin-LR. As summarized in Table 4.2, nearly all of the microcystin-LR (91%) was adsorbed on the most hydrophobic polysulfone (PS) membrane, while the most hydrophilic CA membranes adsorbed little or no microcystin-LR.

However, membrane hydrophobicity does not completely explain the adsorption behavior of microcystin-LR. For example, polyvinylidene fluoride (PVDF) membranes had a lower adsorptive capacity than thin-film (TF) membranes, despite their greater hydrophobicity (see Table 4.1 and 4.2). In addition to hydrophobicity, other factors must also influence the adsorption behavior of microcystins. Previous studies suggest that membrane morphology (e.g., physical structure, porosity, roughness, tortuosity, and thickness) influences attachment of organic molecules [28,29]. For example, thin-film composite membranes exhibited large-scale surface roughness [30], which may lead to an increase in microcystin-LR adsorption, due to the larger surface area and greater contact opportunities for the toxin with the TF membrane surfaces. This explanation is consistent with Elimelech et al. [31] who attributed higher colloid fouling for TF composite membranes to surface roughness.

The lower adsorption of microcystin-LR on the hydrophobic PVDF membranes may also be related to the physical structure and higher porosity of this membrane. The PVDF membranes used in this study were quite hydrophobic but very thin due to the lack of supporting layers (according to the manufacturer). As a result of the thin PVDF layer, the adsorptive sites on the membrane may become quickly saturated, and consequently, rapid breakthrough was observed within 5 minutes (see Figure 4.3a). Also, as shown in Table 4.1, PVDF membranes had a pure water permeability (PWP) twice that of the PS membranes with a similar pore size. This difference may be due to the smaller thickness, as well as higher porosity of the PVDF membrane, since the PWP is related to pore size, porosity, and membrane thickness [32]. Muller and Davis [33] found greater deposition of protein aggregates for membranes with lower surface porosity and larger thickness.

These studies suggest that the high porosity and thin PVDF layer limit adsorption of microcystin-LR to this membrane.

The adsorption of microcystin-LR on the hydrophilic TF membranes may also be influenced by more specific interactions such as hydrogen bonding. As can be seen in Figure 4.1, microcystin-LR has a number of carbonyl and amino functional groups, which make it capable of participating in hydrogen bonding with membrane functional groups. Even though microcystin-LR is negatively charged over most of the pH range, it is only weekly charged [34] and significantly sorbed to negatively charged TF membranes. Previous studies reported that hydrogen bonding was an important mechanism for the adsorption of organic contaminants on polyamide TF membranes [35,36].

Based on our previous research [21], microcystin-LR was easily desorbed from PES membranes by water flushing, likely due to the low activation energy of the hydrophobic interactions between microcystin-LR and membranes. This is consistent with previous research examining the release of cyanobacterial cells, proteins and polyssacharides using water or caustic [37,38,39]. Therefore, UF membranes should be cleaned and regenerated by backwashing or chemical/oxidant cleaning after blooms of cyanotoxins, to minimize the risk of toxin release to the permeate.

4.4.2 Effect of feed concentration on microcystin-LR adsorption

The effect of the initial feed concentration on microcystin-LR adsorption to TF membranes was studied with feed solutions ranging from 10 μg/L to 100 μg/L. Figure 4.4a shows changes in permeate concentrations for various initial feed concentrations.

As the feed concentration of microcystin-LR increased, the time to breakthrough reduced, and the permeate concentration at steady-state increased. The adsorptive capacity of the TF membrane also increased with increasing feed concentration. Figure 4.4b shows the amount of microcystin-LR adsorbed per unit membrane surface area as a function of the final feed concentration. By assuming that the final feed concentration after reaching steady-state was equal to the equilibrium bulk concentration, the adsorbed amount of microcystin-LR is plotted as an adsorption isotherm. As can be seen in Figure 4.4b, a linear isotherm with a constant partition coefficient of 0.018 L/cm^2 was observed. Similar adsorption isotherms were obtained in previous studies for estrogenic hormone [40] and protein adsorption [41]. The linear adsorption isotherm suggests an initial surface adsorption of microcystin-LR followed by deposition of more microcystin molecules on the adsorbed microcystin monolayer, forming a multilayer of microcystin-LR. Previous research also reported that the deposition is influenced by the feed concentration and concentration gradient at the membrane-solution interface. Martinez et al. [41], for example, reported that protein was deposited on membranes mainly by adsorption at low concentration, while accumulation and cake layer formation occurred at high concentration. Gowman and Ethier [42] found that higher initial concentration increased the thickness of the concentration polarization layer, resulting in greater amount of hyaluronan loaded on to the UF membrane.

The constant partition coefficient resulted in rejection values that were relatively independent (15-23%) of feed concentration. This is consistent with previous research demonstrating no significant influence of feed concentration on the rejection of organic compounds (e.g., endocrine-disrupting compounds or pesticides) by NF membranes

[22,43,44].

4.4.3 Size exclusion by thin-film membranes

The pore sizes of CA-20KDa, PS-30KDa, and PVDF-30KDa membranes were at least 20 times greater than the molecular weight of microcystin-LR. Therefore, size exclusion or cake formation was not likely under these conditions, and permeate concentrations were equal to the feed concentrations at steady-state (see Figure 4.3). To examine the importance of size exclusion for tight UF membranes, additional experiments were conducted using thin-film membranes with smaller MWCOs. In Figure 4.5, it can be seen that permeate concentrations of microcystin-LR stabilized at levels below the feed concentrations. The difference between permeate and feed concentration decreased with increasing pore size, indicating some degree of rejection due to a sieving mechanism. Microcystin-LR is very weakly charged [34] and easily sorbed on TF membranes, which suggests that rejection by charge repulsion can be ignored.

Figure 4.6 shows the percent rejection, which considers both adsorption and size exclusion, of microcystin-LR by the three TF membranes. Microcystin-LR transport was retarded across the membrane layer due to the adsorptive effect, and consequently, this resulted in an initially high rejection of microcystin-LR by the TF membranes. Because the adsorptive capacity of the membranes is limited, the percent rejection stabilized when equilibrium between microcystin-LR and the membrane was established. Microcystin-LR rejection was lower at this later filtration time (> 480 min) and size exclusion played a dominant role. Table 4.3 demonstrates that the average rejection of microcystin-LR at

steady-state followed the order: TF-1KDa > TF-2KDa > TF-4KDa. These rejection trends are consistent with the MWCOs of the membranes used (Table 4.1), which further supports the idea that microcystin-LR was mainly rejected through a size exclusion mechanism after reaching steady-state. As can be seen from Table 4.3, the adsorbed amount of microcystin-LR was quite similar for the three TF membranes, indicating that adsorption of microcystin-LR by these UF membranes is independent of pore size.

The results presented here suggest that molecular weight and hydrophobicity (i.e., octanol-water partition coefficient) of cyanotoxins provides an indication for the potential for size exclusion and adsorption by UF membranes, respectively. For example, other alkaloid cyanotoxins such as anatoxin-a and cylindrospermopsin have lower molecular weights (MW) of 166 and 415, respectively, compared with microcystins. UF membranes are not theoretically able to reject these toxins through size exclusion. We also expect greater adsorption for congeners more hydrophobic than microcystin-LR, such as microcystin-LL, -LF, -LV, and –LM [45]. Since nodularin has similar chemical and physical properties to microcystin-LR [46], it would have a similar adsorption behavior as microcystin-LR during membrane filtration. Cook and Newcombe [47] also observed similar adsorption characteristics of nodularin to powdered activated carbon as microcystin-LR. Further research, however, is needed to examine the removal of other cyanotoxins during membrane filtration.

4.4.4 Effect of operating conditions

The influence of system operating parameters, including water recovery and operating pressure, on microcystin-LR rejection was investigated. PES-5KDa or TF-

4KDa membranes were selected for use since they exhibited both adsorptive effects and size exclusion of microcystin-LR. Figure 4.7a shows the adsorption of microcystin-LR by PES membranes as a function of time at water recoveries of 17%, 50%, and 87%. The water recovery is defined as the ratio between the permeate and feed flow rate. An increase in water recovery resulted in an increase in permeate flux since feed flux was fixed at 7.74×10^{-5} m^3/m^2-sec. As shown in Figure 4.7a, higher water recovery (i.e., permeate flux) resulted in a more rapid and greater adsorption of microcystin-LR onto the membranes. Examining adsorption as a function of accumulated permeate volume rather than time (Figure 4.7b), it was found that the adsorption curves for each recovery were identical. This indicates that the increase in adsorption with increasing water recovery was attributable to the increased permeate flux. Table 4.4 presents the effect of water recovery on size exclusion of microcystin-LR. Interestingly, rejection by size exclusion slightly decreased with increasing water recovery. Chellam and Taylor [48] reported that rejection of trihalomethanes (THMs) by NF membranes decreased as feed water recovery increased due to the increasing concentration gradient across the membrane. A negative impact of water recovery on NF performance was also observed by Reiss et al. [49] for natural organic matter (NOM).

Figure 4.8 shows the effect of operating pressure on microcystin-LR rejection by PES and TF membranes. Each membrane filtration test was conducted at two different pressures to obtain two fixed permeate fluxes of 1.29×10^{-5} m^3/m^2-sec and 3.87×10^{-5} m^3/m^2-sec. As shown, a higher applied pressure increased permeate flux and caused a more rapid and greater decrease of microcystin-LR concentration in the feed tank, indicating increased adsorption of microcystin-LR. These results are consistent with

Kimura et al. [50] who reported that NF/RO membrane saturation by hydrophobic organics was achieved more quickly at higher pressure. Tang et al. [51] also found that perfluorooctane sulfonate (PFOS) accumulation was promoted at greater initial flux and/or applied pressure, likely due to increased hydrodynamic permeate drag. On the other hand, the increase in pressure resulted in a drop in size exclusion from 35% to 23% for TF-4KDa, and from 13% to 8% for PES-5KDa membrane, mainly due to the decreased feed concentration. A decrease in size exclusion with increasing pressure was also observed by previous researchers for estrogenic hormone [52] and chloroform [53].

4.5 Conclusions

Microcystin-LR rejection by UF membranes was investigated to determine the effect of membrane surface properties and operating conditions. The dominant rejection mechanism of microcystin-LR by UF membranes at early stages of filtration was adsorption, presumably due to hydrophobic interactions or hydrogen bonding. Membrane surface morphology, such as porosity, surface roughness, and thickness may also play a role in controlling the extent of adsorption. For tight TF membranes, with similar MWCOs to the molecular weight of microcystin-LR, size exclusion was the dominant rejection mechanism once adsorption reached equilibrium. Higher permeate flux resulted from increasing water recovery or operating pressure, led to greater adsorption of microcystin-LR on the membranes and a decrease in size exclusion.

Acknowledgments

The authors acknowledge the support of the Ohio Sea Grant College Program, the Ohio State University Graduate Fellowship program, and the Ohio Water Development Authority (OWDA). Shengnian Wang and Xuejin Wen contributed to zeta potential analyses and contact angle measurements, respectively.

References

[1] Antoniou, M.G., de la Cruz, A.A., Dionysiou, D.D. 2005. *J. Environ. Eng*. 131(9), 1239-1243.

[2] Wiegand, C., Pflugmacher, S. 2005. *Toxicol. Appl. Pharmacol.* 203(3), 201-218.

[3] Gupta, N., Pant, S.C., Vijayarghavan, R., Rao, P.V.L. 2003. *Toxicology* 188, 285-296.

[4] Sielaff, H., Dittmann, E., Tandeau de Marsac, N., Bouchier, C., Von Döhren, H., Börner, T., Schwecke, T. 2003. *Biochem. J*. 373, 909-916.

[5] Lawton, L.A., Robertson, P.K.J. 1999. *Chem. Soc. Rev*. 28, 217-224.

[6] Pendleton, P., Schumann, R., Wong, S.H. 2001. *J. Colloid Interf. Sci*. 240, 1-8.

[7] Vesterkvist, P.S.M., Meriluoto, J.A.O. 2003. *Toxicon* 41, 349-355.

[8] Yoshizawa, S., Matsushima, R., Watanabe, M.F., Harada, K.-I., Ichihara, A., Carmichael, W.W., Fujiiki, H. 1990. *J. Cancer Res. Clin. Oncol*. 116, 609-614.

[9] Nishiwaki-Matsushima, R., Ohta, T., Nishiwaki, S., Suganuma, M., Kohyama, K., Ishikawa, T., Carmichael, W.W., Fujiki, H. 1992. *J. Cancer Res. Clin. Oncol*. 118, 420-424.

[10] WHO. *Cyanobacterial toxins: Microcystin-LR. Guidelines for drinking water quality*. World Health Organization, Geneva. 1998.

[11] USEPA. *Fact sheet: The drinking water contaminant candidate list−The source of priority contaminants for the drinking water program*. EPA 815-F-05-001. Office of Water, US Environmental Protection Agency, Washington, DC. 2005.

[12] Himberg K., Keijola A.-M., Pyysalo, H., Sivonen K. 1989. *Water Res*. 23(8), 979-984.

[13] Hart, J., Stott, P. *Microcystin-LR removal from water*. FR 0367, In: P. Marlow (Ed.), Buckinghamshire, Foundation for Water Research, UK. 1993.

[14] Falconer, I.R., Runnegar, M.T.C., Buckley, T., Huyn, V.L., Bradshaw, P. 1989. *J. Am. Water Works Assoc*. 81(2), 102-105.

[15] Song, W., Teshiba, T., Rein, K., O'Shea, K.E. 2005. *Environ. Sci. Technol.* 39, 6300-6305.

[16] Shawwa, A.R., Smith, D.W. 2001. *Ozone Sci. Eng*. 23(2), 161-170.

[17] Teixeira, M.R., Rosa, M.J. 2006. *Water Res*. 40, 2837-2846.

[18] Teixeira, M.R., Rosa, M.J. 2005. *Sep. Purif. Technol*. 46, 192-201.

[19] Gijsbertsen-Abrahamse, A.J., Schmidt, W., Chorus, I., Heijman, S.G.J. 2006. *J. Membr. Sci*. 276, 252-259.

[20] Chow, C.W.K., Panglisch, S., House, J., Drikas, M., Burch, M.D., Gimbel, R. 1997. *AQUA* 46(6), 324-334.

[21] Lee, J., Walker, H.W. 2006. *Environ. Sci. Technol*. 40(23), 7336 -7342.

[22] Schäfer, A.I., Nghiem, L.D., Waite, T.D. 2003. *Environ. Sci. Technol*. 37(1), 182-188.

[23] Elimelech, M., Chen, W.H., Waypa, J.J. 1994. *Desalination* 95(3), 269-286.

[24] Walker, S.L., Bhattacharjee, S., Vrijenhoek, E.M., Elimelech, M. 2002. *Langmuir* 18, 2193-2198.

[25] Tang, C.Y., Fu, Q.S., Robertson, A.P., Criddle, C.S., Leckie, J.O. 2006. *Environ. Sci. Technol*. 40, 7343-7349.

[26] Neumann, U., Weckesser, J. 1998. *Environ. Toxicol. Water Qual*. 13, 143-148.

[27] Lambert, T.W., Holmes, C.F.B., Hrudey, S.E. 1996. *Water Res*. 30(6), 1411-1422.

[28] Howe, K.J., Clark, M.M. 2002. *Environ. Sci. Technol*. 36, 3571-3576.

[29] Ho, C.-C., Zydney, A.L. 1999. *J. Membr. Sci*. 155, 261-275.

[30] Petersen, R.J. 1993. *J. Membr. Sci*. 83, 81-150.

[31] Elimelech, M., Zhu, X., Childress, A.E., Hong, S. 1997. *J. Membr. Sci*. 127, 101-109.

[32] Yoon, Y., Amy, G., Cho, J., Pellogrino, J. 2004. *Sep. Sci. Technol*. 39(9), 2105-2135.

[33] Muller, J., Davis, R.H. 1996. *J. Membr. Sci*. 116(1), 47-60.

[34] Lawton, L.A., Cornish, B.J.P.A., Macdonald, A.W.R. 1998. *Water Res*. 32(3), 633-638.

[35] Nghiem, L.D., Schafer, A.I., Waite, T.D. 2002. *Wat. Sci. Technol*. 46(4-5), 265-272.

[36] Williams, M.E., Hestekin, J.A., Smothers, C.N., Bhattacharyya, D. 1999. *Ind. Eng. Chem. Res*. 38, 3683-3695.

[37] Farahbakhsh, K., Svrcek, C., Guest, R.K., Smith, D.W. 2004. *J. Environ. Eng. Sci*. 3, 237-253.

[38] Liu, C., Caothien, S., Hayes, J., Caothuy, T., Otoyo, T., Ogawa, T. Membrane Cleaning: from Art to Science. *Proceedings of Membrane Technology Conference*. March 2000.

[39] Gan, Q., Howell, J.A., Field, R.W., England, R., Bird, M.R., McKechinie, M.T. 1999. *J. Membr. Sci*. 155(2), 277-289.

[40] Nghiem, L.D., Schäfer, A.I. 2002. *Environ. Eng. Sci*. 19(6), 441-451.

[41] Martinez, F., Martin, A., Pradanos, P., Calvo, J.I., Palacio, L., Hernandez, A. 2000. *J. Colloid Interf. Sci*. 221, 254–261.

[42] Gowman, L.M., Ethier, C.R. 1997. *J. Membr. Sci*. 131, 107-123.

[43] Van der Bruggen, B., Schaep, J., Maes, W., Wilms, D., Vandecasteele, C. 1998. *Desalination* 117, 139-147.

[44] Kim, T.-U. 2006. *Transport of organic micropollutants through Nanofiltration (NF) and reverse osmosis (RO) membranes: mechanisms, modeling, and applications*. Ph.D. dissertation. University of Colorado at Boulder. 77-83.

[45] Craig, M., MacCready, T.L., Luu, H.A., Smillie, M.A., Dubord, P., Holmes, C.F.B. 1993. *Toxicon* 31(12), 1541-1549.

[46] Svrcek, C., Smith, D.W. 2004. *J. Environ. Eng. Sci*. 3, 155-185.

[47] Cook, D., Newcombe, G. Effect of natural organic matter concentration and character on the adsorption of microcystin analogues onto PAC. *Proceedings of the AWWA−Water Quality Technology Conference*. November 2002.

[48] Chellam, S., Taylor, J.S. 2001. *Water Res*. 35(10), 2460-2474.

[49] Reiss, C.R., Taylor, J.S., Robert, C. 1999. *Desalination* 125, 97-112.

[50] Kimura, K., Amy, G., Drewes, J., Watanabe, Y. 2003. *J. Membr. Sci*. 221, 89-101.

[51] Tang, C.Y., Fu, Q.S., Criddle, C.S., Leckie, J.O. 2007. *Environ. Sci. Technol*. 41, 2008-2014.

[52] Nghiem, L.D., Manis, A., Soldenhoff, K., Schäfer, A.I. 2004. *J. Membrane. Sci*. 242, 37-45.

[53] Ducom, G., Cabassud, C. 1999. *Desalination* 124, 115-123.

Table 4.1 Characteristics of ultrafiltration membranes

Membranes	Membrane surface material	MWCO (Da)	Contact angle (deg)	Zeta potential at pH 7 (mV)	PWP (L/m^2-day-kPa)
CA-20KDa	Cellulose Acetate	20,000	33	-9.6	21.5
PES-5KDa	Polyethersulfone	5,000	49	-14.2	6.6
TF-1KDa	Polyamide	1,000	38	-23.0	1.2
TF-2KDa	Polyamide	2,000	37	-21.8	2.0
TF-4KDa	Polyamide	4,000	37	-18.8	4.2
PS-30KDa	Polysulfone	30,000	64	-17.8	20.7
PVDF-30KDa	Polyvinylidene Fluoride	30,000	51	-15.3	41.3

Table 4.2 Adsorption of microcystin-LR to various UF membranes

Membranes	Adsorption (%) [a]	Adsorbed amount (mg/m^2)
CA-20KDa	0.9	0.1
PES-5KDa	66.8	2.2
TF-4KDa	74.7	2.5
PS-30KDa	91.2	3.0
PVDF-30KDa	35.1	1.4

[a] Average percent adsorption of microcystin-LR at steady-state

Table 4.3 Effect of pore size on the rejection of microcystin-LR using TF membranes

Membranes	Adsorption (%) [a]	Adsorbed amount (mg/m^2)	Size exclusion (%) [b]
TF-1KDa	69.9	2.4	69.5
TF-2KDa	75.9	2.6	55.4
TF-4KDa	70.3	2.5	34.8

[a] Average percent adsorption of microcystin-LR at steady-state
[b] Average percent rejection by size exclusion of microcystin-LR at steady-state

Table 4.4 Effect of water recovery on the rejection of microcystin-LR using PES membranes

Water recovery (%)	Size exclusion (%) [a]
17 %	11.7 (σ^2=1.2)
50 %	8.4 (σ^2=0.9)
87 %	4.3 (σ^2=0.5)

[a] Average percent rejection by size exclusion of microcystin-LR at steady-state

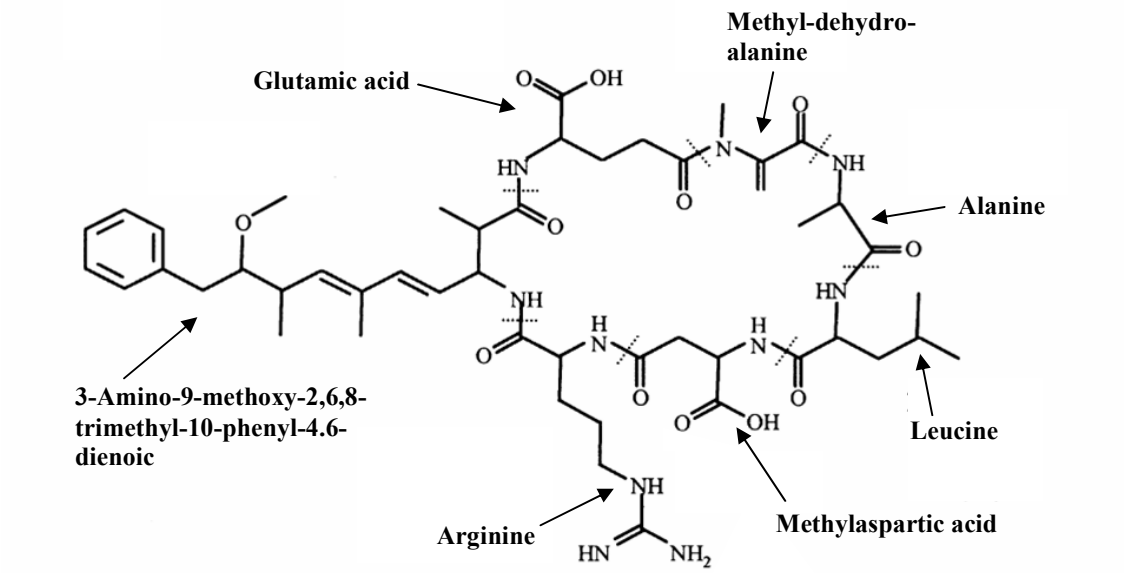

Figure 4.1 General molecular structure of microcystin-LR (after Sielaff et al. [4])

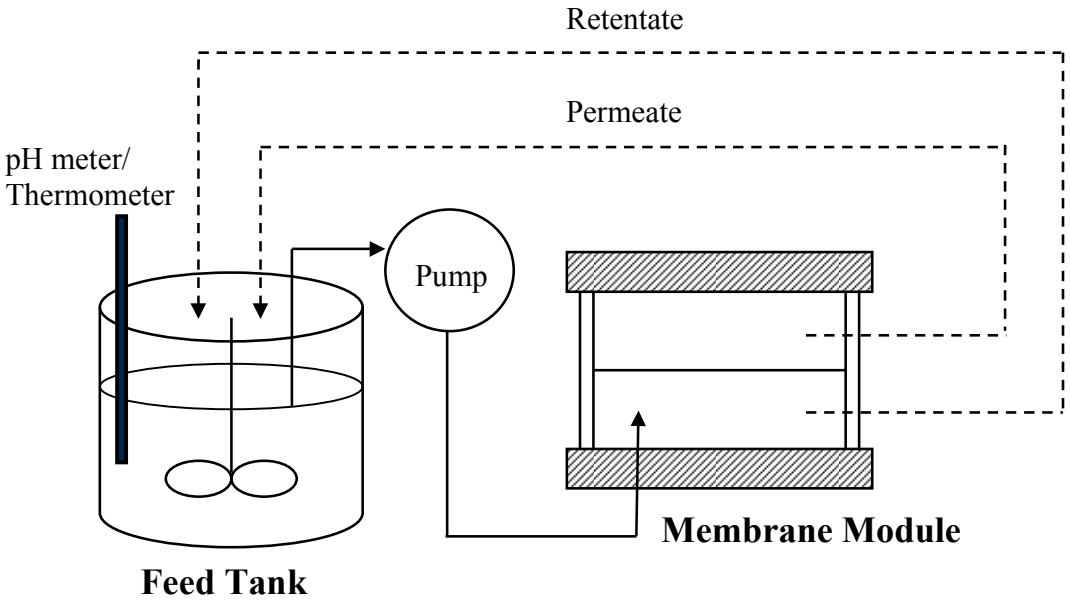

Figure 4.2 Schematic diagram of the bench-scale UF system.

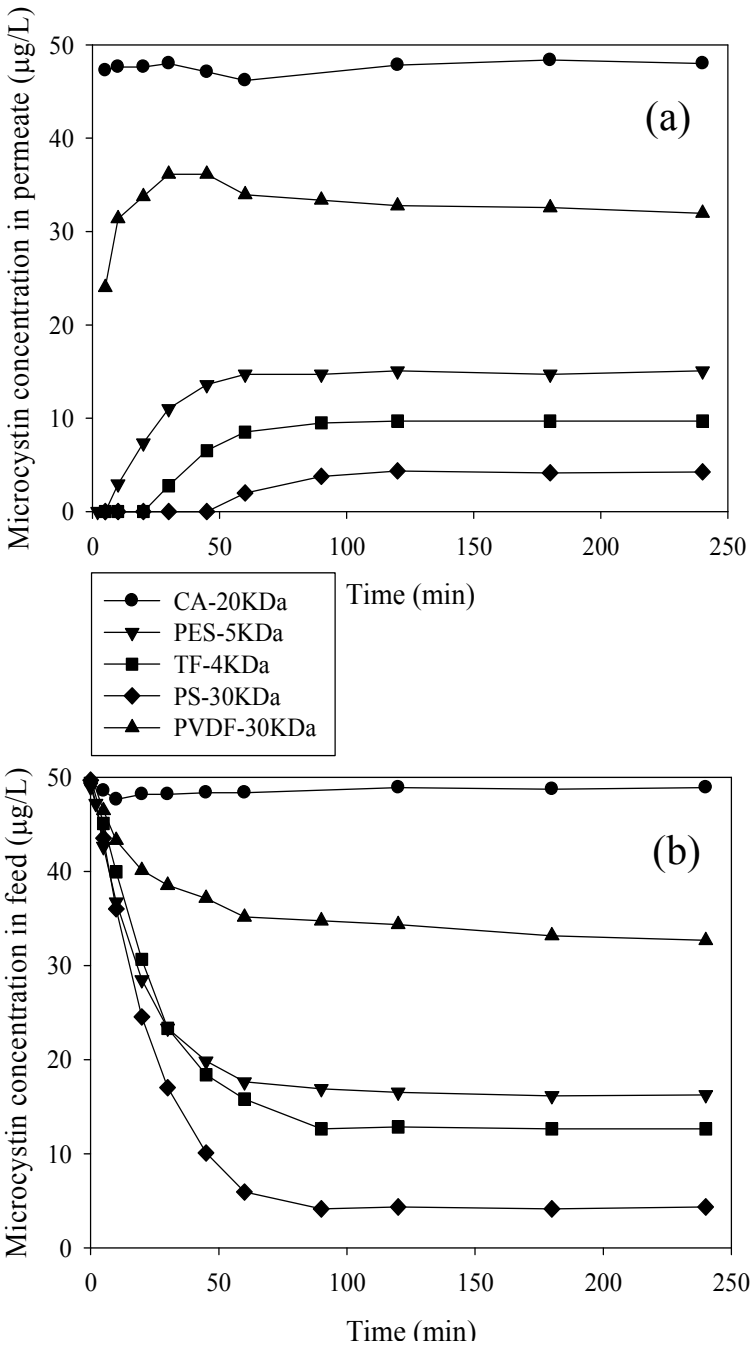

Figure 4.3 Concentration of microcystin-LR in permeate flow (a) and feed tank (b) for various membranes.

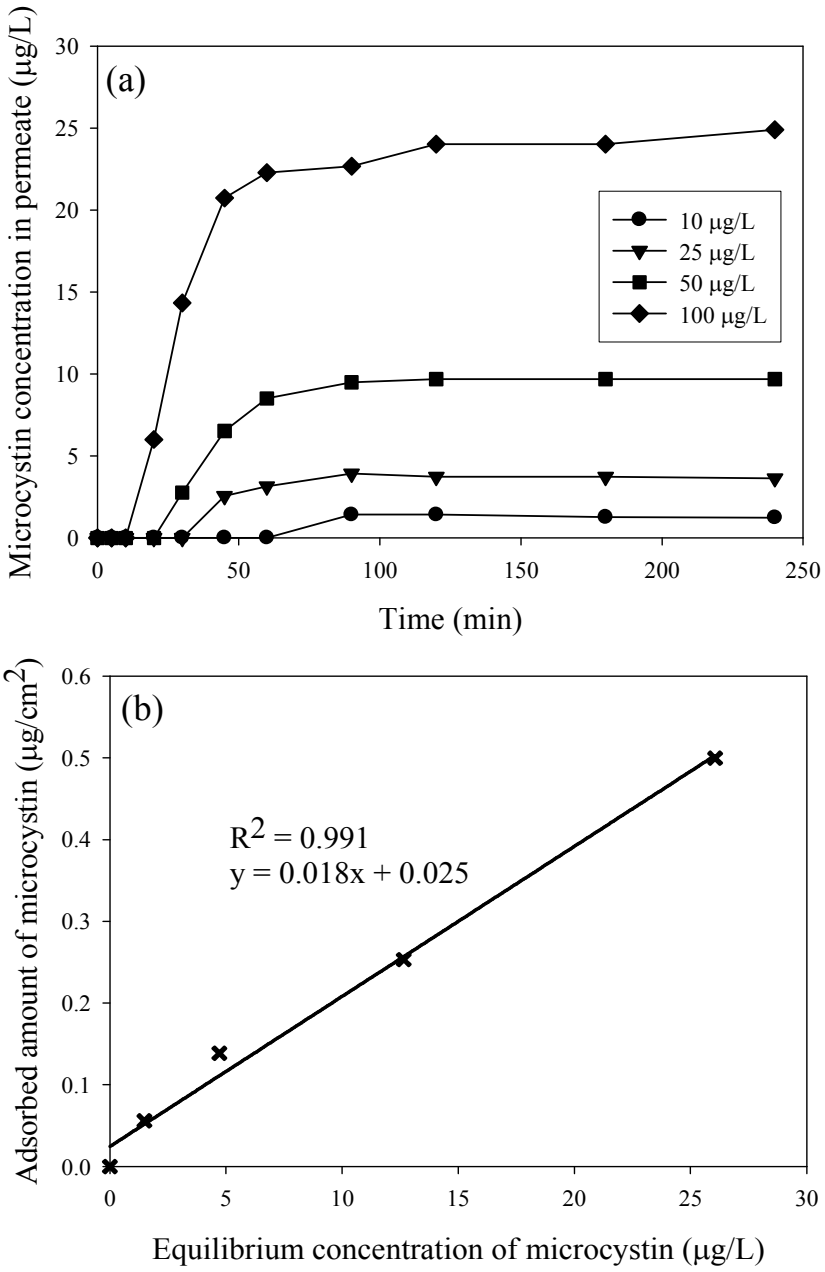

Figure 4.4 Effect of initial feed concentration of microcystin-LR on (a) permeate concentration and (b) amount of microcystin-LR adsorbed on the TF-4KDa membrane.

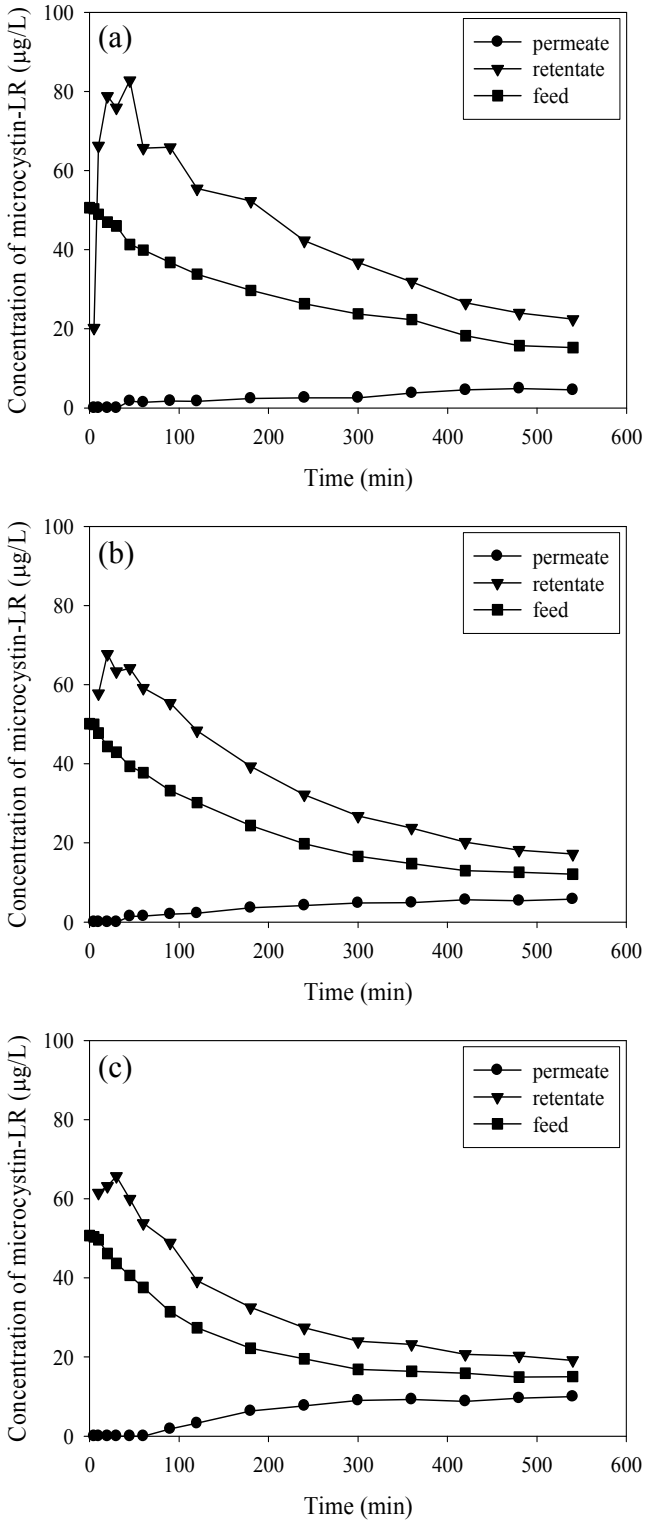

Figure 4.5 The concentrations of microcystin-LR in permeate, retentate, and feed as a function of filtration time for (a) TF-1kDa, (b) TF-2KDa, and (c) TF-4KDa membranes.

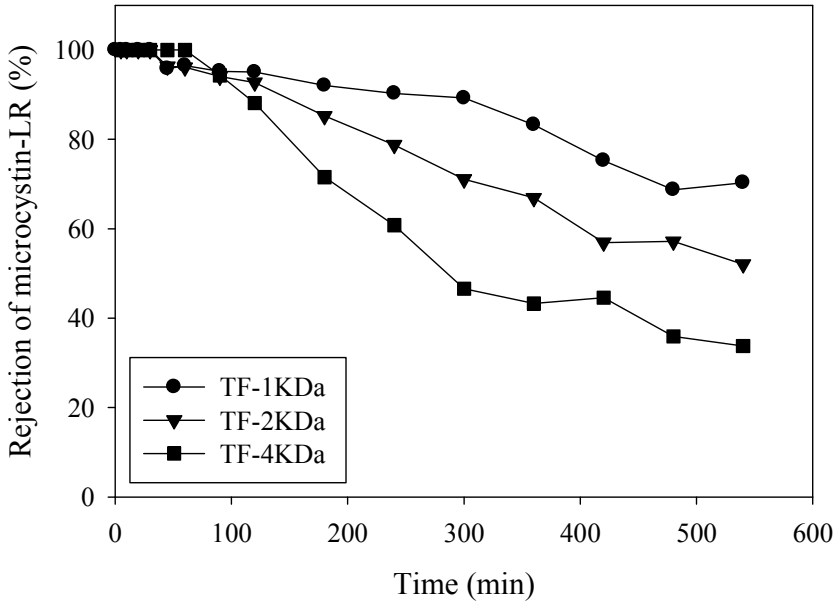

Figure 4.6 Rejection of microcystin-LR by thin-film membranes with different pore sizes. Experimental conditions: microcystin-LR = 50 μg/L, initial permeate flux = 1.29×10^{-5} m^3/m^2-sec, pH = 7.0 ± 0.2, ionic strength = 5 mM, and temperature = 23 ± 1 ^oC. Water recovery was set at 50%.

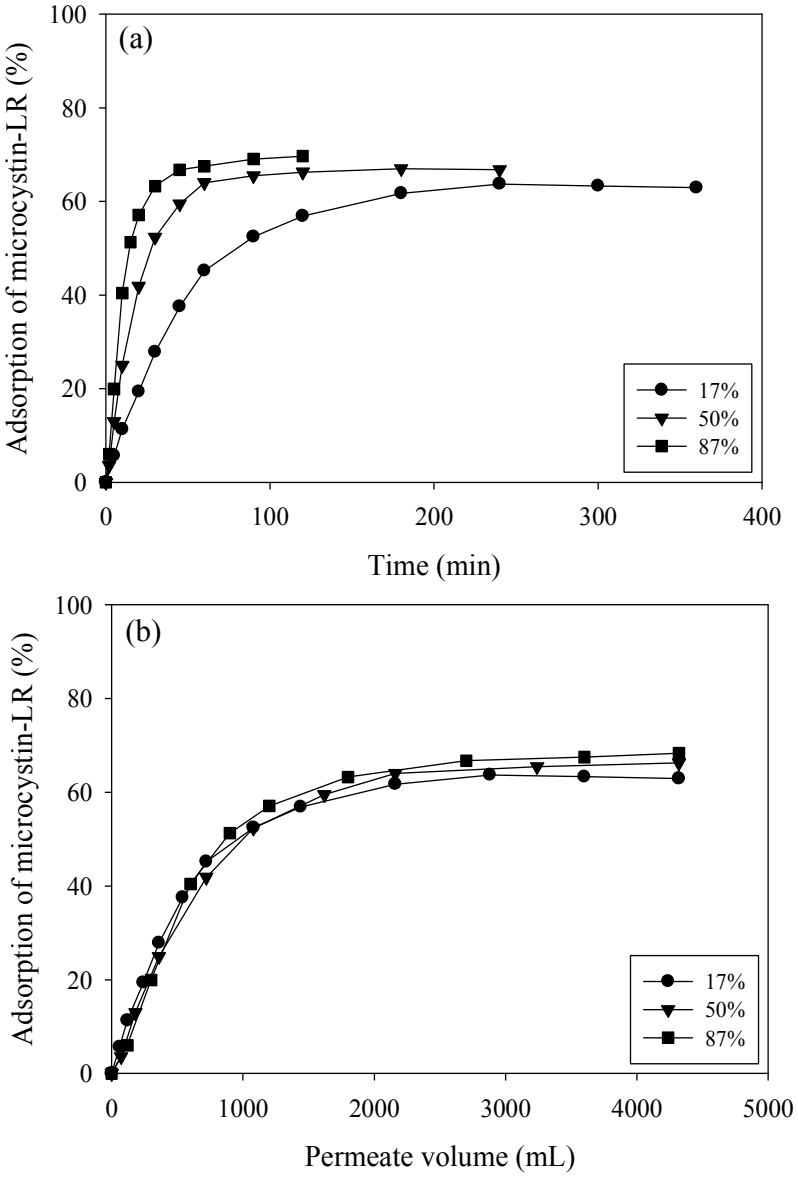

Figure 4.7 The adsorption of microcystin-LR as a function of (a) time and (b) accumulated permeate volume at different water recovery using PES-5KDa membranes. Feed flux was fixed at 7.74×10^{-5} m^3/m^2-sec. Permeate fluxes for water recoveries of 17%, 50%, and 87% were 1.29×10^{-5} m^3/m^2-sec, 3.87×10^{-5} m^3/m^2-sec, and 6.45×10^{-5} m^3/m^2-sec, respectively.

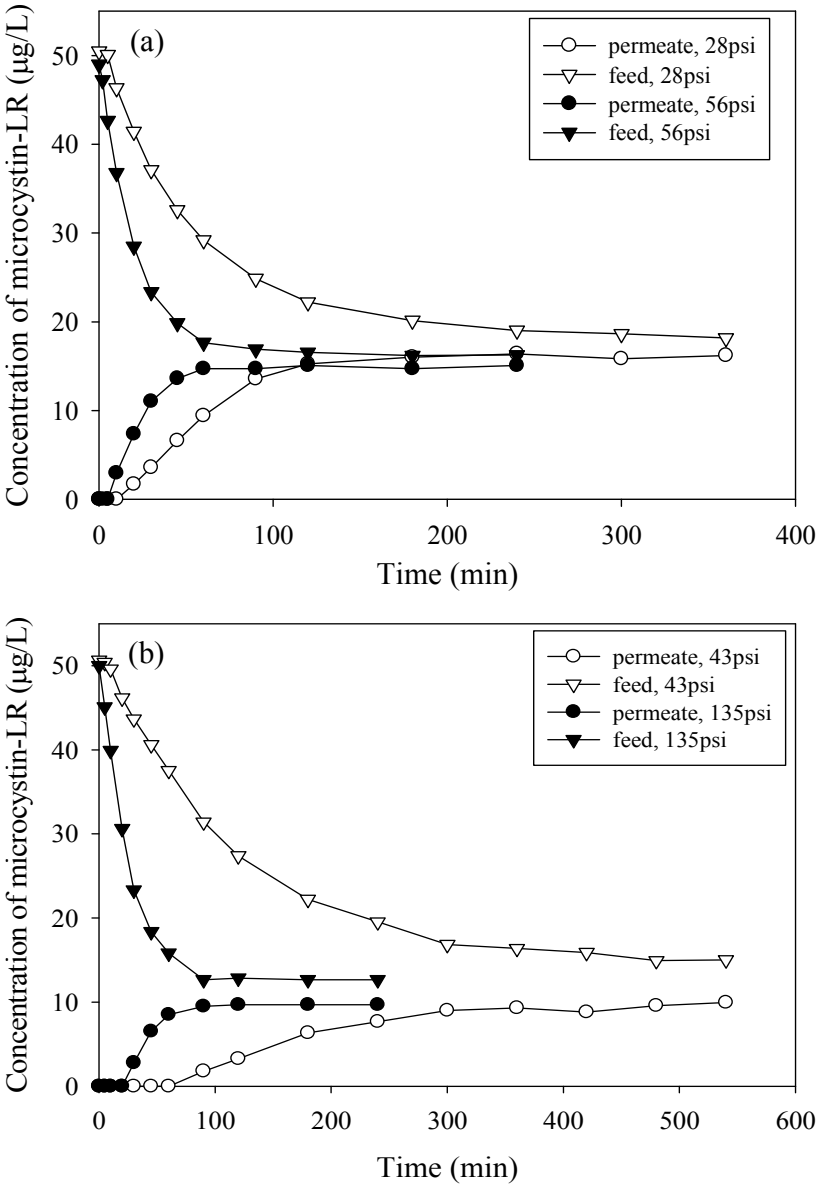

Figure 4.8 Concentration of microcystin-LR in permeate flow and feed tank for (a) PES-5KDa at 28 psi and 56 psi and (b) TF-4KDa at 43 psi and 135 psi. Permeate fluxes were 1.29×10^{-5} m^3/m^2-sec for 28 psi and 43 psi, and 3.87×10^{-5} m^3/m^2-sec for 56 psi and 135 psi. Water recovery was set at 50%.

CHAPTER 5

ADSORPTION OF MICROCYSTIN-LR ONTO IRON OXIDE NANOPARTICLES

To be submitted to *Water Research*

5.1 Abstract

In this study, the effectiveness of iron oxide (maghemite) nanoparticles for the removal of microcystin-LR from water was examined. Factors influencing the sorption behavior were examined, including microcystin and maghemite concentration, pH, ionic strength, and the presence of natural organic matter. Adsorption of microcystin-LR was strongly affected by pH. The adsorption increased with decreasing pH, with a maximum adsorption around pH 3. Adsorption of microcystin-LR on maghemite was primarily attributed to electrostatic interactions, although hydrophobic interactions may also play a role. The extent of microcystin-LR adsorption onto maghemite increased with increasing ionic strength at pH 6.4, since salt ions screened the electrostatic repulsion between adsorbed microcystin molecules. Adsorption of microcystin-LR was not significantly affected in the presence of Suwannee River Fulvic Acid (SRFA) below 2.5 mg/L.

However, adsorption decreased at higher SRFA concentrations (2.5−25 mg/L) due to competitive adsorption between SRFA and microcystin-LR for limited sorption sites.

5.2 Introduction

Microcystins are the most frequently occurring class of cyanobacterial toxins [1]. When consumed or in contact with skin, microcystins can cause serious health problems to humans such as nausea, liver damage, and in extreme cases, liver cancer or death [2,3]. For example, exposure to microcystins has been linked to increased liver cancer in China, the deaths of 76 dialysis patients in Brazil, and elevated kidney failure and liver injury in Australia [4,5]. Due to these adverse health effects, the World Health Organization (WHO) established a drinking water guideline of 1 μg/L for microcystin-LR (L and R stand for Leucine and Arginine, respectively (see Figure 5.1) [6], which is one of the most toxic and frequently detected microcystin congeners [7].

Recently, nanoscale iron oxides such as nanostructured ferric oxides, magnetite, maghemite, and hematite have been used for separation and removal of organic and inorganic contaminants [8,9,10,11,12,13]. Compared with conventional adsorbents such as activated carbon, nanoparticles are extremely small in size (1-100 nm), which can provide large surface area per unit mass and more available sites for chemical reaction [13,14]. For example, Ganesh et al. [8] and Liu [9] reported that nano-ferric oxide (Fe_2O_3) effectively and rapidly removed humic substances and inorganic contaminants (e.g., molybdenum, arsenic). Hagare et al. [10] used nanoscale hematite to remove natural organic substances from water. Nanoscale magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) showed high removal efficiency for arsenic and hexavalent chromium [11,13].

Peng et al. [12] found that the adsorption of bovine serum albumin (BSA) to nanosized magnetite was significantly affected by the solution pH, and maximum adsorption occurred at the isoelectric point of BSA. However, the adsorption of cyanotoxins to nanoscale iron oxides has not yet been explored.

It is also expected that the adsorption of microcystins onto iron oxide particles may play an important role in the fate and transport of these toxins in aquatic environments. Natural waters contain a host of particles including clay, aluminum/iron oxides and hydroxides, and silica. Iron oxides and hydroxides are important components influencing the mobility of organic and inorganic compounds since they are naturally occurring minerals, ubiquitous in soils and sediments, and chemically interactive with many aqueous dissolved species [15,16]. A number of studies addressed the adsorption of natural organic matter (NOM), particularly humic substances, onto iron oxides [17,18,19,20,21]. To date, a few studies have found that microcystins are strongly absorbed on clays and other particulate matter [22,23,24,25,26]. For example, Morris et al. [23] observed that kaolinite and montmorillonite effectively adsorbed microcystins. They proposed clays as a removal technology for microcystins from drinking water. Liu et al. [27] reported that suspended particle matter (SPM) occurring in lake sediments significantly adsorbed microcystins, likely due to hydrophobic interactions between microcystins and organic matter in SPM. No research, however, has been carried out to examine the interaction of microcystins with metal oxides and hydroxides.

In this study, we investigated the adsorption of microcystin-LR on maghemite (γ-Fe_2O_3) nanoparticles from aqueous solution. The influence of various factors, such as pH, ionic strength, microcystin and maghemite concentration, and the presence of NOM,

was examined to better understand the adsorption behavior of microcystin-LR on maghemite surfaces under various conditions.

5.3 Materials and methods

5.3.1 Chemicals

Microcystin-LR was purchased from Calbiochem (San Diego, CA) and was used as received. Microcystin-LR is approximately 3 nm in diameter [7] and has a molecular weight of 995.2. A standard Suwannee River fulvic acid (SRFA) obtained from the International Humic Substances Society (IHSS) was used as a representative natural organic matter. The average molecular weights of 1150 and 2310 were reported for SRFA, measured by field flow fractionation (FFF) [28] and high-performance size exclusion (HPSEC) [29], respectively. Other chemicals such as acetonitrile, ammonium acetate, and sodium chloride were analytical or HPLC grade (Fisher Scientific). All solutions were prepared in Milli-Q water (resistivity 18.2 MΩ-cm).

5.3.2 Iron oxide (Maghemite) nanoparticles

A commercial iron oxide nanoparticle was obtained from Sigma-Aldrich (St. Louis, MO) and used in this study without further purification. Iron oxide solutions of 10 g/L were prepared and acidified to pH 3.5 and stored in the dark prior to use. The identity and purity of the commercial iron oxides were verified by X-ray diffraction (XRD, Scintag PAD-V). The sample's XRD pattern matched standard maghemite (γ-Fe_2O_3). Transmission electron microscopy (TEM) (CM12, Philips) showed that maghemite was composed of roughly spherical particles with a diameter of 10−30 nm.

Surface zeta potentials of maghemite were measured by a zeta potential analyzer (ZetaPlus, Brookhaven Instruments Corp.) at 0.1 M NaCl. The isoelectric point of maghemite was approximately 7.9, as shown in Figure 5.2a. Specific surface area was determined by N_2-BET analysis (Micromeritics), which was 192 ± 0.2 m^2/g.

5.3.3 Batch adsorption experiments

Batch adsorption experiments were conducted over the pH range 2−9 and at background electrolyte concentrations of 0.001−1 M NaCl. Each batch sample was prepared by transferring an aliquot of a stock maghemite suspension (10 g/L) to a 50 mL polycarbonate ultracentrifuge tube to give a final maghemite concentration of 0.3 or 2.3 g/L. Microcystin-LR and NaCl were added to achieve the desired microcystin concentration and ionic strength, respectively. Solution pH was adjusted to a value between 2 and 9 using standardized HCl or NaOH. The sample tubes were then slowly agitated at room temperature using an end-over-end rotator for 48 hours to reach equilibrium. Kinetic experiments indicated that approximately 95% of the adsorption was complete within 24 hours (data not shown). Once equilibrium was reached, the final pH of each batch sample was measured. Prior to quantitative adsorption measurement, the samples were centrifuged for 20 min at 12,000 rpm, and the supernatants were filtered through 0.45-μm polyvinylidene fluoride (PVDF) membrane syringe filters.

For the SRFA adsorption tests, SRFA ranging from 0 to 50 mg/L was added to the centrifuge tubes containing 0.3 g/L of maghemite and 0.01 M NaCl. Solution pH was adjusted to 4.4 or 6.4. To examine the effect of SRFA on microcystin-LR adsorption, various concentrations of SRFA (0−25 mg/L) were simultaneously added to the

centrifuge tubes along with 0.5 mg/L of microcystin-LR and 0.3 g/L of maghemite in 0.01 M NaCl over the pH range 2−9. The concentrations of microcystin-LR and SRFA in the supernatant were analyzed at 238 nm and 254 nm, respectively, using high performance liquid chromatography (Hewlett Packard Series 1100 HPLC) with a UV diode array detector and a 4.6×150 mm C18 analytical column (Agilent Technologies, Wilmington, DE). The HPLC was operated under isocratic conditions using a mobile phase consisting of 28% acetonitrile and 72% 10 mM ammonium acetate buffer adjusted to pH 7.0 at a flow rate of 0.4 ml/min, as modified from previous methods [30,31]. The retention times for SRFA and microcystin-LR were 2.5 and 6.4 min, respectively, indicating good peak separation. The standard calibration curves for microcystin-LR and SRFA showed a strong linear relationship between the peak area and concentration.

5.4 Results and discussion

5.4.1. Effect of maghemite concentration

The adsorption capacity of maghemite nanoparticles for microcystin-LR was initially measured at pH 4.4, with 0.3 g/L or 2.3 g/L of maghemite and varying microcystin-LR concentration (0.1−2.5 mg/L). Figure 5.3 shows the percent adsorption of microcystin-LR as a function of initial microcystin concentration at two different maghemite concentrations. Microcystin-LR was effectively removed from the aqueous solution using iron oxide nanoparticles. The percent adsorption decreased almost linearly with increasing initial concentration of microcystin-LR, from 0.1 mg/L to 2.5 mg/L, as the number of available sorption sites became saturated with the toxins. Higher maghemite concentration (i.e., solid-liquid ratio) resulted in greater removal of

microcystin-LR, probably due to the increased surface area available for adsorption. For example, the adsorption of microcystin-LR at the initial concentration of 100 μg/L was found to be 73 % and 94 % using 0.3 and 2.3 g/L of maghemite, respectively. The maximum adsorption capacities for 0.3 and 2.3 g/L of maghemite were 0.014 and 0.005 μmol/m^2, indicating greater sorption density at a lower solid-liquid ratio.

5.4.2 Effect of pH

Figure 5.4 shows the adsorption isotherms of microcystin-LR on maghemite at pH 4.4 and 6.4. The sorption isotherms were nonlinear over the range of microcystin concentrations tested. In both cases, the slope of the isotherm was relatively steep at low microcystin concentrations (below 0.25 mg/L) and approached a plateau at higher concentrations. This experimental data was fitted using a Langmuir adsorption isotherm model, which can be described as $q = q_{max}KC/(1+KC)$, where q is the amount of microcystin adsorbed per unit surface area at equilibrium (mg/m^2), q_{max} is the maximum amount of microcystin that may be adsorbed (mg/m^2), K is a Langmuir constant (L/mg), and C is the microcystin concentration in the aqueous solution at equilibrium (mg/L). Table 1 shows Langmuir model isotherm parameters for each pH value.

As can be seen in Figure 5.4, microcystin-LR sorption behavior was influenced by solution pH. Greater adsorption of microcystin-LR was observed at pH 4.4 compared to pH 6.4. As shown in Table 1, the maximum adsorption capacity (q_{max}) at pH 4.4 was approximately four times greater than at pH 6.4. The K value was also greater at pH 4.4. The K value is related to the adsorption affinity, indicating that the lower the solution pH, the higher the affinity between microcystin-LR and maghemite.

Additional experiments examined microcystin-LR adsorption over the pH range 2−9 for two different microcystin concentrations of 0.05 mg/L and 0.5 mg/L. All experiments were performed with 0.3 g/L maghemite suspensions using 0.01 M NaCl as a background electrolyte. Figure 5.5 shows the adsorption of microcystin-LR onto nano-sized maghemite as a function of final pH in terms of adsorbed amount (Figure 5.5a) and percent adsorption (Figure 5.5b). As shown, microcystin adsorption was strongly pH dependent for both concentrations. The adsorption behavior of microcystin-LR was similar to that observed for other anionic sorbates interacting with oxide surfaces, namely a maximum sorption at low pH and decreasing sorption as pH increased [32].

The surface charge of both microcystin-LR and maghemite changes as a function of pH, which plays a significant role in adsorption of microcystin-LR onto maghemite. The charge of maghemite can more strongly influence the adsorption since microcystin-LR is negatively charged (−1) at most pH values ($3 < pH < 12$) (see Figure 5.2b). As shown in Figure 5.2a, maghemite surfaces exhibited a strongly positive charge at lower pH. A strong electrostatic attraction occurred between the highly positively charged maghemite surface and the negatively charged microcystin-LR at this low pH. As the pH increased, the number of available adsorption sites decreased due to deprotonation of the surface hydroxyl groups, leading to a decrease in the surface charge of maghemite. The decreasing electrostatic attraction between microcystin-LR and maghemite resulted in the decrease in microcystin adsorption on maghemite with increasing pH values. Little adsorption was observed for pH values close to or greater than the measured isoelectric point of maghemite (≈7.9) where electrostatic interactions are unfavorable for the adsorption of microcystin-LR on maghemite with neutral or negative charge.

Adsorption at pH 2.9 was slightly higher than at pH 2.3, as shown in Figure 5.5. The maximum adsorption observed around pH 3 was likely related to the surface charge of microcystin-LR. Microcystin-LR contains two ionizable carboxyl groups on glutamic acid and methylaspartic acid, and one ionizable amino group on arginine (see Figure 5.1). The pK_a values of the carboxyl in methylaspartic acid and glutamic acid and the amino group in arginine are 2.09, 2.19, and 12.48, respectively [33]. The different species of microcystin-LR as a function of pH are shown in Figure 5.2b. The charge of microcystin-LR is positive at pH<2.09 (i.e., all functional groups are protonated, $R-(COOH)_2NH_2^+$), neutral at a narrow pH range between 2.09 and 2.19 due to loss of a proton from the carboxyl group in methylaspartic acid ($R-(COO^-)(COOH)NH_2^+$), and negative at pH>2.19 due to deprotonation of two carboxylic groups ($R-(COO^-)_2NH_2^+$). At pH 2.9, near 90% of microcystin-LR was in anionic form with -1 charge, while only 50% was ionized at pH 2.3. Thus, the maximum adsorption observed around pH 3 was consistent with the known, surface charge behavior of maghemite and microcystin-LR.

The results above suggest that electrostatic interactions are important in controlling the adsorption of microcystin-LR onto iron oxide nanoparticles. Microcystin-LR sorption to iron oxide is also potentially influenced by specific chemical interactions between the carboxylic functional groups of the toxin and surface hydroxyl groups, such as ligand exchange or hydrogen bonding. A number of studies on the adsorption of NOM onto metal oxides have addressed that ligand exchange between surface hydroxyl groups and organic functional groups, especially carboxyl groups, is an important adsorption mechanism, and resulted in an increase in adsorption with decreasing pH. [17,18,19,34,35,36]. Yoon et al. [37] observed, based on ATR-FTIR analysis, SRFA was

predominantly adsorbed on aluminum oxyhydroxide surfaces in an outer-sphere complexation mode (electrostatic and hydrogen bonding) while inner-sphere complexes by ligand exchange were formed at low pH. Oliva et al. [38] suggested that the adsorption of protein (human serum albumin) onto TiO_2 particles occurred through ligand exchange, hydrogen bonding, as well as electrostatic interactions.

Hydrophobic interactions may play a minor role in microcystin adsorption on iron oxide nanoparticles since microcystin-LR contains an aromatic ring in the ADDA residue and seven peptides exhibiting hydrophobic properties in aqueous media [39]. According to Evanko and Dzombak [32], hydrophobic interactions can be an important mechanism in sorption of aromatic organic acids, such as humic substances, onto iron oxide surfaces. Gert-Jan de Maagd et al. [33] observed that the octanol-water distribution ratio (D_{ow}) of microcystin-LR decreased with increasing pH. When the pH is higher, two carboxyl groups are deprotonated around pH 2−3, causing an increase in microcystin water solubility. This greater solubility, or reduced hydrophobicity, may lead to a decrease in the affinity of microcystin-LR for the iron oxides, as well as other adsorbed microcystin molecules. Liu et al. [27] speculated that the increase in microcystin-LR adsorption on suspended particulate matter with decreasing pH probably resulted from the pH-dependent hydrophobicity of the toxin. Pendleton et al. [39] reported that an increase in microcystin-LR affinity for activated carbon at low pH was due to the decreased water solubility of the toxin.

5.4.3 Effect of ionic strength

The effect of ionic strength on microcystin-LR adsorption to iron oxide nanoparticles was studied with background electrolyte (NaCl) concentrations ranging from 0.001 M to 1 M. Figure 5.6 shows the percent adsorption of microcystin-LR onto maghemite at pH 3.9 and 6.4 as a function of NaCl concentration. As can be seen, little change in microcystin adsorption with NaCl concentration was observed at pH 3.9, while adsorption of microcystin-LR at pH 6.4 slightly increased as the NaCl concentration increased from 0.001 to 1 M.

The change in microcystin adsorption with NaCl concentration is consistent with the electrostatic and hydrophobic interactions discussed above. For example, at low pH the screening of both attractive and repulsive electrostatic interactions resulted in little change in microcystin-LR with increasing NaCl. At the high pH of 6.4, however, an increase in NaCl appears to screen the electrostatic repulsions between adsorbed microcystin-LR molecules, allowing for greater adsorption. Compared to the absence of NaCl, the amount of microcystin-LR adsorption increased by 175.4 % at pH 6.4. This is consistent with the adsorption behavior of other large molecules on iron oxides. An increase in adsorption of natural organic matter with increasing ionic strength on goethite, hematite, and aluminum oxides was observed in many previous studies [19,21,40,41]. For example, adsorption of humic substances (HS) was enhanced with increasing NaCl concentrations since salt ions screened the electrostatic repulsion between the adsorbed HS molecules [19,21].

5.4.4 NOM effects on microcystin adsorption to iron oxides

Natural organic matter (NOM) is ubiquitous in aquatic systems and is strongly associated with metal (oxy)hydroxide minerals (e.g, aluminum and iron oxide) [19,21,37,40,41]. The presence of NOM can affect the performance of iron oxide adsorption for other target compounds by competing for adsorption sites [42], enhancing the solubility of the compounds binding to NOM [43], and changing physicochemical properties of mineral surfaces [37]. Here, we examined how microcystin-LR interacts with iron oxide nanoparticles in the presence of NOM using Suwannee River fulvic acid (SRFA) as a representative NOM compound.

Figure 5.7 shows the adsorption isotherm of SRFA for 0.3 g/L of maghemite at two pH values (4.4 and 6.4) in 0.01 M NaCl. The adsorption isotherms showed an initial high affinity character at low SRFA concentration and continued to increase with increasing SRFA concentration. Compared with microcystin-LR (Figure 5.4), SRFA exhibited higher adsorption affinity and capacity for maghemite than microcystin-LR.

Figure 5.8a shows microcystin-LR sorption to iron oxide particles in the presence of various concentrations of SRFA. At SRFA concentrations greater than 2.5 mg/L, the amount of microcystin-LR adsorption decreased with increasing SRFA concentration. Previous research reported that the larger size, more hydrophobic, and more aromatic fractions of NOM were competitively adsorbed on iron oxides or displaced smaller sized hydrophilic NOM fractions that had been previously adsorbed, due to their higher adsorption affinity [21,37,42,44,45]. For example, Vermeer and Koopal [20] studied adsorption kinetics and competition for a mixture of purified Aldrich humic acid (PAHA) and Laurentian fulvic acid (LFA). They found the large PAHA molecules were adsorbed

more strongly and displaced small LFA molecules from hematite surfaces. Following the same logic, it is expected that SRFA preferentially adsorbed on maghemite surfaces over microcystin-LR in the mixed system, due to its higher affinity for the maghemite surface.

At SRFA concentrations below 2.5 mg/L, adsorption of microcystin-LR increased slightly with increasing SRFA concentration. Perhaps at these low SRFA concentrations, the majority of binding sites were still available for microcystin-LR adsorption, even though microcystin-LR is less competitive than SRFA. Moreover, as the maghemite had at least a partial surface coating of hydrophobic SRFA, microcystin-LR can be further adsorbed though enhanced hydrophobic interactions.

Changes in adsorption of microcystin-LR in the presence of SRFA were examined over the pH range of 2 to 10. As shown in Figure 5.8b, microcystin-LR adsorption for each pH was little affected by 1 mg/L of SRFA, but reduced in the presence of 10 mg/L of SRFA. This observation is similar to and consistent with the previous studies on competitive adsorption. Gu et al. [42] found that adsorption of phthalic acid increased with increasing total concentrations of phthalic acid and polyacrylic acid (PAA) until surface adsorption sites became saturated, although PAA was more competitively adsorbed than phthalic acid. A further increase in total concentration led to decreased adsorption of phthalic acid due to limited sites available to phthalic acid with lower affinity. De Laat and van den Heuvel [46] also observed that both polyvinylalcohol (PVA) and a polyacrylic acid (PAA) were adsorbed from mixtures as long as the amount of more competitive PAA was not enough to reach adsorption saturation, but no adsorption of PVA occurred if excess amounts of PAA were added to the mixtures.

5.4 Conclusions

In this study, we used iron oxide nanoparticles (γ-Fe_2O_3) to investigate the adsorption of the hepatotoxin microcystin-LR from aqueous solution. Electrostatic interactions played an important role in controlling microcystin adsorption. The adsorption of microcystin-LR decreased with increasing pH, likely due to a decrease in the surface charges of maghemite and subsequently, reduced electrostatic attraction. Changes in hydrophobicity of microcystin-LR as a function of pH may also contribute to the pH-dependent adsorption behavior. The ionic strength also affected microcystin adsorption by screening electrostatic interactions. Microcystin-LR adsorption was strongly influenced by the presence of NOM. Sorption of microcystin-LR decreased with increasing SRFA concentration higher than 2.5 mg/L due to competition between SRFA and microcystin-LR for surface sites.

Acknowledgments

The authors acknowledge the support of the Ohio Sea Grant College Program, the Ohio State University Graduate Fellowship program, and the Ohio Water Development Authority (OWDA). Shengnian Wang and Ziqi He contributed to zeta potential analyses and BET measurements, respectively.

References

[1] Carmichael, W.W. 1992. J. *Appl. Bacteriol*. 72(6), 445-459.

[2] Yoshizawa, S., Matsushima, R., Watanabe, M.F., Harada, K.-I., Ichihara, A., Carmichael, W.W., Fujiki, H. 1990. *J. Cancer Res. Clin. Oncol*. 116, 609-614.

[3] Nishiwaki-Matsushima, R., Ohta, T., Nishiwaki, S., Suganuma, M., Kohyama, K., Ishikawa, T., Carmichael, W.W., Fujiki, H. 1992. *J. Cancer Res. Clin. Oncol*. 118, 420-424.

[4] Jochimsen, E.M., Carmichael, W.W., An, J.S., Cardo, D.M., Cookson, S.T., Holmes, C.E.M., Antines, M.B. de Melo Filho, D.A., Lyra, T.M., Burreto, V.S.T., Azevedo, S.M.F.O., Jarvis, W.R. 1998. *New Eng. J. Medicine*. 338(13), 873-878.

[5] McElhiney, J., Lawton, L.A. 2005. *Toxicol. Appl. Pharmacol*. 203, 219-230.

[6] WHO. *Cyanobacterial toxins: Microcystin-LR. Guidelines for drinking water quality*. World Health Organization, Geneva. 1998.

[7] Antoniou, M.G., de la Cruz, A.A., Dionysiou, D.D. 2005. *J. Environ. Eng*. 131(9), 1239-1243.

[8] Ganesh, R., Leong, L.Y.C., Skandan, G., Jain, M., Liu, B., Larson, L.E. Use of nanoscale materials for water treatment to achieve multiple water quality goals. *Proceedings of Water Quality Technology Conference and Exposition*. 2005.

[9] Liu, B.H. 2006. *Contaminants removal from water using nanoparticles*. MS thesis, Dept. of Environmental Science, California State University, Fullerton.

[10] Hagare, P., Thiruvenkatachari, R., Ngo, H.H. 2001. *Sep. Sci. Technol*. 36(11), 2547-2559.

[11] Yavuz, C.T., Mayo, J.T., Yu, W.W., Prakash, A., Falkner, J.C., Yean, S., Cong, L.L. Shipley, H.J. Kan, A., Tomson, M., Natelson, D., Colvin, V.L. 2006. *Science* 314, 964-967.

[12] Peng, Z.G., Hidajat, K., Uddin, M.S. 2004. *J. Colloid Interf. Sci*. 271, 277-283.

[13] Hu, J., Chen, G., Lo, I.M.C. 2005. *Water Res*. 39, 4528-4536.

[14] Rajagopalan, G., Leong, L.Y.C., Jain, M., Larson, L.E. Use of nanoscale adsorbents for water treatment. *Proceedings of the 40th Western Regional Meeting*. Jan. 22-25, 2006.

[15] Liang, L., Morgan, J.J. 1990. *Aquatic Sci*. 52(1), 32-55.

[16] Hanna, K. 2007. *J. Colloid Interf. Sci*. 309, 419-428.

[17] Davis, J.A. 1982. *Geochim. Cosmochim. Acta.* 46, 2381–2393.

[18] Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J.F. 1994. *Environ. Sci. Technol*. 28, 38-46.

[19] Vermeer, A.W.P., Van Riemsdijk, W.H., Koopal, L.K. 1998. *Langmuir* 14, 2810-2819.

[20] Vermeer, A.W.P., Koopal, L.K. 1998. *Langmuir* 14, 4210-4216.

[21] Weng, L., Van Riemsdijk, W.H., Koopal, L.K., Hiemstra, T. 2006. *Environ. Sci. Technol*. 40, 7494-7500.

[22] Tsuji, K., Masui, H., Uemura, H., Mori, Y., Harada, K.-I. 2001. *Toxicon* 39, 687-692.

[23] Morris, R.J., Williams, D.E., Luu, H.A., Holmes, C.F.B., Andersen, R.J., Calvert, S.E. 2000. *Toxicon* 38, 303-308.

[24] Miller, M.J., Critchley, M.M., Hutson, J., Fallowfield, H.J. 2001. *Water Res*. 35, 1461-1468.

[25] Mohamed, Z.A., El-Sharouny, H.M., Ali, W.S. 2007. *Arch. Environ. Contam. Toxicol*. 52, 489-495.

[26] Miller, M.J., Hutson, J. Fallowfield, H.J. 2005. *J. Water Health* 3(4), 339-347.

[27] Liu, G., Qian, Y., Dai, S., Feng, N. 2008. *Water Air Soil Pollut*. 192(1-4), 67-76.

[28] Beckett, R., Jue, Z., Giddings, J.C. 1987. *Environ. Sci. Technol*. 21(3), 289-295.

[29] Chin, Y.-P., Aiken, G., O'Loughlin, E. 1994. *Environ. Sci. Technol*. 28, 1853-1858.

[30] Neumann, U., Weckesser, J. 1998. *Environ. Toxicol. Water Qual*. 13, 143-148.

[31] Lambert, T.W., Holmes C.F.B., Hrudey, S.E. 1996. *Water Res*. 30(6), 1411-1422.

[32] Evanko, C.R., Dzombak, D.A. 1998. *Environ. Sci. Technol*. 32(19), 2846-2855.

[33] Gert-Jan de Maagd, P., Hendriks, A., Seinen, W., Sijm, D.T. H. M. 1999. *Water Res*. 33, 677-680.

[34] Murphy, E.M., Zachara, J.M., Smith, S.C. 1990. *Environ. Sci. Technol*. 24, 1507-1516.

[35] Parfitt, R.L. Fraser, A.R., Farmer, V.C. 1977. *J. Soil Sci*. 28, 289-296.

[36] Tipping E. 1981. *Geochim. Cosmochim. Acta* 45, 191–199.

[37] Yoon, T.H., Johnson, S.B., Musgrave, C., Brown, G.E., Jr. 2005. *Langmuir* 21(11), 5002-5012.

[38] Oliva, F.Y., Avalle, L.B., Camara, O.R., De Pauli, C.P. 2003. *J. Colloid Interf. Sci.*261, 299-311.

[39] Pendleton, P., Schumann, R., Wong, S.H. 2001. *J. Colloid Interf. Sci*. 240(1), 1-8.

[40] Saito, T., Koopal, L.K., Van Riemsdijk, W.H., Nagasaki, S., Tanaka, S. 2004. *Langmuir* 20, 689-700.

[41] Schlautman, M.A., Morgan, J.J., 1991. *Soil Sci. Soc. Am. J*. 55, 34-42.

[42] Gu, B., Mehlhorn, T.L, Liang, L., McCarthy, J.F. 1996. *Geochimica et Cosmochimica Acta* 60(11), 1943-1950.

[43] Kördel, W., Dassenakis, M., Lintelmann, J., Padberg, S. 1997. *Pure&Appl. Chem*. 69(7), 1571-1600.

[44] Meier, M., Namjesnik-Dejanovic, K., Maurice, P.A., Chin, Y.–P, Aiken, G.R. 1999. *Chemical Geology* 157, 275-284.

[45] Zhou, Q., Maurice, P.A., Cabaniss, S.E. 2001. *Geochimica et Cosmochimica Acta* 65(5), 803-812.

[46] de Laat A.W.M., van den Heuvel G.L.T. 1993. *Colloid Surf. A: Physico-chem. Eng. Aspects*. 70(2), 179-187.

[47] Sielaff, H., Dittmann, E., Tandeau de Marsac, N., Bouchier, C., Von Döhren, H., Börner, T., Schwecke, T. 2003. *Biochem. J*. 373, 909-916.

Table 5.1 Langmuir model isotherm parameters for microcystin-LR adsorption on maghemite at pH 4.4 and 6.4

pH	q_{max} (mg/m^2)	K (L/mg)	R^{2*}
4.4 ± 0.1	0.0142	2.96	0.989
6.4 ± 0.1	0.0034	2.18	0.995

* The correlation coefficient R^2 describes the goodness of fit to the linearized Langmuir model by Sigma Plot.

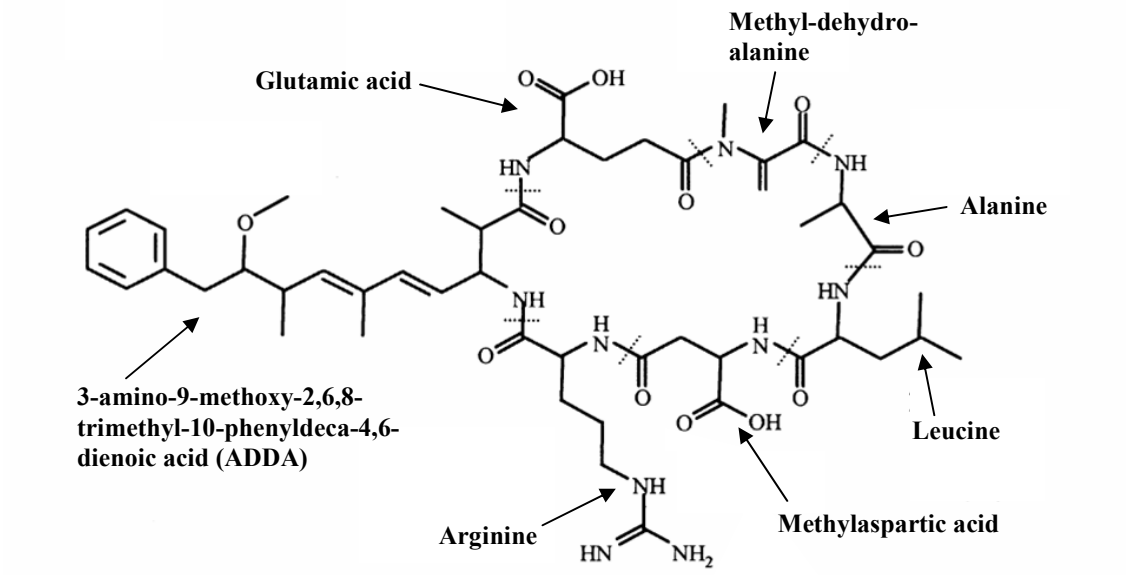

Figure 5.1 Molecular structure of microcystin-LR (after Sielaff et al. [47])

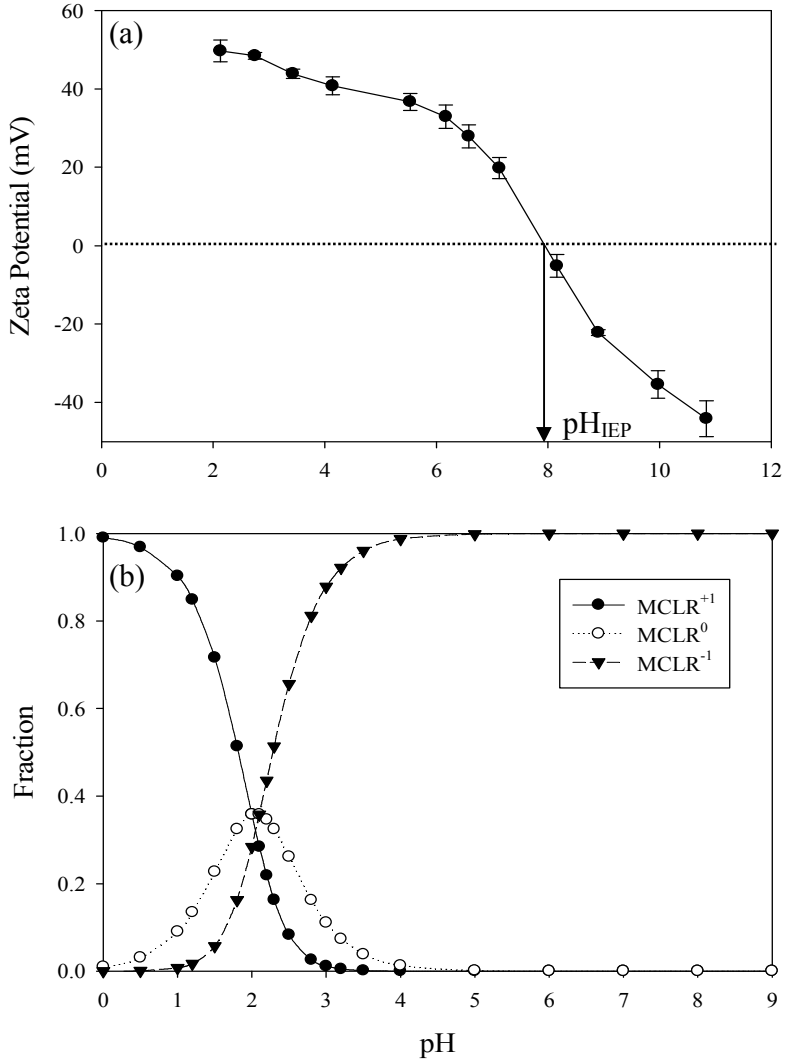

Figure 5.2 (a) Zeta potential of maghemite (0.5 g/L) as a function of pH in the presence of 0.01 M NaCl, and (b) The distribution of microcystin-LR species in aqueous solution at an ionic strength of 0.01 M over the pH range 0 to 9.

.

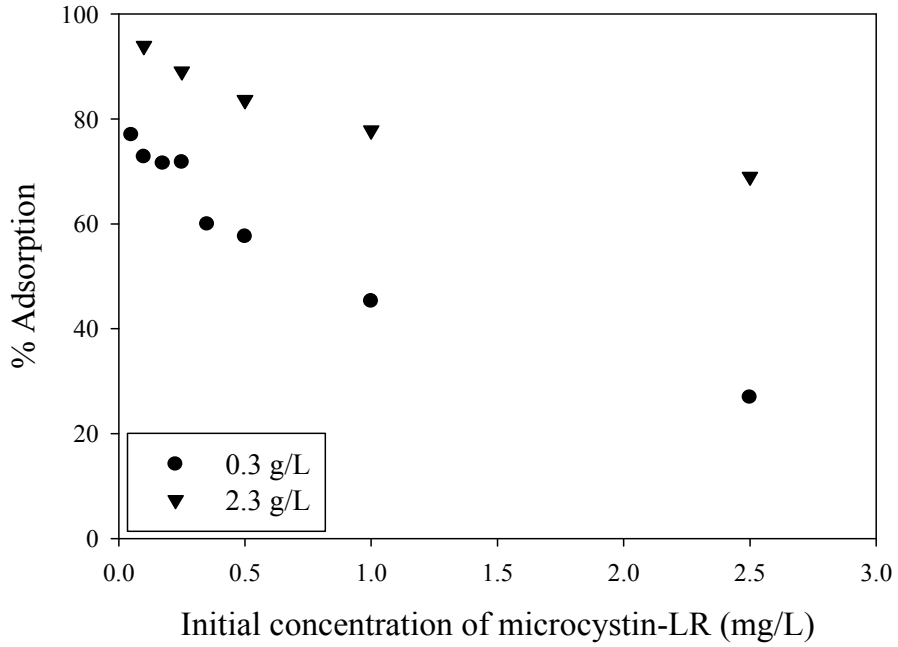

Figure 5.3 Effect of the maghemite concentration (i.e., solid-liquid ratio) on microcystin-LR adsorption at pH 4.4.

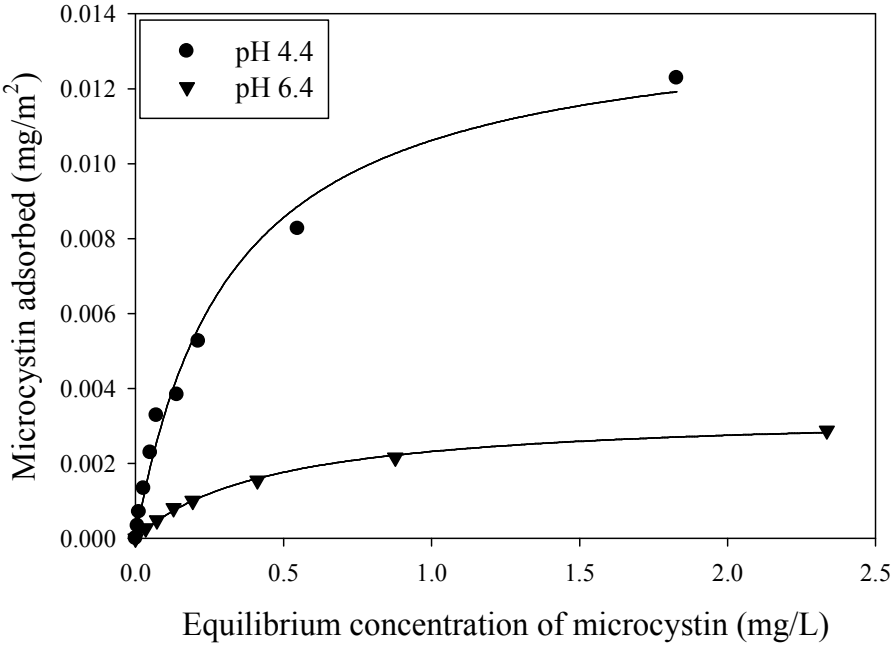

Figure 5.4 Adsorption isotherms for microcystin-LR on maghemite (0.3 g/L) at pH 4.4 and 6.4 in 0.01M NaCl.

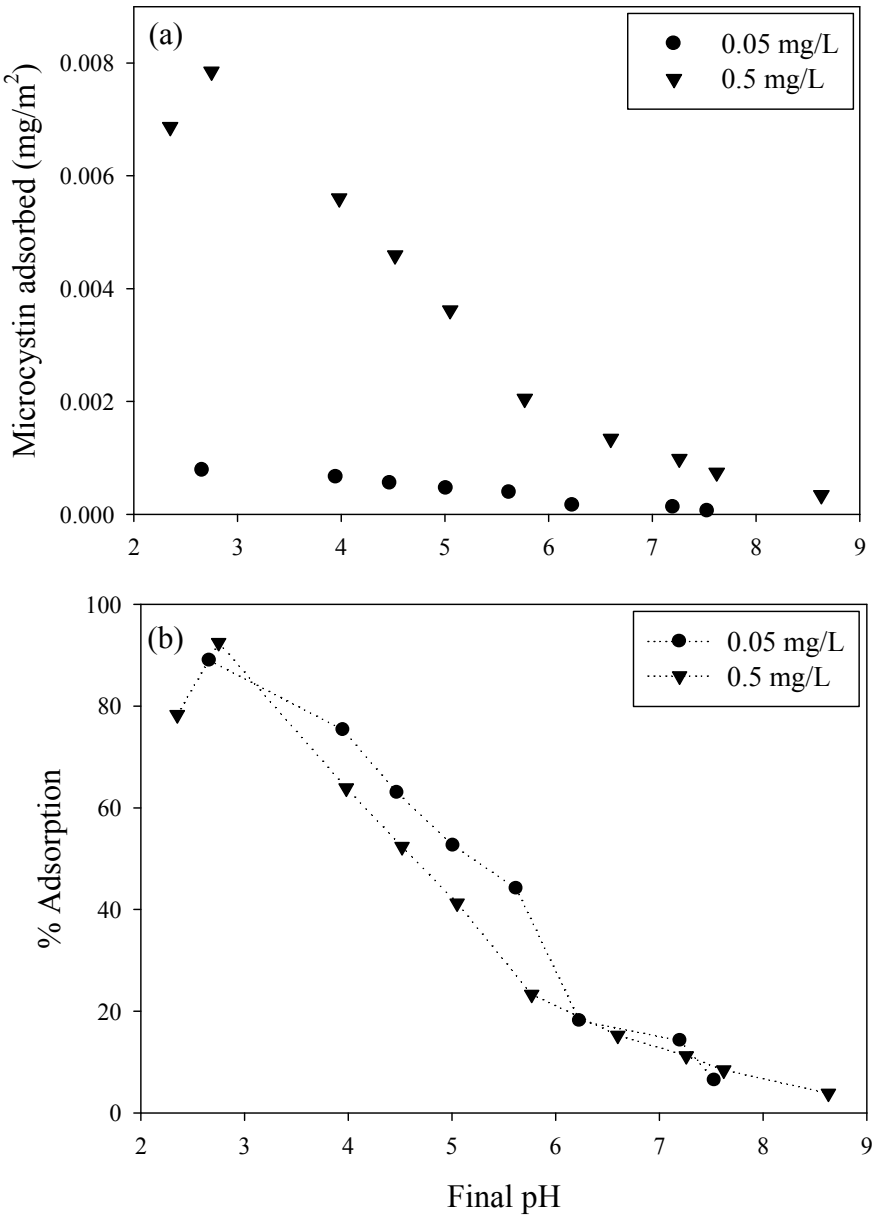

Figure 5.5 The effect of pH on the adsorption of microcystin-LR onto iron oxide nanoparticles (0.3 g/L) at different initial microcystin concentrations (0.05 and 0.5 mg/L); (a) adsorbed amounts vs. pH and (b) percent adsorption vs. pH.

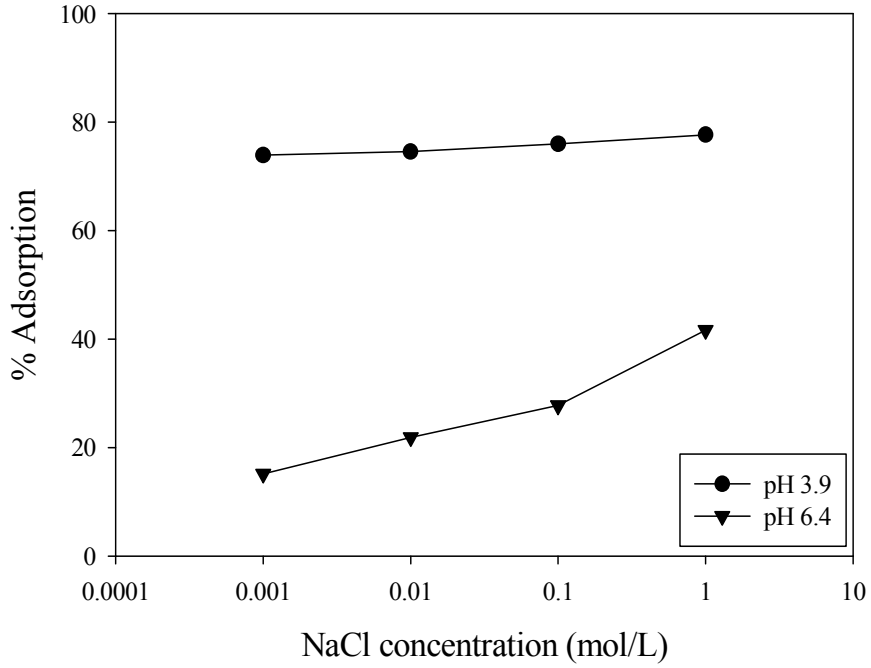

Figure 5.6 Effect of the ionic strength (i.e., NaCl concentration) on microcystin-LR adsorption at pH 3.9 and 6.4. The initial concentration of microcystin-LR is 0.25 mg/L.

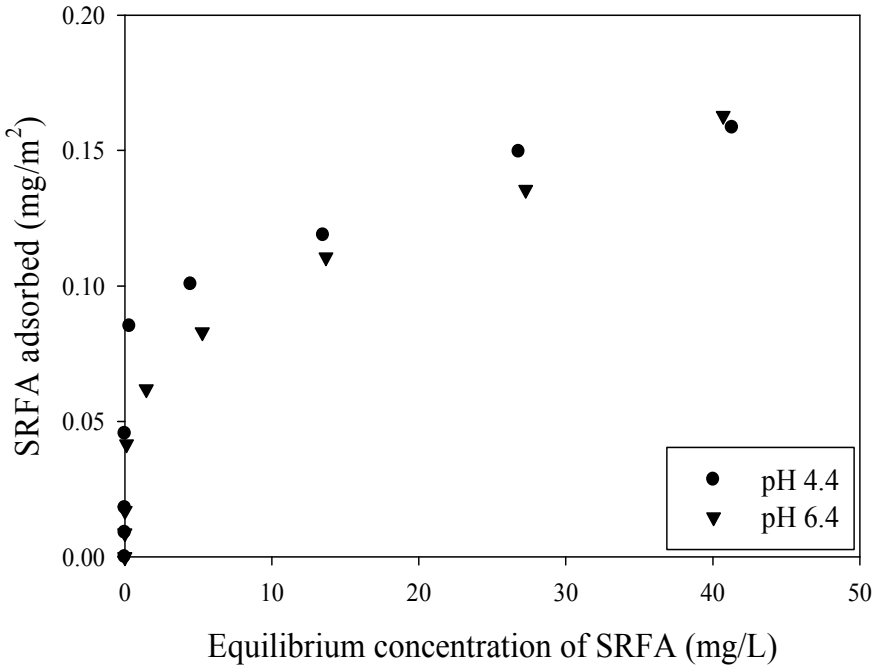

Figure 5.7 Adsorption isotherms at pH 4.4 and 6.4 for SRFA on maghemite (0.3 g/L) in 0.01M NaCl.

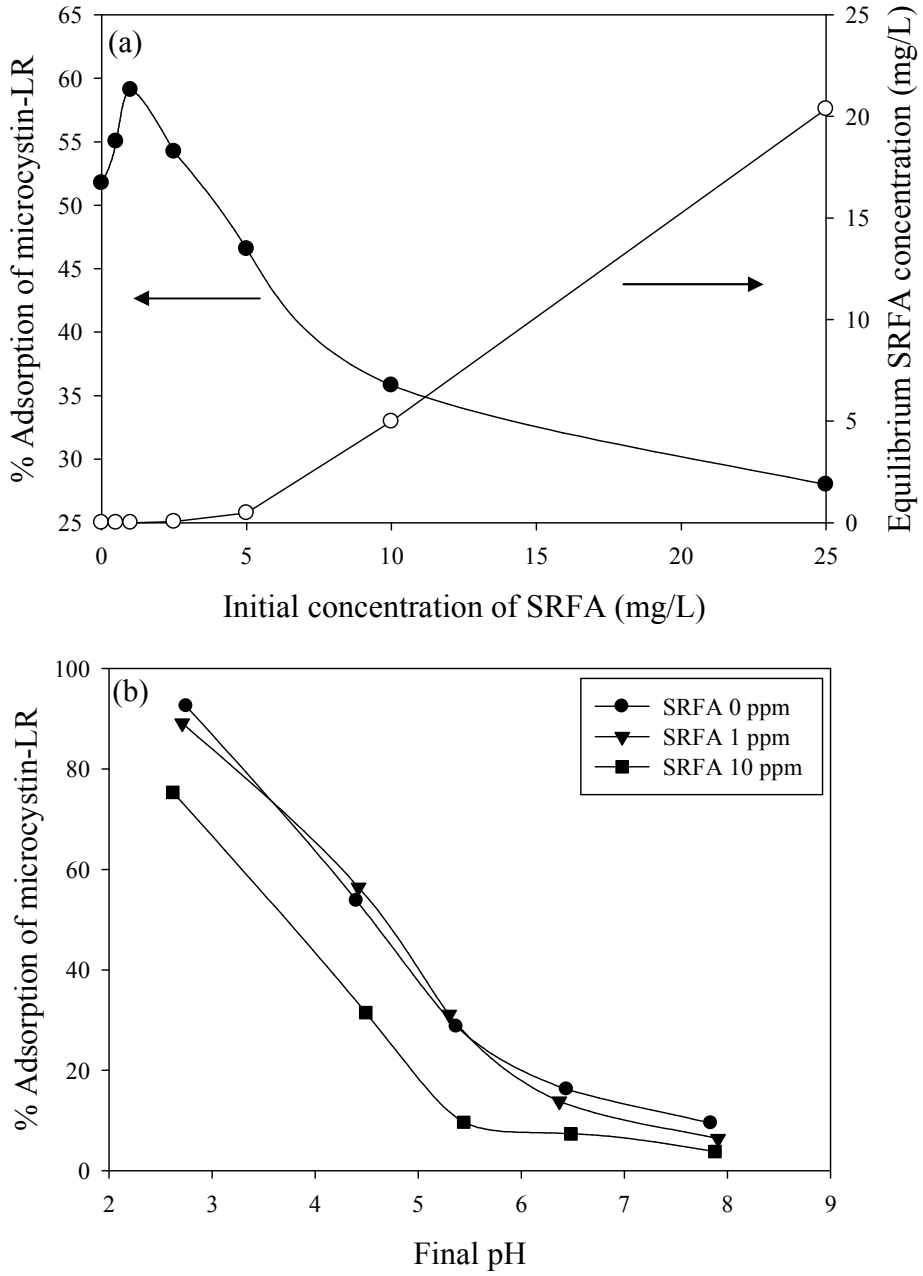

Figure 5.8 The effect of SRFA on the adsorption of microcystin-LR (0.5 mg/L) to maghemite nanoparticles (0.3 g/L) in 0.01M NaCl solution, (a) as a function of SRFA concentration (0−25 mg/L) at pH 4.4 and (b) as a function of final pH (2−8) in the presence of SRFA (0, 1, 10 ppm).

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 Summary and Conclusions

In this dissertation, an investigation of adsorption by activated carbon or iron oxide nanoparticle, as well as membrane filtration, was conducted for the effective treatment of source water contaminated with harmful cyanotoxins. The major observations from this research are given below.

Objective 1. Investigate the application of ultrafiltration for the rejection of microcystin-LR and elucidate the rejection mechanisms (Chapter 4).

Microcystin-LR rejection by ultrafiltration (UF) membranes was investigated in Chapter 4. Membrane properties (e.g., material and pore size) strongly influenced the extent of adsorption, and subsequently microcystin removal. The main rejection mechanism of microcystin-LR by UF membranes at early stages of filtration was adsorption, presumably due to hydrophobic interactions or hydrogen bonding. However, the sorption of microcystin-LR to the membranes was reversible due to the low activation

energy of the hydrophobic interactions. In addition to hydrophobicity, membrane morphology may also influence the extent of microcystin adsorption. Once adsorption reached equilibrium, size exclusion was a dominant mechanism in controlling rejection, especially for tight TF membranes, with similar pore sizes to the molecular weight of microcystin-LR. An increase in water recovery and/or operating pressure led to an increase in the adsorption of microcystin-LR and a decrease in size exclusion, which was attributable to the increased permeate flux.

Objective 2. Determine the optimum operational condition of PAC-UF system for the effective removal of microcystin-LR from drinking water (Chapter 3).

The removal efficiency of the PAC-UF system proposed in Chapter 3 was greater than that of either individual membrane filtration or activated carbon binding alone. Of two types of activated carbon (e.g., wood-based carbon, coconut-based carbon) tested, wood-based activated carbon was more effective at removing microcystin than coconut-based carbon. In addition, of the two ultrafiltration membranes tested, the membrane composed of more hydrophobic polyethersulfone was found to attach microcystins on its surfaces and hence had better removal of microcystins than the hydrophilic cellulose acetate membrane. The removal of microcystin-LR by the PAC-UF system as a function of time followed a similar trend as PAC adsorption alone, which suggests that PAC adsorption was the dominant removal mechanism during the PAC-UF process. When we increased the amount of activated carbon to 5 mg/L, PAC-UF systems using either membrane removed nearly all of the microcystin toxin (above 95%) from the water and

microcystin concentrations less than the WHO guideline were detected in the treated water.

Objective 3. Investigate how natural organic matter (NOM) influences the removal of microcystin-LR by ultrafiltration or PAC-UF (Chapter 3)

The effect of organic matter existing in natural waters on the removal of microcystin-LR by ultrafiltration alone or PAC-UF was examined. From the study using Suwannee river fulvic acid (SRFA) in Chapter 3, it was found that the presence of SRFA in the water negatively affected either UF or PAC-UF process performances. When SRFA and microcystin-LR were added to the feed tank simultaneously during UF stand-alone process, the removal of microcystin-LR was not reduced for either the CA or PES membranes. For the sequential addition, on the other hand, the association of SRFA with the PES membranes resulted in a decline of permeate flux due to blocking membrane pores as well as a decrease in removal of microcystin-LR due to fewer available adsorption sites in the membrane pores and external surfaces for microcystin-LR. The presence of SRFA inhibited microcystin binding to activated carbon, thus reducing removal of microcystin-LR by a PAC-UF system. Similar trends were observed when either Suwannee River humic acid (SRHA) or Lake Erie water was used. This result suggests that the level of NOMs in the water must be monitored, if the level is high, additional activated carbon must be added to the treatment process to maintain optimum removal of cyanotoxins.

Objective 4. Examine the interaction between microcystin-LR and iron oxide nanoparticles to determine the applicability of metal oxide adsorption as an efficient removal technology (Chapter 5).

The application of iron oxide (maghemite) nanoparticles for the removal of microcystin-LR was investigated under various conditions in Chapter 5. The results from this chapter elucidated the adsorption mechanisms and important factors influencing the adsorption of microcystin-LR by nano-scale maghemite. The dominant mechanism of microcystin-LR adsorption onto maghemite was electrostatic interactions, although hydrophobic interactions may also play a role. The adsorption decreased with increasing pH, which was primarily attributable to a decrease in the positive surface charge of maghemite. An increase in ionic strength (NaCl concentration) led to increased microcystin adsorption onto maghemite at pH 6.4, due to the screening effect by salt ions. SRFA exhibited higher adsorption affinity and capacity for the iron oxides than microcystin-LR. Adsorption of microcystin-LR decreased with increasing SRFA concentration (> 2.5 ppm) due to the preferential adsorption of SRFA and limited sites available to microcystin-LR with a lower affinity.

6.2 Recommendations for Future Research

Results of this research suggest that advanced treatment technologies, such as adsorption process using activated carbon or metal oxide nanoparticles and membrane filtration (either stand-alone or combination with adsorbents), could effectively treat the source water contaminated with cyanotoxins. However, further investigations are needed

to address the following aspects before the application of these technologies to drinking water treatment facilities.

(1) In this research, only one individual compound of microcystin-LR was used for each treatment process. During cyanobacterial blooms, however, cyanotoxins exist as mixtures with other cyanotoxins rather than as a single compound. Therefore, it would be interesting to examine the removal of other cyanotoxins such as anatoxin-a, cylindrospermopsin, and other microcystin congeners, by both adsorption and membrane filtration processes. Further studies on the competition between microcystin-LR and other cyanobacteria toxins would be also valuable. It is expected that the properties of cyanotoxins such as molecular weight and hydrophobicity would provide an indication for the potential for the toxin removal.

(2) One of most important results from this research was a significant influence of NOM on process performance during either adsorption (PAC, maghemite nanoparticle) or membrane filtration processes. It was suggested that the concentration and composition of NOMs would be key factors affecting microcystin removal by these advanced processes. Further studies are still required such as the information relating the concentration, composition and molecular weight distribution of NOMs to microcystin removal to provide reliable prediction for system performance.

(3) It would be necessary to investigate the influence of traditional treatment processes such as coagulation and softening on microcystin removal during the advanced processes proposed in this research. Coagulation and lime-soda softening are widely practiced in the water utilities for reducing levels of organic matter and hardness, respectively. These processes might be used as a pre-treatment prior to PAC-UF. Thus,

the effect of these pre-treatment processes on microcystin removal during PAC-UF should be examined to ensure successful incorporation of this advanced process into current water treatment facilities. Moreover, it would be interesting to assess the feasibility of iron oxide nanoparticles as a coagulant aid and optimize the operating conditions. The concentration of iron oxide nanoparticles can be reduced if they are used to aid other coagulants.

(4) As suggested in Chapter 5, metal oxide nanoparticles could be used as an effective adsorbent to remove microcystins from drinking water. In this research, however, only one type of metal oxides (maghemite) was used to evaluate this process effectiveness. Thus, it would be required to examine the adsorption of microcystins onto other metal oxide nanoparticles, such as magnetite, hematite, and aluminum/titanium oxides, under various conditions, and determine the most effective process configurations. It is expected that the properties of metal oxides (e.g., surface charge, particle size) would significantly influence the microcystin removal. Comparison with the adsorption efficiency of either nano-scale clay minerals or carbonaceous materials (PAC or carbon nanotube) would be also interesting.

BIBLIOGRAPHY

Adham, S.S., Snoeyink, V.L., Clark, M.M., Bersillon, J.L. 1991. Predicting and verifying organics removal by PAC in an ultrafiltration system. *J. Am. Water Works Assoc*. 83, 81-91.

Adham, S.S., Snoeyink, V.L., Clark, M.M., Anselme, C. 1994. Predicting and verifying TOC removal by PAC in pilot-scale UF systems. *J. Am. Water Works Assoc*. 85, 58-68.

Antoniou, M.G., de la Cruz, A.A., Dionysiou, D.D. 2005. Cyanotoxins: New generation of water contaminants. *J. Environ. Eng*. 131(9), 1239-1243.

Aoustin, E., Schafer, A.I., Fane, A.G., Waite, T.D. 2001. Ultrafiltration of natural organic matter. *Sep. Purif. Technol*. 22-23, 63-78.

AWWA (American Water Works Association). *Water Quality and Treatment: A Handbook of Community Water Supplies*. McGraw-Hill Inc. New York, 1999.

AWWARF (American Water Works Association Research Foundation). Project No. 256, Denver, Colorado, 2001.

Balannec, B., Vourch, M., Rabiller-Baudry, M., Chaufer, B. 2005. Comparative study of different nanofiltration and reverse osmosis membranes for dairy effluent treatment by dead-end filtration. *Sep. Purif. Technol.* 42, 195-200.

Bandala, E.R., Martinez, D., Martinez, E., Dionysiou, D.D. 2004. Degradation of microcystin-LR toxin by Fenton and Photo-Fenton processes. *Toxicon* 43(7), 829-832.

Beckett, R., Jue, Z., Giddings, J.C. 1987. Determination of molecular weight distributions of fulvic and humic acids using flow field-flow fractionation. *Environ. Sci. Technol*. 21(3), 289-295.

Bellona, C., Drewes, J.E., Xu, P., Amy, G. 2004. Factors affecting the rejection of organic solutes during NF/RO treatment–a literature review. *Water Res*. 38, 2795-2809.

Bischoff, K. 2001. The toxicology of microcystin-LR: occurrence, toxicokinetics, toxicodynamics, diagnosis and treatment. *Vet. Hum. Toxicol*. 43(5), 294-297.

Bottero, J.-Y., Rose, J., Wiesner, M.R. 2006. Nanotechnologies: tools for sustainability in a new wave of water treatment processes. Integr. Environ. Assess. Manag. 2(4), 391-395.

Braghetta, A., DiGiano, F.A., Ball, W.P. 1997. Nanofiltration of natural organic matter: pH and ionic strength effects. *J. Environ. Eng.* 123(7), 628-641.

Bruchet, A., Bernazeau, F., Baudin, I., Pieronne, P. 1998. Algal toxins in surface water: analysis and treatment. *Water Supply* 16(1-2), 619-623.

Campos, C., Mariñas, B.J. Snoeyink, V.L. Baudin, I., Lainé, J.M. 2000. PAC-Membrane filtration process. I: Model development. *J. Environ. Eng*. 126(2), 97-103.

Carmichael, W.W. 1992. Cyanobacteria secondary metabolites--the cyanotoxins. J. *Appl. Bacteriol*. 72(6), 445-459.

Carmichael, W.W. 1997. The cyanotoxins. *Adv. Bot. Res.* 27, 211-256.

Chellam, S., Taylor, J.S. 2001. Simplified analysis of contaminant rejection during ground and surface water nanofiltration under the information collection rule. *Water Res*. 35(10), 2460-2474.

Childress, A.E., Elimelech, M. 2000. Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristics. *Environ. Sci. Technol*. 34, 3710-3716.

Chin, Y.-P., Aiken, G., O'Loughlin, E. 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environ. Sci. Technol*. 28, 1853-1858.

Cho, J., Amy, G., Pellegrino, J., Yoon, Y. 1998. Characterization of clean and natural organic matter (NOM) fouled NF and UF membranes, and foulants characterization. *Desalination* 118, 101-108.

Chow, C.W.K., Panglisch, S., House, J., Drikas, M., Burch, M.D., Gimbel, R. 1997. A study of membrane filtration for the removal of cyanobacterial cells, *AQUA* 46(6), 324-334.

Cleveland, C.T., Seacord, T.F., Zander, A.K. 2002. Standardized membrane pore size characterization by polyethylene glycol rejection. *J. Environ. Eng.* 128, 399-407.

Cook, D., Newcombe, G. 2002. Effect of natural organic matter concentration and character on the adsorption of microcystin analogues onto PAC. *Proceedings of the AWWA−Water Quality Technology Conference*. November 2002.

Craig, M., MacCready, T.L., Luu, H.A., Smillie, M.A., Dubord, P., Holmes, C.F.B. 1993. Identification and characterization of hydrophobic microcystins in Canadian freshwater cyanobacteria. *Toxicon* 31(12), 1541-1549.

Davis, J.A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochim. Cosmochim. Acta* 46, 2381-2393.

De Laat A.W.M., van den Heuvel G.L.T. 1993. Competitive and displacement adsorption of polyvinyl alcohol and the ammonium salt of a polyacrylic acid on $BaTiO_3$. *Colloid Surf. A: Physico-chem. Eng. Aspects*. 70(2), 179-187.

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

Drikas, M., Newcombe, G., Nicholson, B. 2001. Water treatment options for cyanobacteria and their toxins. *Proceedings of AWWA-Water Quality Technology Conference (WQTC)*, Nashville, TN, November 2001, 2006-2033.

Ducom, G., Cabassud, C. 1999. Interests and limitations of nanofiltration for the removal of volatile organic compounds in drinking water production. *Desalination* 124, 115-123.

Elimelech, M., Chen, W.H., Waypa, J.J. 1994. Measuring the zeta (electrokinetic) potential of reverse osmosis membranes by a streaming potential analyzer, *Desalination* 95(3), 269-286.

Elimelech, M., Zhu, X., Childress, A.E., Hong, S. 1997. Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes. *J. Membr. Sci*. 127, 101-109.

Eriksson J. E. Gronberg, L., Nygard, S., Slotte, J.P., Meriluoto, J.A.O. 1990. Hepatocellular uptake of 3H-dihydromicrocystin-LR, a cyclic peptide toxin. *Biochimica Biophysica Acta*. 1025, 60-66.

Evanko, C.R., Dzombak, D.A. 1998. Influence of structural features on sorption of NOM-analogue organic acids to goethite. *Environ. Sci. Technol*. 32(19), 2846-2855.

Falconer I.R., Runnegar, M.T.C., Buckley, T., Huyn, V.L., Bradshaw P. 1989. Using activated carbon to remove toxicity from drinking water containing cyanobacteria blooms. *J. Am. Water Works Assoc*. 81(2), 102-105.

Falconer, I.R. 1999. An overview of problems caused by toxic blue-green algae (cyanobacteria) in drinking and recreational water. *Env. Toxicol*. 14, 5-12.

Farahbakhsh, K., Svrcek, C., Guest, R.K., Smith, D.W. 2004. A review of the impact of chemical pretreatment on low-pressure water treatment membranes. *J. Environ. Eng. Sci*. 3, 237-253.

Fawell, J., Hart, J., James, H., Parr, W. 1993. Blue-green algae and their toxins: analysis, toxicity, treatment, and environmental control. *Water Supply*. 11(3-4), 109-121.

Fawell, J.K., James C.P., James, H.A. *Toxins from blue-green algae: toxicological assessment of microcystin-LR and a method for its determination in water*. FWR Report No. FR0359/2/DoE 3358/2. Foundation of Water Research, Medmenham, Marlow, Bucks, UK. 1994.

Feitz, A.J., Waite, D., Jones, G.J., Boyden, B.H., Orr, P.T. 1999. Photocatalytic degradation of the blue green algal toxin microcystin-LR in a natural organic-aqueous matrix. *Environ. Sci. Technol*. 33, 243-249.

Fitzgerald, D.J., Cunliffe, D.A., Burch, M.D. 1999. Development of health alerts for cyanobacteria related toxins in South Australia. *Environ. Toxicol*. 14(1), 203-209.

Gajdek, P., Lechowski, Z., Bochnia, T., Kepczynski, M. 2001. Decomposition of microcystin-LR by Fenton oxidation. *Toxicon* 39(10), 175-1578.

Gan, Q., Howell, J.A., Field, R.W., England, R., Bird, M.R., McKechinie, M.T. 1999. Synergetic cleaning procedure for a ceramic membrane fouled by beer microfiltration. *J. Membr. Sci*. 155(2), 277-289.

Ganesh, R., Leong, L.Y.C., Skandan, G., Jain, M., Liu, B., Larson, L.E. Use of nanoscale materials for water treatment to achieve multiple water quality goals. *Proceedings of Water Quality Technology Conference and Exposition*. 2005.

Geffroy, C., Cohen Stuart, M.A., Wong, K., Cabane, B., Bergeron, V. 2000. Adsorption of nonionic surfactants onto polystyrene: Kinetics and reversibility. *Langmuir* 16, 6422-6430.

Gert-Jan de Maagd, P., Hendriks, A., Seinen, W., Sijm, D.T. H. M. 1999. pH-dependent hydrophobicity of the cyanobacteria toxin microcystin-LR. *Water Res*. 33, 677-680.

Gijsbertsen-Abrahamse, A.J., Schmidt, W., Chorus, I., Heijman, S.G.J. 2006. Removal of cyanotoxins by ultrafiltration and nanofiltration. *J. Membr. Sci*. 276, 252-259.

Gowman, L.M., Ethier, C.R. 1997. Concentration and concentration gradient measurements in an ultrafiltration concentration polarization layer. Part II: Application to hyaluronan. *J. Membr. Sci*. 131, 107-123.

Grutzmacher, G., Bottcher, G., Chorus, I., Bartel, H. 2002. Removal of microcystins by slow sand filtration. *Environ. Toxicol*. 17(4), 386-394.

Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J.F. 1994. Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. *Environ. Sci. Technol*. 28, 38-46.

Gu, B., Mehlhorn, T.L, Liang, L., McCarthy, J.F. 1996. Competitive adsorption, displacement, and transport of organic matter on iron oxide: I. competitive adsorption. *Geochimica et Cosmochimica Acta* 60(11), 1943-1950.

Gupta, N., Pant, S.C., Vijayarghavan, R., Rao, P.V.L. 2003. Comparative toxicity evaluation of cyanobacterial cyclic peptide toxin microcystin variants (LR, RR, YR) in mice. *Toxicology* 188, 285-296.

Hagare, P., Thiruvenkatachari, R., Ngo, H.H. 2001. A feasibility study of using hematite to remove dissolved organic carbon in water treatment. *Sep. Sci. Technol*. 36(11), 2547-2559.

Hanna, K. 2007. Sorption of two aromatic acids onto iron oxides: Experimental study and modeling. *J. Colloid Interf. Sci*. 309, 419-428.

Harada, K.-I., Tsuji, K. 1998. Persistence and decomposition of hepatotoxic MCYSTs produced by cyanobacteria in natural environment. *J. Toxicol Toxicon Rev*. 61, 385-403.

Hart, J., Stott, P. *Microcystin-LR removal from water*. FR 0367, In: P. Marlow (Ed.), Buckinghamshire, Foundation for Water Research, UK. 1993.

Himberg K., Keijola A.-M., Pyysalo, H., Sivonen K. 1989. The effect of water treatment processes on the removal of hepatotoxins from Microcystis and Oscillatoria cyanobacteria: A laboratory study. *Water Res*. 23(8), 979-984.

Ho, C.-C., Zydney, A.L. 1999. Effect of membrane morphology on the initial rate of protein fouling during microfiltration. *J. Membr. Sci*. 155, 261-275.

Hoek, E.M.V., Kim, A.S., Elimelech, M. 2003. Cake-enhanced concentration polarization: A new fouling mechanism for salt-rejecting membranes. *Environ. Sci. Technol*. 37, 5581-5588.

Hong, S., Elimelech, M. 1997. Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *J. Membr. Sci*. 132(9), 159-181.

Hooser, S.B., Beasley, V.R., Basgall, E.J., Carmichael, W.W., Haschek, W.M. 1990. Microcystin-LR-induced ultrastructural changes in rats. *Vet Pathol*. 27(1), 9-15.

Howe, K.J., Clark, M.M. 2002. Fouling of microfiltration and ultrafiltration membranes by natural waters. *Environ. Sci. Technol*. 36, 3571-3576.

Hu, J., Chen, G., Lo, I.M.C. 2005. Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles. *Water Res*. 39, 4528-4536.

Hu, J., Chen, G., Lo, I.M.C. 2006. Selective removal of heavy metals from industrial wastewater using maghemite nanoparticles: performance and mechanisms. *J. Environ. Eng*. 132(7), 709-715.

International Humic Substances Society (IHSS) website, http://www.ihss.gatech.edu

Izumi, Y, Masih, D., Aika, K.-I., Seida, Y. 2005. Characterization of intercalated iron(III) nanoparticles and oxidative adsorption of arsenite on them monitored by X-ray absorption fine structure Combined with fluorescence spectrometry. *J. Phys. Chem. B* 109(8), 3227-3232.

Jochimsen, E.M., Carmichael, W.W., An, J.S., Cardo, D.M., Cookson, S.T., Holmes, C.E.M., Antines, M.B. de Melo Filho, D.A., Lyra, T.M., Burreto, V.S.T., Azevedo, S.M.F.O., Jarvis, W.R. 1998. Liver failure and death after exposure to microcystins at a hemodialysis center in Brazil. *New Eng. J. Medicine*. 338(13), 873-878.

Jones, K.L., O'Melia, C.R. 2000. Protein and humic acid adsorption onto hydrophilic membrane surfaces: Effects of pH and ionic strength. *J. Membr. Sci*. 165, 31-46.

Jucker, C., Clark, M.M. 1994. Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes. *J. Membr. Sci.* 97, 37-52.

Kim, J.-S., Lee, S.-J., Yoon, S.-H., Lee, C.-H. 1996. Competitive adsorption of trace organics on membranes and powdered activated carbon in powdered activated carbon-ultrafiltration system. *Water. Sci. Technol*. 34(9), 223-229.

Kim, T.-U. 2006. *Transport of organic micropollutants through Nanofiltration (NF) and reverse osmosis (RO) membranes: mechanisms, modeling, and applications*. Ph.D. dissertation. Dept. of Civil, Environmental, and Architectural Engineering, University of Colorado at Boulder. 77-83.

Kimura, K., Amy, G., Drewes, J., Watanabe, Y. 2003. Adsorption of hydrophobic compounds onto NF/RO membranes: an artifact reading to overestimation of rejection. *J. Membr. Sci*. 221, 89-101.

Kimura, K., Amy, G., Drewes, J.E., Heberer, T., Kim, T.-U., Watanabe, Y. 2003. Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes. *J. Membr. Sci*. 227, 113-121.

Kördel, W., Dassenakis, M., Lintelmann, J., Padberg, S. 1997. The importance of natural organic material for environmental processes in water and soils. *Pure&Appl. Chem*. 69(7), 1571-1600.

Kotak, B.G., Kenefick, S.L., Fritz, D.L., Rousseaux, C.G., Prepas, E.E., Hrudey, S.E. 1993. Occurrence and toxicological evaluation of cyanobacterial toxins in Alberta lakes and farm dugouts. *Water Res*. 27(3), 495-506.

Krisdhasima, V., Vinaraphong, P., McGuire, J. 1993. Adsorption kinetics and elutability of α-lactalbumin, β-casein, β-lactoglobulin, and bovine serum albumin at hydrophobic and hydrophilic interfaces. *J. Colloid Interf. Sci.* 161, 325-334.

Lahti, K., Rapala, J., Fardig, M., Niemela, M., Sivonen, K. 1997. Persistence of cyanobacterial hepatotoxin, microcystin-LR in particulate material and dissolved in lake water. *Water Res*. 31, 1005-1012.

Lambert, T.W., Holmes C.F.B., Hrudey, S.E. 1996. Adsorption of microcystin-LR by activated carbon and removal in full scale water treatment. *Water Res*. 30(6), 1411-1422.

Lawton, L.A., Cornish, B.J.P.A., Macdonald, A.W.R. 1998. Removal of cyanobacterial toxins (microcystins) and cyanobacterial cells from drinking water using domestic water filters. *Water Res*. 32(3), 633-638.

Lawton L.A., Robertson, P.K.J. 1999. Physico-chemical treatment methods for the removal of microcystins (cyanobacterial hepatotoxins) from potable waters. *Chem. Soc. Rev.* 28, 217-224.

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

Liang, L., Morgan, J. J. 1990. Chemical aspects of iron oxide coagulation in water: Laboratory studies and implications for natural systems, *Aquatic Sci*. 52(1), 32-55.

Liu, B.H. 2006. *Contaminants removal from water using nanoparticles*. MS thesis, Dept. of Environmental Science, California State University, Fullerton.

Liu, C., Caothien, S., Hayes, J., Caothuy, T., Otoyo, T., Ogawa, T. 2000. Membrane Cleaning: from Art to Science. *Proceedings of Membrane Technology Conference*. March 2000.

Liu, G., Qian, Y., Dai, S., Feng, N. 2008. Adsorption of microcystin LR and LW on suspended particulate matter (SPM) at different pH. *Water Air Soil Pollut*. 192(1-4), 67-76.

Mackintosh, C., Beattie, K.A., Klumpp, S., Cohen, P., Codd, G.A. 1990. Cyanobacterial microcystin-LR is a potent and specific inhibitor of protein phosphatases 1 and 2A from both mammals and higher plants. *FEBS Lett*. 264, 187-192.

Martinez, F., Martin, A., Pradanos, P., Calvo, J.I., Palacio, L., Hernandez, A. 2000. Protein adsorption and deposition onto microfiltration membranes: the role of solute-solid interactions. *J. Colloid Interf. Sci*. 221, 254–261.

Matsui, Y., Colas, F., Yuasa, A. 2001. Removal of a syntetic organic chemical by PAC-UF systems. II: Model Application. *Water Res*. 35(2), 464-470.

Matthiasson, E. 1983. The role of macromolecular adsorption in fouling of ultrafiltration membranes. *J. Membr. Sci.* 16, 23-36.

McElhiney, J., Lawton, L.A. 2005. Detection of the cyanobacterial hepatotoxins microcystins. *Toxicol. Appl. Pharmacol*. 203, 219-230.

Meier, M., Namjesnik-Dejanovic, K., Maurice, P.A., Chin, Y.–P, Aiken, G.R. 1999. Fractionation of aquatic natural organic matter upon sorption to goethite and kaolinite. *Chemical Geology* 157, 275-284.

Meriluoto, J., Gueimonde, M., Haskard, C.A., Spoof, L. 2005. Removal of the cyanobacterial toxin microcystin-LR by human probiotics. *Toxicon* 46, 111-114.

Metcalf, J.S., Godd, G.A. Cyanobacterial toxins in the water environment. FWR Report No. FR/R0009. Foundation for Water Research, UK. February 2004.

Miller, M.J., Critchley, M.M., Hutson, J. Fallowfield, H.J. 2001. The adsorption of cyanobacterial hepatotoxins from water onto soil during batch experiments. *Water Res*. 35, 1461-1468.

Miller, M.J., Hutson, J. Fallowfield, H.J. 2005. The adsorption of cyanobacterial hepatoxins as a function of soil properties. *J. Water Health* 3(4), 339-347.

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

Mohamed, Z.A., El-Sharouny, H.M., Ali, W.S. 2007. Microcystin concentration in the Nile River sediments and removal of microcystin-LR by sediments during batch experiments. *Arch. Environ. Contam. Toxicol*. 52, 489-495.

Mohammad, A.W., Ali, N. 2002. Understanding the steric and charge contributions in NF membranes using increasing MWCO polyamide membranes. *Desalination* 147, 205-212.

Morris, R.J., Williams, D.E., Luu, H.A., Holmes, C.F.B., Andersen, R.J., Calvert, S.E. 2000. The adsorption of microcystin-LR by natural clay particles. *Toxicon*, 38, 303-308.

Mouchet, P., Bonnelye, V. 1998. Solving algae problems: French expertise and world-wide applications. *AQUA* 47(3), 125-141.

Mozia, S., Tomaszewska, M., Morawski, A.W. 2005. Studies on the effect of humic acids and phenol on adsorption-ultrafiltration process performance. *Water Res*. 39, 501-509.

Muller, J., Davis, R.H. 1996. Protein fouling of surface-modified polymeric microfiltration membranes. *J. Membr. Sci*. 116(1), 47-60.

Murphy, E.M., Zachara, J.M., Smith, S.C. 1990. Influence of mineral-bound humic substances on the sorption of hydrophobic organic compounds. *Environ. Sci. Technol*. 24, 1507-1516.

Neumann, U., Weckesser, J. 1998. Elimination of microcystin peptide toxins from water by reverse osmosis. *Environ. Toxicol. Water Qual*. 13, 143-148.

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

Nghiem, L.D., Schafer, A.I., Waite, T.D. 2002. Adsorption of estrone on nanofiltration and reverse osmosis membranes in water and wastewater treatment. *Wat. Sci. Technol*. 46(4-5), 265-272.

Nghiem, L.D., Schafer, A.I., Waite, T.D. 2002. Adsorptive interactions between membranes and trace contaminants. *Desalination* 147, 269-274.

Nghiem, L.D., Schäfer, A.I. 2002. Adsorption and transport of trace contaminant estrone in NF/RO membranes. *Environ. Eng. Sci*. 19(6), 441-451.

Nghiem, L.D., Schafer, A.I., Elimelech, M. 2004. Removal of natural hormones by nanofiltration membranes: measurement, modeling, and mechanisms. *Environ. Sci. Technol*. 38(6), 1888-1896.

Nghiem, L.D., Manis, A., Soldenhoff, K., Schäfer, A.I. 2004. Estrogenic hormone removal from wastewater using NF/RO membranes. *J. Membr. Sci*. 242, 37-45.

Nghiem, L.D., Schäfer, A.I., Elimelech, M. 2005. Pharmaceutical retention mechanisms by nanofiltration membranes. *Environ. Sci. Technol*. 39, 7698-7705.

Nicholson, B.C. Rositano, J. Burch, M.D. 1994. Destruction of cyanobacterial peptide hepatotoxins by chlorine and chloramines. *Water Res*. 28, 1297-1303.

Nishiwaki-Matsushima, R., Ohta, T., Nishiwaki, S., Suganuma, M., Kohyama, K., Ishikawa, T., Carmichael, W.W., Fujiki, H. 1992. Liver tumour promotion by cyanobacterial cyclic peptide toxin microcystin-LR. *J. Cancer Res. Clin. Oncol*. 118, 420-424.

NOAA (National Oceanic and Atmospheric Administration). Harmful algal blooms in the Great Lakes. NOAA Great Lakes Environmental Research Laboratory. 2006. http://www.glerl.noaa.gov/res/Centers/HumanHealth/hab/EventResponse/

O'Loughlin, E., Chin, Y.-P. 2001. Effect of detector wavelength on the determination of the molecular weight of humic substances by high-pressure size exclusion chromatography. *Water Res*. 35(1), 333-338.

Oliva, F.Y., Avalle, L.B., Camara, O.R., De Pauli, C.P. 2003. Adsorption of human serum albumin (HAS) onto colloidal TiO_2 particles, Part I. *J. Colloid Interf. Sci.*261, 299-311.

Ozaki, H., Li, H. 2002. Rejection of organic compounds by ultralow pressure reverse osmosis membrane. *Water Res*. 36(1), 123-130.

Parfitt, R.L. Fraser, A.R., Farmer, V.C. 1977. Adsorption on hydrous oxides. III. Fulvic acid and humic acid on goethite, gibbsite and imogolite. *J. Soil Sci*. 28, 289-296.

Pendleton, P., Schumann, R., Wong, S.H. 2001. Microcystin-LR adsorption by activated carbon. *J. Colloid Interf. Sci*. 240(1), 1-8.

Peng, Z.G., Hidajat, K., Uddin, M.S. 2004. Adsorption of bovine serum albumin on nanosized magnetic particles. *J. Colloid Interf. Sci*. 271, 277-283.

Petersen, R.J. 1993. Composite reverse osmosis and nanofiltration membranes. *J. Membr. Sci*. 83, 81-150.

Rajagopalan, G., Leong, L.Y.C., Jain, M., Larson, L.E. 2006. Use of nanoscale adsorbents for water treatment. *Proceedings of the 40th Western Regional Meeting*. Jan. 22-25, 2006.

Reiss, C.R., Taylor, J.S., Robert, C. 1999. Surface water treatment using nanofiltration-pilot testing results and design considerations. *Desalination* 125, 97-112.

Renolds, K.A. 2004. Cyanobacteria: Natural organisms with toxic effects. *Wat. Cond. Pur*. 46(3), 78-80.

Robertson, P.K.J., Lawton, L.A., Munch, B., Cornish, B. 1999. The destruction of cyanobacterial toxins by titanium dioxide photocatalysis. *J. Adv. Oxid. Technol*. 4(1), 20-26.

Rositano, J., Nocholson, B.C. 1994. *Water treatment techniques for removal of cyanobacteiral toxins from water*. Australian Centre for Water Quality Research, Salisbury, South Australia.

Rositano, J., Nicholson, B.C., Pieronne, P. 1998. Destruction of cyanobacterial toxins by ozone. *Ozone Sci. Eng*. 20(3), 223-238.

Saito, T., Koopal, L.K., Van Riemsdijk, W.H., Nagasaki, S., Tanaka, S. 2004. Adsorption of humic acid on goethite: Isotherms, charge adjustments, and potential profiles. *Langmuir* 20, 689-700.

Santos, J.H., Matsuda, N., Qi, Z., Yoshida, T., Takatsu, A., Kato, K. 2003. Experimental evidence of the reversibility of the first stage of protein adsorption at a hydrophobic quartz surface near the isoelectric point. *Surf. Interface Anal.* 35, 432-436.

Savage, N., Diallo, M. 2005. Nanomaterials and water purification: Opportunities and challenges. *J. Nanoparticle Research* 7, 331-342.

Schaeffer, K. Match treatment type to carbon type. 2008. *Water Technol. Magazine*. 31(1), Technical pages.

Schäfer, A.I., Fane, A.G., Waite, T.D. 2000. Fouling effects on rejection in the membrane filtration of natural waters. *Desalination* 131, 215-224.

Schäfer, A.I., Nghiem, L.D., Waite, T.D. 2003. Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis. *Environ. Sci. Technol*. 37(1), 182-188.

Schlautman, M.A., Morgan, J.J., 1991. Adsorption of aquatic humic substances on colloidal-size aluminum-oxide surfaces on clay-minerals. *Soil Sci. Soc. Am. J*. 55, 34-42.

Shawwa, A.R., Smith, D.W. 2001. Kinetics of microcystin-LR oxidation by ozone. *Ozone Sci. Eng*. 23 (2), 161-170.

Shumidt, W., Willmitzer, H., Bornmann, K., Pietsch, J. 2002. Production of drinking water from raw water containing cyanobactreria pilot plant studies for assessing the risk of microcystin break through. *Environ. Toxicol*. 17(4), 375-385.

Sielaff, H., Dittmann, E., Tandeau de Marsac, N., Bouchier, C., Von Döhren, H., Börner, T., Schwecke, T. 2003. The *mcyF* gene of the microcystin biosynthetic gene cluster from *Microcystis aeruginosa* encodes an aspartate racemase. *Biochem. J.* 373, 909-916.

Song, W., Ravindran, V., Koel, B.E., Pirbazari, M. 2004. Nanofiltration of natural organic matter with H_2O_2/UV pretreatment: fouling mitigation and membrane surface characterization. *J. Membr. Sci.* 241, 143-160.

Song, W., Teshiba, T., Rein, K., O'Shea, K.E. 2005. Ultrasonically induced degradation and detoxification of microcystin-LR (Cyanobacterial toxin). *Environ. Sci. Technol.* 39, 6300-6305.

Svrcek, C., Smith, D.W. 2004. Cyanobacteria toxins and the current state of knowledge on water treatment options: a review. *J. Environ. Eng. Sci*. 3, 155-185.

Tang, C.Y., Fu, Q.S., Robertson, A.P., Criddle, C.S., Leckie, J.O. 2006. Use of reverse osmosis membranes to remove perfluorooctane Sulfonate (PFOS) from semiconductor wastewater. *Environ. Sci. Technol*. 40, 7343-7349.

Tang, C.Y., Fu, Q.S., Criddle, C.S., Leckie, J.O. 2007. Effect of flux (transmembrane pressure) and membrane properties on fouling and rejection of reverse osmosis and nanofiltration membranes treating perfluorooctane sulfonate containing wastewater, *Environ. Sci. Technol*. 41, 2008-2014.

Taniguchi, M., Kilduff, J.E., Belfort, G. 2003. Modes of natural organic matter fouling during ultrafiltration. *Environ. Sci. Technol*. 37, 1676-1683.

Teixeira, M.R., Rosa, M.J. 2005. Microcystins removal by nanofiltration membranes. *Sep. Purif. Technol*. 46, 192-201.

Teixeira, M.R., Rosa, M.J. 2006. Neurotoxic and hepatotoxic cyanotoxins by nanofiltration. *Water Res*. 40, 2837-2846.

Thurman, E.M., Wershaw, R.L., Malcolm, R.L., Pinckney, D.J. 1982. Molecular size of aquatic humic substances. *Org. Geochem*. 4, 27-35.

Tipping E. 1981. The adsorption of aquatic humic substances by iron oxides. *Geochim. Cosmochim. Acta* 45, 191-199.

Tomaxzewska, M., Mozia, S. 2002. Removal of organic matter from water by PAC/UF system. *Water Res*. 36, 4137-4143.

Tomaszewska, M., Mozia, S. 2003. Effectiveness of organics removal in hybrid process. *Proceedings of ARS separatoria*, Zloty Potok, Poland, 190-193.

Tsuji, K., Naito, S., Kondo, F., Ishikawa, N., Watanabe, M.F., Suzuki, M., Harada, K.-I. 1994. Stability of microcystins from cyanobacteria: Effect of light on decomposition and isomerization. *Environ. Sci. Technol*. 28, 173-177.

Tsuji, K., Watanuki, T., Dondo, F., Watanabe, M.F., Nakazawa, H., Suzuki, M., Uchida, H., Harada, K.-I. 1997. Stability of microcystins from cyanobacteria – IV. Effect of chlorianation on decomposition. *Toxicon* 35(7), 1033-1041.

Tsuji, K., Masui, H., Uemura, H., Mori, Y., Harada, K.-I. 2001. Analysis of microcystins in sediments using MMPB method. *Toxicon*. 39, 687-692.

Turker, M., Hubble, J. 1987. Membrane fouling in a constant-flux ultrafiltration cell. *J. Membr. Sci.* 34, 267-281.

Uheida, A., Salazar-Alvarez, G., Björkman, E., Yu, Z., Muhammed, M. 2006. Fe_3O_4 and γ-Fe_2O_3 nanoparticles for the adsorption of Co^{2+} from aqueous solution. *J. Colloid and Interf. Sci*. 298, 501-507.

USEPA. *Fact sheet: The drinking water contaminant candidate list−The source of priority contaminants for the drinking water program*. EPA 815-F-05-001. Office of Water, US Environmental Protection Agency, Washington, DC. 2005.

Van der Bruggen, B., Schaep, J., Maes, W., Wilms, D., Vandecasteele, C. 1998. Nanofiltration as a treatment method for the removal of pesticides from ground waters. *Desalination* 117, 139-147.

Van der Bruggen, B., Schaep, J., Wilms, D., Vandecasteele, C. 1999. Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *J. Membr. Sci*. 156, 29-41.

Vermeer, A.W.P., van Riemsdijk, W.H., Koopal, L.K. 1998. Adsorption of humic acid to mineral particles. 1.specific and electrostatic interaction. *Langmuir* 14, 2810-2819.

Vermeer, A.W.P., Koopal, L.K. 1998. Adsorption of humic acid to mineral particles. 2.Polydispersity effects with polyelectrolyte adsorption. *Langmuir* 14, 4210-4216.

Vesterkvist, P.S.M., Meriluoto, J.A.O. 2003. Interaction between microcystins of different hydrophobicities and lipid monolayers. *Toxicon*. 41. 349-355.

Vrijenhoek, E.M., Hong, S., Elimelech, M. 2001. Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes. *J. Membr. Sci*. 188, 115-128.

Walker, S.L., Bhattacharjee, S., Vrijenhoek, E.M., Elimelech, M. 2002. A novel asymmetric clamping cell for measuring streaming potential of flat surface. *Langmuir* 18, 2193-2198.

Walker, S.R. 2005. Nebraska Experience. *Proceedings of International Symposium on Cyanobacterial Harmful Algal Blooms (ISOC-HAB)*, USEPA, Research Triangle Park, NC, September 2005.

Wannemacher, M.F., Harada, K.I., Matsuura, K., Watanbe M., 1989. Heptapeptide toxin production during the batch culture of two microcystis species (cyanobacteria). *J. Appl. Phycol*. 1, 161-165.

Watanabe, M.F., Park, H.-D., Kondo, F., Harada, K.-I., Hayashi, H., Okino, T. 1997. Identification and estimation of microcystins in freshwater mussels. *Nat. Toxins*. 5, 31-35.

Welker, M., Steinberg, C. 2000. Rates of humic substance photosensitized degradation of microcystin-LR in natural waters. *Environ. Sci. Technol*. 34, 3415-3419.

Weng, L., Van Riemsdijk, W.H., Koopal, L.K., Hiemstra, T. 2006. Adsorption of humic substances on goethite: Comparison between humic acids and fulvic acids. *Environ. Sci. Technol*. 40, 7494-7500.

WHO. *Cyanobacterial toxins: Microcystin-LR. Guidelines for drinking water quality*. World Health Organization, Geneva. 1998.

Wiegand, C., Pflugmacher, S. 2005. Ecotoxicological effects of selected cyanobacterial secondary metabolites a short review. *Toxicol. Appl. Pharmacol*. 203(3), 201-218.

Williams, D.E., Dawe, S.C., Kent, M.L., Andersen, R.J., Craig, M., Homes, C.F.B. 1997. Bioaccumulation and clearance of microcystins from salt water mussels, Mytilus edulis, and in vivo evidence for covalently bound microcystins in mussel tissues. *Toxicon*. 35(11), 1671-1625.

Williams, M.E., Hestekin, J.A., Smothers, C.N., Bhattacharyya, D. 1999. Separation of organic pollutants by reverse osmosis and nanofiltration membranes: Mathematical models and experimental verification. *Ind. Eng. Chem. Res*. 38, 3683-3695.

Xu, Y., Lebrun, R.E. 1999. Investigation of the solute separation by charged nanofiltration membrane: effect of pH, ionic strength, and solute type. *J. Membr. Sci*. 158, 93-104.

Yavuz, C.T., Mayo, J.T., Yu, W.W., Prakash, A., Falkner, J.C., Yean, S., Cong, L.L. Shipley, H.J. Kan, A., Tomson, M., Natelson, D., Colvin, V.L. 2006. Low-field magnetic separation of monodisperse Fe_3O_4 nanocrystals. *Science* 314, 964-967.

Yoon, T.H., Johnson, S.B., Musgrave, C., Brown, G.E., Jr. 2005. Adsorption of organic matter at mineral/water interfaces. *Langmuir* 21(11), 5002-5012.

Yoon, Y., Amy, G., Cho, J., Pellogrino, J. 2004. Systematic bench-scale assessment of perchlorate (ClO_4^-) rejection mechanisms by nanofiltration and ultrafiltration membranes. *Sep. Sci. Technol*. 39(9), 2105-2135.

Yoon, Y., Westerhoff, P., Snyder, S.A., Wert, E.C. 2006. Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products. *J. Membr. Sci.*, 270, 88-100.

Yoshizawa, S., Matsushima, R., Watanabe, M.F., Harada, K.-I., Ichihara, A., Carmichael, W.W., Fujiiki, H. 1990. Inhibition of protein phosphatases by microcystis and nodularin associated with hepatotoxicity. *J. Cancer Res. Clin. Oncol*. 116, 609-614.

Zander, A.K., Curry, N.K. 2001. Membrane and solution effects on solute rejection and productivity. *Water Res*. 35, 4426-4434.

Zhou, Q., Maurice, P.A., Cabaniss, S.E. 2001. Size fractionation upon adsorption of fulvic acid on goethite: Equilibrium and kinetic studies. *Geochimica et Cosmochimica Acta* 65(5), 803-812.