Sorption of Microconstituents onto Primary and Activated Sludge to which Alum Has Been Added

by

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Abstract

Microconstituents (MCs) have become an emerging concern to scientists and researchers. Due to the development of analytical technology, it is now possible to study MCs at ηg/L to μg/L levels.

Wastewater treatment plants (WWTPs) are the major point source for MCs entering the environment based on the literature. WWTPs are known to be unable to remove many MCs to a safe level. In order to fully understand the fate of MCs in WWTPs and to further improve the design of WWTPs in terms of MC removal, it is necessary to examine removal mechanisms such as sorption and biodegradation in WWTPs.

Three MCs, bisphenol A (BPA), 17-α-ethinylestradiol (EE2) and triclosan (TCS), were chosen for this study. They are chemicals reported to be hydrophobic and have low vapor pressure, which makes sorption a highly potential removal mechanism.

Primary sludge and activated sludge (AS) were used to perform sorption kinetics and isotherm experiments for BPA, EE2 and TCS. Primary sludge was collected from local WWTPs, and AS was generated from a lab-scale continuous flow bioreactor system maintained at solids retention times of 15, 10 and 5 d and hydraulic retention time (HRT) of 6 h. Alum was added to synthetic wastewater influent at concentrations typically used for phosphorus removal at some plants. Alum has the potential to change sludge structure and influence the sorption process. A comparison was made with AS as the adsorbent with and without alum addition to the AS to study the influence of alum on the sorption processes.

The selected MCs were found to reach sorption equilibrium with primary sludge within 7 h. A pseudo second-order kinetic model was an excellent fit to describe the sorption processes of selected MCs.

The solids-liquid partitioning coefficient (K_d) was determined for the three chosen MCs. The K_d values found for primary sludge and AS are very close. The K_d for MCs sorbed to AS in this study were compared with the K_d for AS without alum addition. Although alum addition showed no influence on effluent soluble chemical oxygen demand, it decreases the K_d for BPA and EE2 sorbed to AS. In contrast, a much higher K_d for TCS was observed for AS with alum addition.

Judging from the R^2 values, the linear sorption model is not suitable for some of the isotherms. Langmuir and Freundlich sorption isotherms were further used to fit the experimental data by applying linear regression and nonlinear regression approaches. The Freundlich isotherm was found to be the most suitable model to describe the experiment data.

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This paper would not have been possible without my parents' continuous moral support. They have always believed in my potential and gave me unconditional support, even though I was not able to accompany them all the time.

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Glossary

17β-estradiol	E2
17-α-ethinylestradiol	EE2
Activated Sludge	AS
American Water Works Association	AWWA
Biochemical Oxygen Demand	BOD
Bisphenol-A	BPA
Chemical Oxygen Demand	COD
Dichloro-diphenyl-trichloroethane	DDT
Dissolved Oxygen	DO
Endocrine Disrupting Compound	EDC
Environmental Protection Agency	EPA
High Performance Liquid Chromatography Coupled with Ultraviolet Detection	HPLC-UV
Hydraulic Retention Time	HRT
Microconstituent	MC
Polynuclear Aromatic Hydrocarbons	PAH
Polychlorinated Biphenyl	PCB
Pharmaceutical and Personal Care Products	PPCP
Robert O. Pickard Environmental Center	ROPEC
Sludge Retention Time	SRT

Solid Phase Extraction	SPE
Total Suspended Solids	TSS
Triclosan	TCS
Ultraviolet	UV
Volatile Suspended Solids	VSS
Water Environment Federation	WEF
Wastewater Treatment Plant	WWTP

Symbol	**Definition**
C_o	Initial Liquid Phase Concentration，μg/L
C_e	Liquid Phase Concentration at Equilibrium，μg/L
C_{inf}	Influent Liquid Phase Concentration, μg/L
C_{eff}	Effluent Liquid Phase Concentration, μg/L
C_{liquid}	Volume of Liquid Part, L
C_{solid}	Tested Concentration of MCs in Solid Phase, μg/g
f_{oc}	Fraction of Organic Carbon Present on the Solid，g/g
K_1	Rate Constant of Pseudo First-order Sorption, h^{-1}
K_2	Rate Constant of Pseudo Second-order Sorption, h^{-1}
K_d	Solid-liquid Partitioning Coefficient, L/kg
K_f	Freundlich Constant
K_l	Langmuir Constant, L/kg
K_{oc}	Organic Carbon Distribution Coefficient, L/kg

m	Mass of Solids, kg
n	Freundlich Exponent
Q_o	Initial Solid Phase Concentration, μg/kg
Q_e	Solid Phase Concentration under Equilibrium, μg/kg
Q_m	Monolayer Adsorption Capacity, μg/kg
Q_t	Solid Phase Concentration at Different Time Sequence, g/g
v	Volume of Solution, L
V	Volume of the Bioreactor, L
V_{inf}	Volume of the Influent Daily, L/d
V_{wasted}	Volume of Sludge Wasted Daily, mL
W_{RC}	Total Weight of MCs Recovered, μg
W_{solid}	Weight of solid Part, μg
X_v	VSS Concentration in Bioreactor, mg/L
X_{ve}	VSS Concentration of Effluent, mg/L
X_{vr}	VSS Concentration of Wasted Activated Sludge, mg/L
θ_x	Sludge Retention Time, d
θ_w	Flow rate of Wasted Activated Sludge, L/d

Chapter 1 Introduction

1.1 General Introduction and Research Needs

From the early nineties of the last century, the concern for the presence of microconstituents (MCs) in the environment and the need to assess their environmental risk have greatly increased (Mi ège et al., 2009; Kosma et al., 2014; Lishman et al., 2006; Huerta-Fontela et al., 2011; Yu et al., 2013). The focus of environmental research has partly turned from conventional pollutants to these so-called emerging contaminants (Bu et al., 2013). Such change can be partially attributed to the development of chemical analytical techniques. Lofrano et al. (2010) reviewed the history of wastewater management dating back to 3500 BC. Wastewater management is largely limited by the analytical techniques. From Table 1.1, it is clear that not until the 1990s that chemicals could be analyzed at parts per quadrillion concentration. This is when researchers began to focus on trace organic contamination, i.e., MCs.

As defined by the Water Environment Federation (WEF), MCs are "natural and human made substances, including elements and inorganic and organic chemicals, detected within water and the environment, for which a prudent course of action is suggested for the continued assessment of the potential effect on human health and the environment" (Hunt, 2007). Thousands of compounds were labeled as MCs according to this definition; however, only a few of them have been thoroughly studied.

Organic MCs mainly include pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs) (Huang et al., 2011), herbicides, pesticides alkylphenols, etc. (Salveson et al., 2008; Reeves et al., 2010). PPCPs and EDCs are two commonly used terms in the literature. PPCPs include non-prescription or prescription pharmaceuticals for human and veterinary use and the active or inert ingredients in personal care products (Lishman et al., 2006). Examples of PPCPs are drugs such as

analgesics, blood lipid regulators, synthetic hormones including oral contraceptives, antidepressant and anxiolytics, disinfectants in detergent, body cleaning products and lotions, sun screens, fragrances and cosmetics (Lishman et al., 2006; Yu et al., 2013, Bu et al., 2013, Mi ège et al., 2009).

Table 1.1 Evolution of Analytical Chemistry, Modified from Lograno et al. (2010)

Time	Advances
1990	20th Ed. Standard Methods: 350 separate methods
	Dioxin analysis> 1 part per quadrillion
1980	First US Environmental Protection Agency (EPA) manual on hazardous waste analysis
	Polychlorinated biphenyls (PCB) Aroclor and separation refinement
	Gas chromatography refinements (cleanup, flame ionization, electron capture)
	Ms and nuclear magnetic resonance refinements
	Inductively coupled plasma atomic emission spectrophotometry
	First EPA manual on organic and trace metal analysis
1970	11th Ed. standard Methods: wet chemistry inorganics
	Gas chromatography advances
	Fluorescence spectroscopy
	Infrared Advances
	PCB and DDT detection by gas chromatography
	First commercial atomic adsorption spectroscopy
1960	Portable dissolved oxygen (DO)
	Introduction of mass spectrometry
	Introduction of atomic adsorption spectroscopy
	IR method advances
`	Column chromatography

Table 1.1 continued

Time	Advances
1950	Infrared method for some inorganics > 500 mg/L
	Benzene > 100 mg/L
	DO by mercury electrode
	Ultraviolet (UV) photometry for some organics > 30mg/L
	Total petroleum
1940	8th Ed. Standard Methods: general parameters
	Biochemical oxygen demand (BOD), chemical oxygen demand (COD) and DO methods improvement
	Phenol > 10 mg/L
	Petroleum hydrocarbon fractions
1930	BOD and DO methods improvements
	Phenol > 10 mg/L
1920	3th Ed. Standard Methods: general parameters
	BOD and DO methods improvements
	Phenol >100 mg/L
1910	1st Ed. Standard Methods: general parameters

EDCs are defined as substances that cause adverse biological effects by interfering with the endocrine system (Hunt, 2007). Natural steroidal estrogens, synthetic estrogens, phytoestrogens and various industrial chemicals are the four main classes of EDCs, among which, synthetic estrogens display much stronger estrogenic effects than other classes (Auriol et al., 2006). Some of the PPCPs, such as oral contraceptives, are also EDCs. Pesticides, herbicides heavy metals and plasticizers also have endocrine-disrupting effects. Other PPCPs are believed to have potential adverse health effects on human and animals. Studies shows that there may be some ecological harm when certain PPCPs are present in the environment (USEPA, 2010). There is no clear boundary between PPCPs and EDCs, one chemical can belong to both PPCPs and

EDCs. In comparison, MCs is a boarder term than PPCPs or EDCs. In addition, since there is no standardized method to evaluate the adverse health impact of a chemical, MCs is a term to avoid the trouble to prejudge the health impact of various trace-level chemicals detected in water (Salveson et al., 2008).

The consumption and application of synthetic MCs have been increasingly consistent in recent years (Jelic et al., 2011). These MCs are discharged to the natural environment by various routes. MCs such as PPCPs are widely used in households and hospitals to treat all kinds of diseases. 17-α-ethinylestradiol (EE2), a commercial oral contraceptive belongs to EDCs, is widely used in households as well. Antibiotics, which are a large group of pharmaceuticals, are also extensively used for animals to treat microbial infections and also as a feed additive to promote growth of livestock animals (Ying et al., 2013). Pharmaceuticals that cannot be completely metabolized by humans or animals will be excreted in original or conjugated form. When the conjugates reach a wastewater treatment plant (WWTP), they will be easily cleaved at the WWTP's operating conditions (Heberer, 2002). Natural hormones are excreted through urine and feces by humans or animals. Unused pharmaceuticals will be inappropriately disposed via the toilet by humans as well. As for personal care products, they find their way into the sewage system when people clean themselves. When PPCPs and EDCs reach WWTPs, part of them will be sorbed to the solids matrix and released to the environment via sludge land application; others remain in the liquid matrix.

Some of the pharmaceuticals are subject to certain forms of transformation, such as biodegradation and photodegradation. While others remain unchanged through the whole treatment process and eventually are discharged to the aquatic environment. MCs such as herbicides and pesticides are mainly used in agriculture. These agricultural chemical residues will remain in the soil or enter the aquatic environment through surface run-off (Solomon et al., 2012). Once MCs reach the natural environment, they pose potential exposure to humans through the drinking water system and agriculture products. Fig. 1.1 shows the pathway of MCs in the environment.

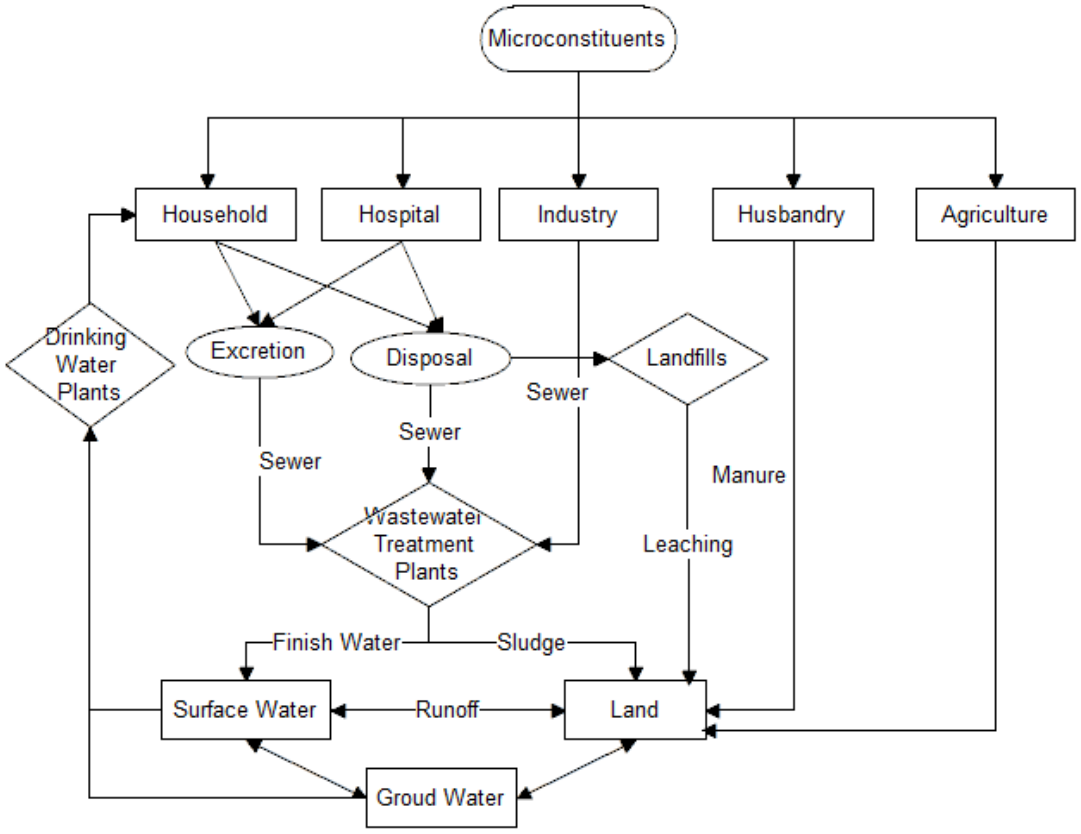


Figure 1.1 Pathways of Microconstituents in the Environment, Modified from Mompelat et al. (2009); Petrović et al. (2003)

As mentioned previously, WWTPs are a significant point source for MCs. Conventional WWTPs, such as activated sludge (AS) systems, provide good performance in terms of removing particulates, carbonaceous substrate, pathogens and nutrients such as nitrogen and phosphorus. However, WWTPs fail to remove many MCs to a safe level. As a matter of fact, WWTPs are one of the major sources for MCs entering the natural environment (Michael et al., 2013, Sathyamoorthy et al, 2013). The concentration of MCs in the influents to WWTPs range from hundreds of ηg/L to μg/L (Sun et al., 2013, Jelic et al., 2011, Huerta-Fontela et al., 2011). Many researchers have published their findings about WWTPs removal efficiency for selected MCs. Most of the literature only focuses on the aqueous removal efficiency, while ignoring the concentration and removal in the solid phase. Part of the reason is that detection of MCs in the solid phase is not easy. Removal efficiencies for MCs based on aqueous phase concentrations varies from 20% to above 90% (Kosma et al., 2014, Yu et al., 2013, Jelic et al., 2011, Sun et

al., 2013). However, when solid phase concentrations were taken into consideration, many researchers found the removal efficiency for MCs by WWTPs is actually insufficient. A detailed literature review will be presented in Section 2.2.

Different conclusions obtained by different studies may be because different target MCs were chosen. Hydrophobic and nonbiodegradable compounds tend to attach to and accumulate in the sludge. One of the pathways for MCs entering into the environment is through the disposal of wasted sludge (Ternes et al., 2004). As a result, it is necessary to study the sorption kinetics and isotherms of MCs in WWTPs. Section 2.2 provides information about MCs concentrations in sludge.

Sorption is the term used here because it is not clear weather MCs will absorb to the surface of the solids or travel further into the interior of the solids. Sorption kinetics and isotherms of MCs are influenced by the characteristics of MCs, the physicochemical characteristics, the organic carbon content of the sludge and some other environmental conditions such as water temperature or pH.

In this study three MCs were selected for study: bisphenol-A (BPA), EE2 and triclosan (TCS). All three compounds were reported as hydrophobic with low volatility, which makes sorption a potentially high removal mechanism for the chosen MCs. Detailed introduction to the three chosen MCs is provided in Section 2.9.

Primary and secondary sludges (i.e. AS) exist in WWTPs in significant amounts which provides massive sorption sites for MCs. For WWTPs which have high production of primary sludge or are operated under low sludge retention times (SRTs), sorption may be an important mechanism to remove MCs from the aqueous phase in WWTPs.

Another factor this study focused on is the addition of alum. Alum is a commonly used coagulant and phosphorus precipitation agent in WWTPs. Alum may alter the characteristics of sludge, including changing the particle size, surface charge, pH and so on. These are basic elements that could possibly change the sorption of the MCs to

solids in WWTPs. A comparison between the sorption isotherms with adsorbents being AS with and without alum addition will be made in this study.

1.2 Research Objectives

The objective of this research is to assess the sorption behavior of elected MCs with adsorbents being primary sludge and AS. More specifically, the goals are to:

1) Investigate the sorption kinetics of selected MCs sorbed to primary sludge;

2) Investigate the sorption isotherms of selected MCs sorbed to primary sludge and AS from reactors operated at different SRTs with alum addition;

3) Explore linear, Freundlich and Langmuir sorption isotherm models with experimental data to determine if these models are suitable to describe MCs sorption behavior at low concentrations, find the corresponding parameters for each models;

4) Compare results with AS without alum addition to find the influence of alum on MCs sorption behavior.

1.3 Experimental Plan

The above stated objectives are achieved by the following tasks:

1) A detailed literature review to find typical concentrations of MCs in WWTPs influent, effluent and solid phase, sorption behavior of selected MCs in WWTPs and relevant sorption isotherm models, and the potential influence by alum addition;

2) Establish a bench scale continuous flow porous pot bioreactor system to simulate WWTPs at SRTs of 15, 10 and 5 days and hydraulic retention time (HRT) of 6 h with alum addition in the influent at dosages of 0.28, 0.48 and 0.72 $\times 10^{-3}$mol/L as Al;

3) Carry out a series batch experiments using primary sludge as the adsorbents to study the sorption kinetics, and using both primary sludge and lab-generated AS as adsorbents to study sorption isotherms for the selected MCs;

4) Calculate R^2 values for experimental data by performing linear regression for linear, Freundlich and Langmuir models, calculate relevant sorption isotherm models parameters. Using non-linear regression for experiment data to fit Freundlich and Langmuir models.

5) Compare experimental data with adsorbents being lab-generated AS without alum addition and determine the effect of alum on MCs sorption isotherms.

1.4 Structure of the Thesis

Chapter 1 provides an introduction to MCs as an emerging concern and sorption as an important mechanism removing MCs from WWTPs.

Chapter 2 provides a detailed literature review about physicochemical characters of selected MCs, typical concentrations of MCs in WWTPs influent, effluent and solid phase, sorption isotherm models for organic contaminants in WWTPs and the role of alum in WWTPs and its potential influence to sorption.

Chapter 3 describes the experimental setup and plan and the analytical technique applied to test selected MCs concentrations

Chapter 4 shows the results of the experiments. Relative parameters are calculated for sorption kinetics and isotherm models. The fits of the models to the experimental data are evaluated. A comparison of sorption between AS with and without alum addition is made with a discussion of the influence of alum. The best fit isotherm is determined based on defined error function. A discussion based on the findings is presented.

Chapter 5 presents conclusions on major findings and defines potential future work.

Appendix A contains the figures of TSS, VSS and effluent COD of the bioreactors.

Appendix B contains the linear regression for Langmuir and Freundlich sorption isotherms.

Appendix C contains the nonlinear regression for Langmuir and Freundlich sorption isotherms.

Appendix D contains information about verification of experimental methods.

Chapter 2 Literature Review

2.1 Microconstituents and Related Environmental Concerns

Even though a standardized method to evaluate the related adverse health and ecological effects of MCs has not been established, studies focusing on this topic are abundant. Current environmental concerns about MCs are primarily due to adverse health effects observed in laboratory experimental animals, in certain wildlife and the increased incidence of certain human diseases (Damstra et al., 2011) or observed ecological effects. Although environmental concentrations of MCs are not likely to cause an acute toxic effect, the persistence of and wide occurrence of MCs makes chronic exposure a potential danger to human beings and animals, or even to the ecosystem (Liu et al., 2013).

Antibiotics are a large group of chemicals that were believed to cause various issues to humans, wildlife and the ecosystem. For human beings, early life exposure to antibiotics may increase the incidence of allergies and asthma (Kuo et al., 2013). Ecosystems are vulnerable to antibiotics as a result of antibiotics' inhibition to algae and bacteria growth (Manzetti, 2014) as well as the development of antibiotic resistant genes and bacteria (Rizzo et al., 2013).

As indicated by the name, EDCs interfere with endocrine systems of humans and animals. Although the mechanisms are still poorly understood, it is at least clear that EDCs can "act at multiple sites via multiple mechanisms of action" (Damstra et al., 2011). Endocrine systems abnormality can further influence other systems, such as brain, immune, and cardiovascular systems, lungs, mammary glands, liver, kidneys, reproductive tract, adipose tissue, and bones (Chang et al., 2009). Chloroform, a by-product of water disinfection, has been proven to cause reproductive health effects, including intrauterine growth retardation, low birth weight, preterm birth, congenital malformations, and stillbirth (Chen et al., 2011). A team of reproductive specialists in

Demark found that the sperm counts of males have dropped by 50% since 1938 when people started to use synthetic chemicals, most of which are classified as EDCs, in large amounts (Colborn, 1995). Field studies and surveys of various kinds of fish in natural waters polluted by EDCs show links between abnormalities in sexual development of fish and low-level exposure to EDCs (Stentiford et al., 2005; Sun et al., 2009; Barnhoorn et al., 2010; Barry, 2009).

Chemicals such as herbicides, pesticides and heavy metals were also proven to cause more complicated adverse health effects to animals and human beings. Dichloro-diphenyl-trichloroethane (DDT), a synthetic pesticides, is believed to have toxic effects such as increasing the incidence of cancer and hepatic-cell hypertrophy and necrosis, impacting the nerve system (Rogan et al., 2005) and causing intersex in aquatic species (Barnhoorn et al., 2010). Although DDT was banned in the USA in 1970s, the research focus on this chemical did not stop because of its persistence in the environment.

Cadmium is a heavy metal usually used in rechargeable nickel-cadmium batteries. The major source for cadmium entering human beings is food which is grown in cadmium contaminated soil. Cadmium will accumulate in kidneys with a very long biological half-life time causing genetic tubular dysfunction (Suwazono et al., 2011). PCBs, a class of chemicals widely used in industry since the 1930s, were found to have adverse effect on children in terms of neurodevelopment. Like DDT, PCBs were banned in the United States since 1979. The general distribution and persistence of PCBs in the environment leads to presence of such chemicals in human tissues even today (Schell et al., 2001).

2.2 Typical Concentrations of MCs in WWTPs and Drinking Water Treatment Plant

As mentioned in the previous section, MCs can cause many adverse health problems and also bring issues to the ecosystem. One of the major sources for MCs entering the environment is the effluents of WWTPs. In this section, typical concentrations of various MCs detected in WWTPs influent, effluent and in solid phase will be reported. Lishman et al. (2006) investigated ten acidic pharmaceuticals, TCS and five polycyclic musks in 12 WWTPs throughout Ontario, Canada. The treatment processes applied in these WWTPs include lagoons, conventional AS systems and conventional AS plus filtration systems. Among the ten acidic pharmaceuticals, removal efficiency varied from 20 to 99%. TCS was removed by 74 to 98% in the 12 WWTPs investigated. Lagoons showed a better performance since the TCS was at non-quantifiable concentrations in their effluents. The removal efficiency for musk ranged from 34 to 68%. Filtration did not provide additional removal for musk as expected.

Another study conducted by Kosma et al. (2014) in Greece investigated 18 compounds in eight WWTPs. According to their results, anti-inflammatory drugs have relatively high removal efficiency, ranging from 60-100%. Even higher removal efficiencies were found for caffeine in all WWTPs (77-100%). Low to medium removal efficiencies were observed for trimethoprim, carbamazepine, diclofenac and budesonide. Bezafibrate (26–90%) and naproxen (25–98%) “presented removals that ranged between very low and very high values”.

Yu et al. (2013) studied 14 MCs for 5 WWTPs in both summer and winter seasons. They tested the WWTPs influent and effluent concentrations together with solid phase (biomass) concentrations of MCs. They found that over 90% of the MCs were removed. Two mechanisms were considered to contribute to total removal of MCs, sorption to biomass and biodegradation. Since low MCs concentrations were found in biomass, the removal efficiency attributed to sorption was low. In that case they stated that biodegradation was the major mechanism contributing to MCs removal.

In contrast, some studies found opposite results from Yu et al., finding that WWTPs provide poor performance for removal of MCs. A study conducted in Spain by Jelic et al. (2011) shows that MCs concentrations in sludge can be as high as 100 ηg/g. When this occurs, simply comparing the influent and soluble effluent MC concentrations will lead to high overestimation of the amount of removal due to biodegradation; most of the MCs were actually retained in the biomass. As a result, they concluded that the removal of MCs by WWTPs is inadequate.

Sun et al. (2013) studied 50 MCs in one WWTP in China over a period of one year, among which 39 MCs were detectable in the influent. They took samples from influent to the plant, influent and effluent of the AS bioreactor, and final effluent of the WWTP. They found that only 14 compounds were removed by more than 50% by the AS treatment process. Sorption to particles in primary treatment and transformation under UV radiation also contributed to the total removal rate.

Removal efficiencies of different categories of MCs are quite different. It appears that there is no logical pattern to their fate even after dividing MCs into different categories based on similar characteristics (Yu et al., 2013).

Studies focusing on MCs concentrations in WWTPs influents and effluents are abundant. Table 2.1 has the concentrations of MCs of WWTPs influent, effluent and sludge reported in several studies.

Table 2.1 Reported MCs Concentrations in WWTPs

Chemical	Influent (ng/L)	Effluent (ng/L)	Sludge (ng/g)	Reference
17-α-ethinylestradiol	4.84	1.4	-	(Auriol et al., 2006)
	2.5-125	0.3-30	-	(Ratola et al., 2012)
17β-Estradiol	5-28.1	<1-4	-	(Auriol et al., 2006)
	1.5-17.2	0.1-3.1	-	(Ratola et al., 2012)
2,4-Dichlorophenol	83	16	-	((Auriol et al., 2006)
4-n-nonylphenol	220-870	n.d [a].-50	35-1307	(Yu et al.. 2013)
4-tert-octylphenol	80-3,900	n.d.-100	74-3263	(Yu et al.. 2013)

Table 2.1 continued

Chemical	Influent (ng/L)	Effluent (ng/L)	Sludge (ng/g)	Reference
Acebutolol	-	0-4	-	(Ratola et al., 2012)
Acetaminophen	3,540-10,234	0-27	-	(Ratola et al., 2012)
	1,570-56,900	n.d.-0.03	-	(Luo et al., 2014)
Acetyl Salicylic Acid	2,040-	n.d.-193,000	-	(Ratola et al., 2012)
Acetyl Salicylic Acid	1,731,000			(Ratola et al., 2012)
Amitriptyline	341-5,143	53-357	-	(Ratola et al., 2012)
Asprin	170-230	n.d.-70	33-75	(Yu et al.. 2013)
Atenolol	9	9	0.7	(Ratola et al., 2012)
	n.d.-33,106	10-7,602	-	(Ratola et al., 2012)
Atorvastain	4	2	2.5	(Jelic et al., 2011)
Azithromycin	6-1140	138	-	(Ratola et al., 2012)
Bezafibrate	4	0.4	0.4	(Jelic et al., 2011)
	n.d.-7,600	20-4,800	-	(Ratola et al., 2012)
Bisphnol A	60-600	n.d.-44	53-196	(Yu et al.. 2013)
	130-1,766	n.d.-210	-	(Auriol et al., 2006)
Butylparaben	274-1,595	-	-	(Ratola et al., 2012)
Caffeine	1,160-120,000	n.d.-60	-	(Ratola et al., 2012)
Carbamazepine	34-350	n.d.-62	n.d.-197	(Yu et al.. 2013)
	2	2	0.2	(Jelic et al., 2011)
	43-21,600	n.d.-15,000	-	(Ratola et al., 2012)
Celestoide	-	n.d.-92	-	(Ratola et al., 2012)
Chloramophenicol	2	0.6	0.2	(Jelic et al., 2011)
	<4-319	<6	-	(Ratola et al., 2012)
Cimetidine	0.6	0.4	0.2	(Jelic et al., 2011)
Ciprofloxacin	n.d.-34,600	1-3080	-	(Ratola et al., 2012)
Clarithromycin	5	4	7.1	(Jelic et al., 2011)
	647	359	-	(Ratola et al., 2012)
Clesrolide	34.5	20	-	(Jelic et al., 2011)
Clofibric Acid	57-420	n.d.-81	n.d.-135	(Yu et al.. 2013)
	n.d.-651	-	-	(Jelic et al., 2011)
Codenie	1,732-32,295	2,940-15,593	-	(Ratola et al., 2012)
Dextroproxphere	22-33	37-64	-	(Ratola et al., 2012)

Table 2.1 continued

Chemical	Influent (ng/L)	Effluent (ng/L)	Sludge (ng/g)	Reference
Diazepam	3	1.2	4.1	(Jelic et al., 2011)
Diclofenac	86-580	n.d.-120	n.d.-187	(Yu et al.. 2013)
	40	4	2	(Jelic et al., 2011)
	140	140	-	(Lishman et al., 2006)
	n.d.-203,000	n.d.-19,200	-	(Ratola et al., 2012)
	<0.0001-94,200	<0.001-690	-	(Luo et al., 2014)
Estriol	57.29-381.5	2.3-11.71	-	(Auriol et al., 2006)
	14.6-802	0-275	-	(Ratola et al., 2012)
Estrogen	n.d.-160	n.d.-30	n.d.-32	(Yu et al.. 2013)
	8.1	-	-	(Lishman et al., 2006)
Estrone	31.1-44	12.3-24	-	(Auriol et al., 2006)
	2.4-670	0-95	-	(Ratola et al., 2012)
Ethylparaben	715-3,312	0.6-43	-	(Ratola et al., 2012)
Famotidine	1	0.1	0.7	(Jelic et al., 2011)
Fenofibrate	0.5	0.5	2.5	(Jelic et al., 2011)
Furosemide	836-5,111	538-1,956	-	(Auriol et al., 2006)
Gabapentin	2,059-37,426	3,001-42,611	-	(Ratola et al., 2012)
Galaxolide	1,701	876	-	(Lishman et al., 2006)
	790-16,600	32-3,750	-	(Ratola et al., 2012)
Gemfibrozil	1,090-8,500	n.d.-650	38-172	(Yu et al.. 2013)
	3	1	1.7	(Jelic et al., 2011)
	418	255	-	(Lishman et al., 2006)
	14-3,000	n.d.-1,340	-	(Ratola et al., 2012)
Glibenclamide	5	4	3.5	(Jelic et al., 2011)
Hydrochlorthiazide	13	6	0.5	(Jelic et al., 2011)
Ketoprofen	n.d.-8,500	n.d.-3,920	-	(Ratola et al., 2012)
Ibuprofen	8,600-56,500	13-92	37-216	(Yu et al.. 2013)
	8,840	353	-	(Lishman et al., 2006)
	n.d.-603,000	n.d.-55,000	-	(Ratola et al., 2012)
Indomethacine	3	2	1	(Jelic et al., 2011)
	196	149	-	(Lishman et al., 2006)
Ketoprofen	150-1,300	n.d.-65	n.d.-27	(Yu et al.. 2013)

Table 2.1 continued

Chemical	Influent (ng/L)	Effluent (ng/L)	Sludge (ng/g)	Reference
Ketoprofen	13	7	1.3	(Jelic et al., 2011)
	136	114	-	(Lishman et al., 2006)
Lecofloxacin	552	301	-	(Ratola et al., 2012)
Lorazepam	7	4	5.1	(Jelic et al., 2011)
Mefenamic Acid	16	5	0.4	(Jelic et al., 2011)
	n.d.-36,400	n.d.-2,400	-	(Ratola et al., 2012)
Methylparaben	4,550-30,688	<3-36	-	(Ratola et al., 2012)
Metoprolol	n.d.-4,680	3-688	-	(Ratola et al., 2012)
Mevastain	2	2	4.5	(Jelic et al., 2011)
Naproxen	9,300-210,000	n.d.-150	8-53	(Yu et al.. 2013)
	21	3	0.9	(Jelic et al., 2011)
	5,220	351	-	(Lishman et al., 2006)
	n.d.-611,000	n.d.-39,300	-	(Ratola et al., 2012)
Nicotine	-	72-3,857	-	(Ratola et al., 2012)
Nitrophenol	11	-	-	(Auriol et al., 2006)
Norfloxacin	250-900	1-301	-	(Ratola et al., 2012)
NP	1.5-73	<0.05-47.5	-	(Auriol et al., 2006)
NP1EO	140.03	1.99	-	(Auriol et al., 2006)
Paracetamol	370-218,000	n.d.-210	n.d.-81	(Yu et al.. 2013)
	40-4822,687	n.d.-6760	-	(Ratola et al., 2012)
PCBs	46	-	-	(Auriol et al., 2006)
Pentoxifyllin	-	500-600	-	(Ratola et al., 2012)
Phantolide	22	-	-	(Lishman et al., 2006)
Phenol	6	-	-	(Auriol et al., 2006)
Pravastain	25	9	2.4	(Jelic et al., 2011)
Propanolol	50-1,962	16-615	-	(Ratola et al., 2012)
	820-8,286	1-84	-	(Ratola et al., 2012)
Ranitidine	3	2	0.3	(Jelic et al., 2011)
	820-8,286	1-84	-	(Ratola et al., 2012)
Ranitidine	3	2	0.3	(Jelic et al., 2011)
Roxithromycin	n.d.-117	45-125	-	(Ratola et al., 2012)
Salbutamol	0.3	0.2	0.3	(Jelic et al., 2011)

Table 2.1 continued

Chemical	Influent (ng/L)	Effluent (ng/L)	Sludge (ng/g)	Reference
Simvastain	<7-798	<3-20	-	(Jelic et al., 2011)
Solatol	n.d.-1,080	82-466	-	(Ratola et al., 2012)
Ssalicylic Acid	14,100	104	-	(Lishman et al., 2006)
Sulfamethazine	2	1	0.8	(Jelic et al., 2011)
	n.d.-189,0000	n.d.-25,400	-	(Ratola et al., 2012)
Sulfamethoxazole	29-309,000	3-24,800	-	(Ratola et al., 2012)
Tetacyclin	240-790	50-850	-	(Ratola et al., 2012)
Tonalide	687	298	-	(Lishman et al., 2006)
	210-12,500	24-2,670	-	(Ratola et al., 2012)
Tramdol	8,505-89,026	24,132-97,616	-	(Ratola et al., 2012)
Tranalide	131	47	-	(Lishman et al., 2006)
Triclosan	180-4,400	n.d.-160	158-3277	(Yu et al.. 2013)
	1,860	106	-	(Lishman et al., 2006)
	247-785	70-430	-	(Lishman et al., 2006)
Trimethoprim	1	0.4	0.6	(Jelic et al., 2011)
	n.d.-162,000	<10-95,100	-	(Ratola et al., 2012)
Trimolol	0.3	0.3	0.9	(Jelic et al., 2011)

a. n.d.: concentration below detection level of the analytical method applied.

As mentioned in Section 1.1, one of the major pathway for MCs entering the environment is through the disposal of wasted sludge. In one of the research works conducted by USEPA in 2010, thirty eight (54%) of 72 PPCPs tested were detected in at least one of the 110 sewage sludge samples, with concentration ranging from 0.002 to 48 mg/kg dry weight. The research concluded that "the loading to U.S. soils from nationwide biosolids recycling was estimated at 210–250 metric tons per year for the sum of the 72 PPCPs investigated" (McClellan K. et al., 2010). Hamid et al. (2012) studied the fate of estrogenic hormones in wastewater and sludge treatment. Their results regarding sludge treatment show that aerobic digestion had better attenuation of estrogenic compounds; however, anaerobic digestion increased the overall estrogenicity of biosolids. Narumiya et al. (2013) studied the phase distribution and removal of PPCPs during anaerobic sludge digestion. They found out that among the

48 PPCPs they tested, sulfamethoxazole and trimethoprim were degraded by over 90%, triclosan and triclocarbon were moderately degraded, while carbamazepine showed no elimination at all.

Although effluents of WWTPs will be diluted by the receiving water and MCs will be degraded gradually in the natural environment, MCs still remain at detectable levels in the feed water of drinking water treatment plants located down stream of WWTPs (Bros áıs et al., 2009; Trenholm et al., 2006; Yoon et al., 2003).

The first reported MC found in drinking water is clofibric acid, which is the metabolite of some blood lipid regulators. Afterwards, more trace level chemicals in drinking water were found. The most frequently detected groups are non-steroidal anti-inflammatory drugs, anticonvulsants and X-ray contrast media according to a recently published literature (Mompelat et al., 2009). Boleda et al. (2011) studied the ability of advanced treatment processes applied in drinking water treatment plants to remove MCs. Evidence shows that some pharmaceuticals can react with oxidants commonly used in water treatment processes. Ultrafiltration and reverse osmosis also show better removal efficiency than conventional techniques. However, it does not mean that such techniques can render MCs harmless in drinking water. The reaction products of MCs from the water treatment process may be more harmful. Shen et al. (2011) studied 20 PPCPs and results showed that all of the chemicals are able to form corresponding nitrosamines, a group of widely studied disinfection by-products from chloramine disinfection. The amount of transformation ranged from 1 to 77%.

2.3 Introduction to the Activated Sludge System

AS is the most commonly used biological treatment system in WWTPs. The basic components for an AS system are a bioreactor which contains suspended and aerated biomass responsible for contaminants removal, a clarifier that separates liquid and solids and recycle systems to return a portion of the separated solids to the bioreactor.

Usually pretreatment and post-treatment are needed for an AS system. Pretreatment is commonly accomplished by a primary clarifier to remove settleable solids in sewage, while post-treatment is usually disinfection for pathogen removal. Fig. 2.1 shows a scheme of a conventional WWTP at the secondary treatment level.

In medium and larger cities conventional WWTPs at a secondary treatment level were the most commonly used method to remove BOD and total suspended solids (TSS) up until the 1990s. In recent years, AS systems were also designed to remove nutrients; however, such treatment processes are only used in special circumstances, such as the Great Lakes area (Metcalf & Eddy, 2003).

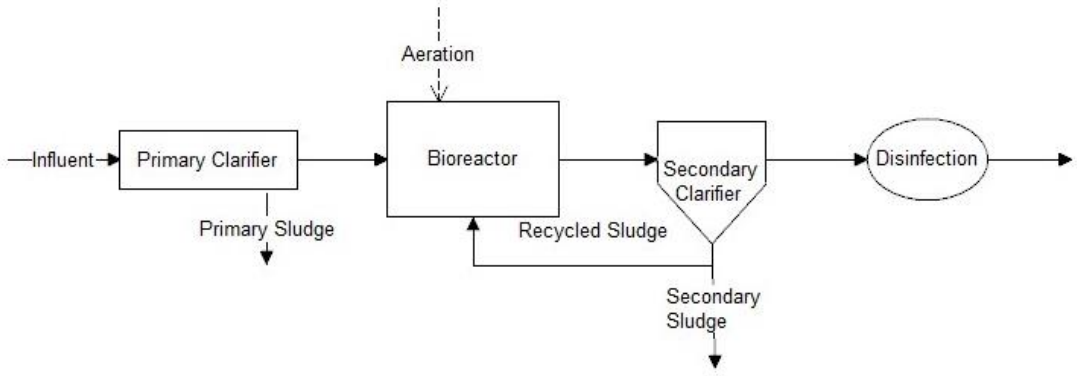


Figure 2.1 Scheme of Conventional WWTPs

Two major operation parameters that distinguish one AS system from another are SRT and food to biomass (F/M) ratio (Metcalf & Eddy, 2003). SRT is the average amount of time the sludge spends in the aeration basin which can be controlled by the amount of sludge removed from the WWTPs every day. A relatively small amount of solids are removed in the overflow from a secondary clarifier; most of the sludge is removed from the secondary clarifier as thickened AS. SRT is important because it influences the performance of an AS system, aeration tank volume, sludge production and oxygen requirements. SRT has a large influence on microbial species. Microbes that have generation times longer than the SRT will eventually be eliminated from the bioreactor. Nitrifying bacteria have generation times in the range of 48 to 72 h (Gerardi, 2002) and heterotrophic denitrifying bacteria have generation times as low as 12 h (Komor et al.,

2002). Nitrification is close to zero in a system operated at a SRT of 2 to 5 days (AWWA, 2006).

The relationship between SRT and MCs removal has not yet been determined. Clara et al. (2005) found out that SRT was the crucial deign parameter to WWTP to remove MCs. A conventional AS system and membrane bioreactor showed no difference in terms of MCs removal efficiency when operating at comparable SRTs. Servos et al. (2005) concluded that SRT has no influence on EDCs removal based on their research of EDCs in Canadian WWTPs.

Since SRT will influence the nature of the sludge, it may influence the sorption behavior of MCs onto AS. Also, SRT has a large influence on the amount of sludge produced; so if certain MCs have a strong tendency to sorb onto AS, then sorption could be a predominant elimination pathway in WWTPs running at low SRTs (Silva et al., 2012).

2.4 Alum's Application in WWTPs

Alum is usually used in water works and WWTPs as a coagulant or chemical precipitation agent. The primary purposes of using alum are to enhance removal of suspended solids in primary sedimentation and meet phosphorus discharge regulations (Metcalf & Eddy, 2003). Coagulation is an important process in both water works and WWTPs where particles are destabilized so that particle growth can occur as a result of particle collisions. Commonly used coagulants are natural and synthetic organic polymers, metal salts such as alum and ferric sulfate and prehydrolized metal salts (Metcalf & Eddy, 2003). However, alum used in WWTPs is more likely used to remove excess phosphorus.

Alum [$Al_2(SO_4)_3 \cdot 18H_2O$] was added into the synthetic wastewater in this study. If a simpler scenario is considered, i. e., only phosphorus and alum exists in water, the concentration of total soluble aluminum and phosphorus can be predicted.

Al^{3+} forms precipitate, $Al(OH)_3$, the solubility product equation is described by Eq. 2.1.

$Al(OH)_3 \rightarrow Al^{3+} + 3OH^-$, $\log K_{SO1} = -33$ Eq. 2.1

where K_{SO1} is the solubility product,

Al^{3+} will form both mononuclear and polynuclear hydroxo complexes, $AlOH^{2+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al(OH)_4^-$, $Al_2(OH)_2^{4+}$, among which, only Al^{3+}, $AlOH^{2+}$ and $Al(OH)_4^-$ will be significant (Snoeyink, et al, 1980).

$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+$, $\log K_1 = -5.0$ Eq. 2.2

$Al^{3+} + 4\,H_2O \rightarrow Al(OH)_4^- + 4H^+$, $\log K_4 = -21.7$ Eq. 2.3

where K_1 and K_4 are the equilibrium constants,

Defining C_{TAl} as the total soluble aluminum concentration:

$C_{TAl} = [Al^{3+}] + [AlOH^{2+}] + [Al(OH)_4^-]$ Eq. 2.4

C_{TAl} can be expressed in terms of $[Al^{3+}]$, $[H^+]$, K_1 and K_4:

$$C_{TAl} = [Al^{3+}] + \frac{K_1}{[H^+]}[Al^{3+}] + \frac{K_4}{[H^+]^4}[Al^{3+}] \quad \text{Eq. 2.5}$$

So $[Al^{3+}]$ is expressed by the following equation:

$$[Al^{3+}] = C_{TAl}\left(1 + \frac{K_1}{[H^+]} + \frac{K_4}{[H^+]^4}\right)^{-1} \quad \text{Eq. 2.6}$$

When phosphorus is added into the solution, the following relationships need to be considered:

$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$, $\log K_{a1} = -2.1$ Eq. 2.7

$H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$, $\log K_{a2} = -7.2$ Eq. 2.8

$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$; $\log K_{a3} = -12.3$ Eq. 2.9

where K_{a1}, K_{a2} and K_{a3} are equilibrium constants,

Defining C_{TP} as the total soluble phosphorus in the solution,

$$C_{TP} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \quad \text{Eq. 2.10}$$

C_{TP} can be expressed in terms of $[PO_4^{3-}]$, $[H^+]$, K_{a1} and K_{a2} and K_{a3}:

$$C_{TP} = \frac{[PO_4{}^{3-}][H^+]^3}{K_{ai}K_{a2}K_{a3}} + \frac{[PO_4{}^{3-}][H^+]^2}{K_{a2}K_{a3}} + \frac{[PO_4{}^{3-}][H^+]}{K_{a3}} + [PO_4{}^{3-}] \quad \text{Eq. 2.11}$$

So PO_4^{3-} can be expressed as

$$[PO_4{}^{3-}] = C_{TP}(1 + \frac{[H^+]^3}{K_{ai}K_{a2}K_{a3}} + \frac{[H^+]^2}{K_{a2}K_{a3}} + \frac{[H^+]}{K_{a3}})^{-1} \quad \text{Eq. 2.12}$$

The solubility product equation is shown by Eq. 2. 13

$AlPO_4 \rightarrow Al^{3+} + PO_4^{3-}$, $\log K_{SO2} = -21$ Eq. 2.13

Where K_{SO2} is the solubility product,

So that

$$K_{SO2} = [Al^{3+}][PO_4{}^{3-}] \quad \text{Eq. 2.14}$$

Substituting Eqs. 2.6 and 2.12 into Eq. 2. 14 ,

$$K_{SO2} = C_{TAl}(1 + \frac{K_1}{[H^+]} + \frac{K_4}{[H^+]^4})^{-1} \cdot C_{TP}(1 + \frac{[H^+]^3}{K_{ai}K_{a2}K_{a3}} + \frac{[H^+]^2}{K_{a2}K_{a3}} + \frac{[H^+]}{K_{a3}})^{-1}$$

Eq. 2.15

Assuming the molar ratio of C_{TAl} over C_{TP} is 1, i.e. $C_{TAl} = C_{TP}$, then C_{TAl} can be expressed by Eq. 2.16.

$$C_{TAl} = \sqrt{K_{SO2} \times (1 + \frac{K_1}{[H^+]} + \frac{K_4}{[H^+]^4}) \times (1 + \frac{[H^+]^3}{K_{ai}K_{a2}K_{a3}} + \frac{[H^+]^2}{K_{a2}K_{a3}} + \frac{[H^+]}{K_{a3}})}$$

Eq. 2.16

In Fig. 2.2 the pC_{TAl} (pC_{TAl} =-log C_{TAl}) is plotted against pH according to Eqs. 2.5 and 2.16.

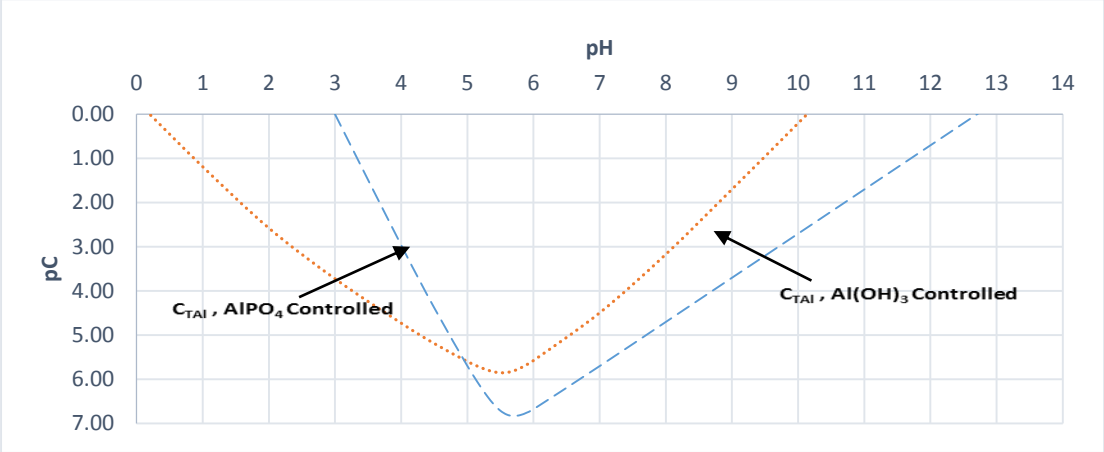


Figure 2.2 Total Soluble Aluminum Concentration against pH (Plotted According to Eqs. 2.5 and 2.16)

It can be seen from Fig. 2.2, above pH = 5, C_{TAl} is controlled by $Al(OH)_3$, which means above pH=5 $Al(OH)_3$ is the main precipitate formed. While under pH=5, the precipitates will mainly be $AlPO_4$. In that case, the corresponding C_{TP} concentration will also be controlled by Al $(OH)_3$ or $AlPO_4$.

In Fig. 2.3, the C_{TP} is added to Fig. 2.2.

In Fig. 2.3, two solid lines represent C_{TP} at scenarios $Al(OH)_3$ or $AlPO_4$ being the major precipitates. C_{TP} and C_{TAl} when $AlPO_4$ controls overlap since the relationship C_{TAl} = C_{TP} is assumed. The minimum C_{TP} occurs at pH slightly above 5.

Figs. 2.2 and 2.3 show the situation where C_{TAl} = C_{TP} is assumed. In Fig. 2.4, the relationship C_{TAl} = 10 C_{TP} is considered and added in the figure. As indicated by the graph, increasing C_{TAl} can lower C_{TP}.

According to Figs. 2.3 and 2.4, the C_{TP} is determined by pH and alum dosage. Judging from the figures, increasing alum dosage and maintaining wastewater in the low pH range is favorable to of phosphorus removal. Usually after adding alum into the wastewater influent, a drop in pH will be observed. However, in WWTPs, the pH of wastewater needs to be maintained in the range of 6.5 to 7.5 which is more favorable for growth of microorganisms. As a result, pH adjustment is usually needed after phosphorus removal.

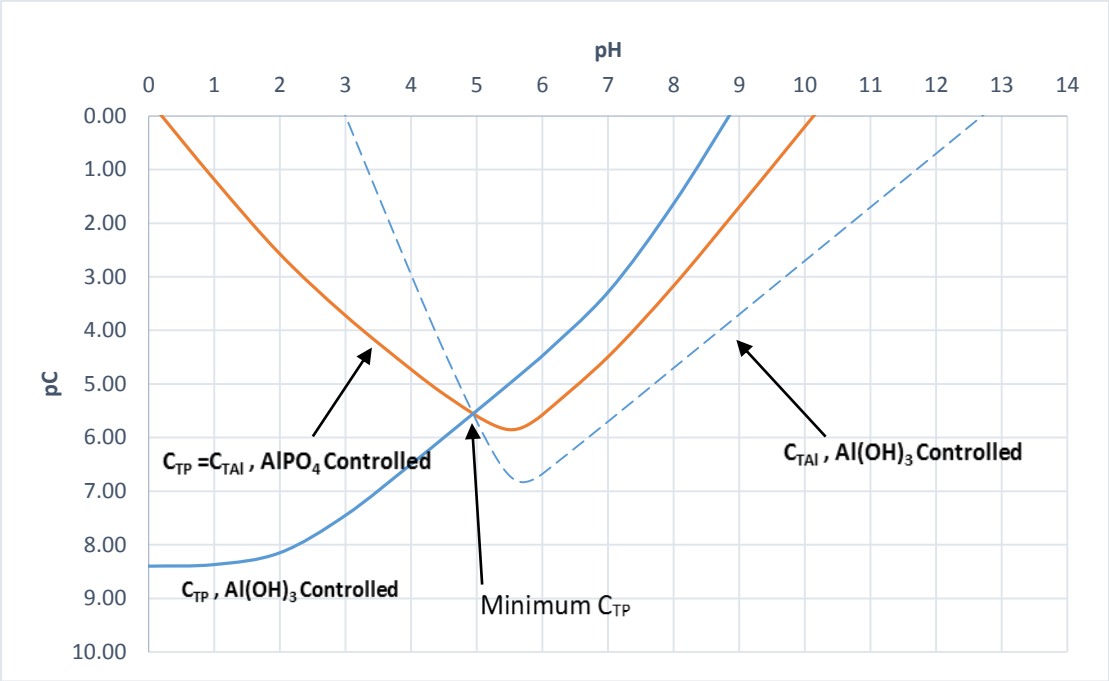


Figure 2.3 Total Soluble Phosphorus (C_{TAl} = C_{TP}) and Aluminum Concentrations against pH

In Section 3.2, details about the alum dosage, alum dosing site in WWTP and the corresponding phosphorus removal will be provided.

Although alum is commonly used in WWTPs to remove phosphorus in a WWTP, the removal efficiencies of alum is not the focus of this study. Alum is related to sorption. Metal salts such as alum can alter the surface charge of particles and potentially influence the sorption behavior of MCs onto particles. Also as alum encourages the growth of larger particles, the specific area of solids would change as a result and leads to a change in number of sorption sites. Adding alum can also alter the pH of wastewater. Clara et al. (2004) claimed that a high pH might encourage the sorbed BPA and EE2 to be dissolved into the liquid phase.

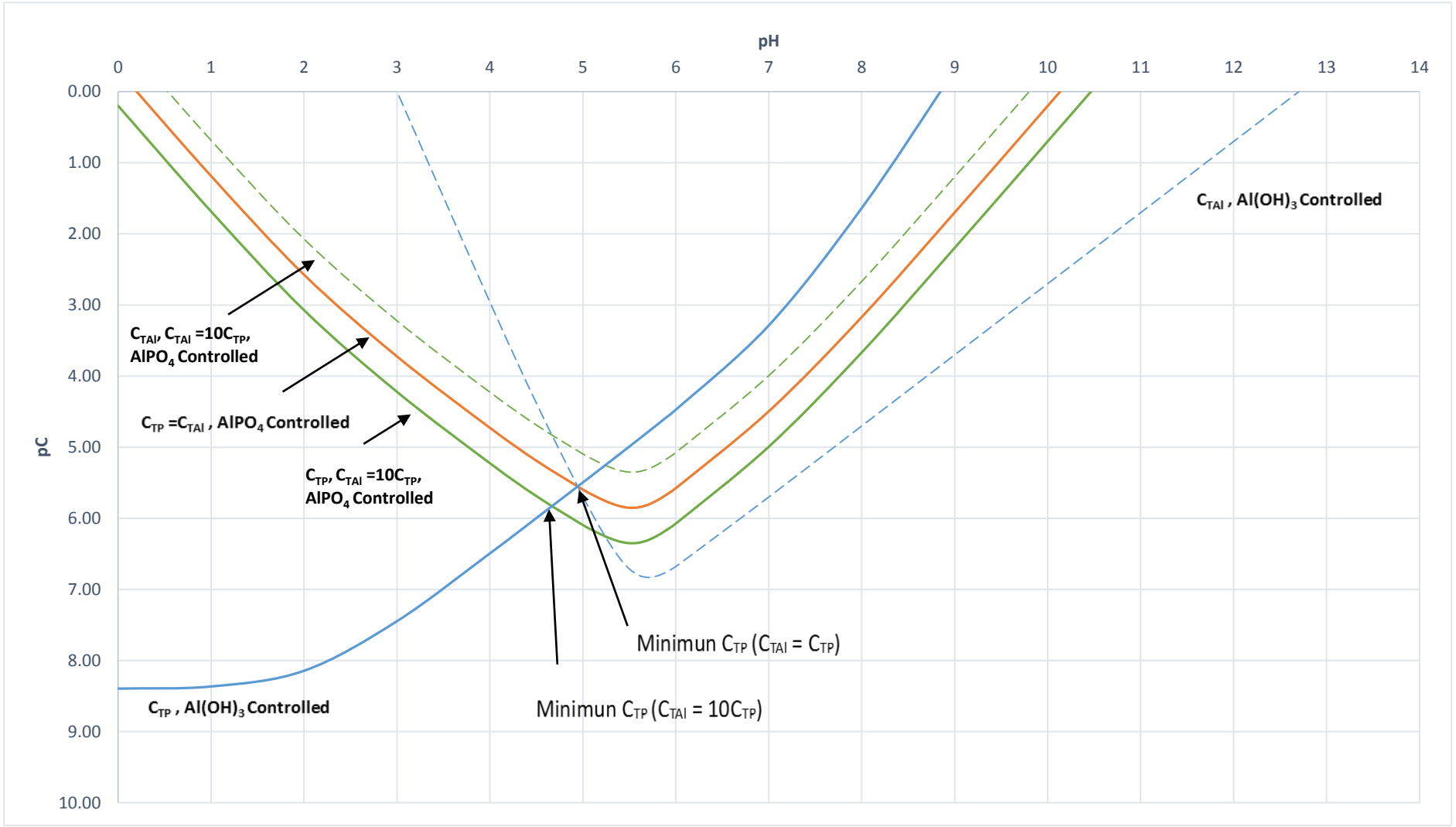


Figure 2.4 Total Soluble Phosphorus (C_{TAl} = 10 C_{TP}, C_{TAl} = C_{TP}) and Aluminum Concentrations against pH

A few case studies reported low removal efficiencies of MCs by coagulation; however, as a pretreatment process, coagulation can enhance the performance of activated carbon filtration and membrane filtration in terms of removing MCs. Jar tests carried out by Vieno et al. (2006) proved that coagulants, alum and ferric sulfate, were not effective to remove selected MCs. However, the presence of dissolved humic acid enhances the removal efficiencies of MCs. In general, ferric sulfate is more effective than alum. Hua et al. (2006) concluded in their study that a combination of coagulation, flocculation and dual media filtration showed no removal of tested MCs, while the above combination plus ozonation reduces MCs by 66-100%. Vieno et al. (2007) reported similar results for 13 MCs. The average removal efficiencies were 13% by coagulation, sedimentation and rapid sand filtration. Ozonation with a dose of 1 mg/L significantly increased the removal rates. Okuda et al.(2008), found that UV radiation combined with coagulation shows no efficiencies in term of MCs removal.

2.5 Mechanisms to Remove MCs in WWTPs

To investigate the ability of WWTPs to remove MCs, numerous factors need to be considered. Generally speaking, in WWTPs, decreased concentrations of any contaminants are caused by either degradation or transformation. To be specific, degradation includes biodegradation, chemical reaction and photodegradation, while transformation refers to sorption and volatilization. All of these phenomena happen within various treatment operations units in WWTPs.

Photodegradation could be an important removal mechanism for photodegradable chemicals in WWTPs equipped with UV treatment. Kim et al. (2009) studied 30 PPCPs removal in water by UV exposure. Results showed that most of the chemicals studied can be easily removed under UV light at wavelengths of 254 and 185 ηm. But this study was conducted in pure water; they did not consider the scattering and shielding effects of UV light by particles contained in finishing water. Photodegradation, like any other

mechanism, is affected by many environmental factors. Xu et al. (2014) simulated sun irradiation to remove sulfapyridine. They found that sulfapyridine is more easily photodegraded in alkaline than in acidic environments

Chemical reactions in WWTPs usually occur in treatment process such as oxidation or coagulation-flocculation. Ternes et al. (2002) studied removal efficiencies of 5 pharmaceuticals by flocculation (using $FeCl_3$) and ozonation. Flocculation had no significant elimination for all 5 pharmaceuticals while ozonation was effective to remove carbamazepine and diclofenac. Another study showed that electron-rich organic compounds, such as phenol, olefin, amine and aniline moieties, can be easily removed by ferrate [Fe (VI)] (Yang et al., 2012).They further suggested that Fe (VI) treatment should be applied in WWTPs as a promising tertiary treatment to remove MCs.

Volatilization happens in a bioreactor since intense aeration to supply oxygen is used in this process. However, volatilization is only effective for compounds that have a high Henry's constant.

Biodegradation could be the result of either catabolism or co-metabolism. Since most MCs are high molecular weight compounds, they cannot be effectively used by microbes as a source for energy (Nzila, 2013). However, co-metabolism is a promising removal mechanism for MCs. Co-metabolism is defined as "the transformation of non-growth-substrate in the obligate presence of a growth-substrate or another transformable compound" (Dalton et al., 1982). Thus co-metabolism cannot occur without the presence of other substrates. Although Vasiliadou et al. (2013) pointed out that high-concentration MCs can activate some enzymes to allow catabolism to happen in the bioreactor. Their study shows that sufficient elimination was achieved within 20 days for caffeine, sulfamethoxazole, ranitidine and ibuprofen when the biomass was exposed to a concentration of 50 μg/L.

Sorption is a universal phenomenon which is important in WWTPs because there is a large amount of sludge produced every day. The transformation of MCs will be discussed in detail in the next section.

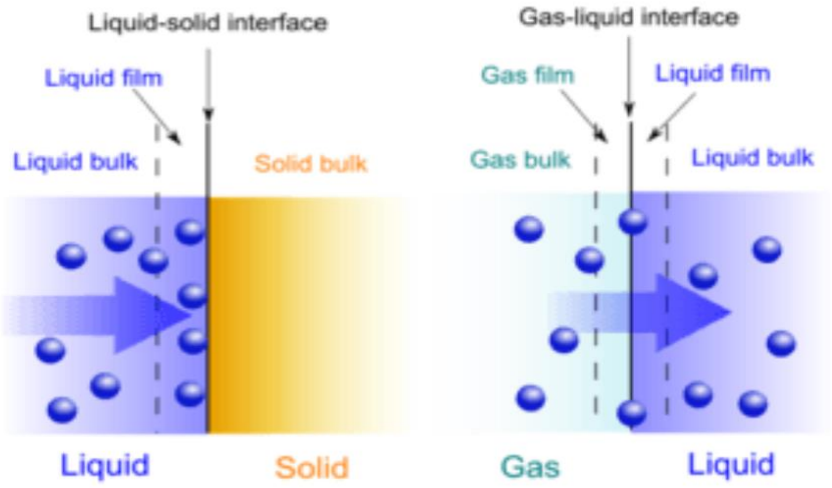
2.6 Sorption of MCs to Sludge

Adsorption is defined as the adhesion of atoms, ions or molecules of gas, liquid or dissolved solids to a surface, while absorption is when these atoms, ions or molecules of gas, liquid or dissolved solids further migrate into the bulk phase (Schönhoff et al., 2013). Adsorption or absorption are used to isolate target compounds or they contribute to removal of trace-level impurities from aqueous solution. The difference between adsorption and absorption is shown in Fig. 2.5. Unlike indicated by the figure, adsorption or absorption can happen in any interface. In fact, these two phenomena usually happen at the same time. Sorption, the absorbent being sludge, is the term usually used in the literature since it is not clear whether the absorbate is just attached to the surface or migrates into the interior of the sludge.

In wastewater and drinking water treatment, technologies involving adsorption or absorption are usually based on exploiting activated carbon (Davankov et al., 2011). Studies focusing on sludge being the sorbent are rare. However, Versino et al. (1982) studied the possibility of AS as sorbing media to remove heavy metals They used both living and dried AS to sorb chromium, iron, copper, zinc and lead. The results shows that dried AS could be a good sorbent for heavy metals at low concentrations (less than 10 ppm), while lower pH or high grease content can lower the maximum sorption capacity. Living AS, on the contrary, had comparatively lower sorption capacity.

Sorption of MCs in the whole wastewater treatment processes could happen at two sites. First of all, in the sewer system, where MCs discharged from households will enter the sewer system and come into contact with solids contained in the sewage. Long travel times in sewer systems will be beneficial to equilibrium being attained between the

soluble and solid phase concentrations. When wastewater reaches WWTPs, most of the settleable solids (that contain sorbed MCs) would be removed by the grit chamber and/or primary clarifier.



(a) **(b)**

Figure 2.5 Adsorption (a) and Absorption (b)

The next unit is the bioreactor. Under typical WWTP operation conditions, sorption equilibrium is considered to reach between MCs and AS. Only the newly generated AS has sorbing capacity to remove MCs. As mentioned in the Section 2.3, the reason why sorption is important is that WWTPs usually produce a large amount of sludge every day.

Parker et al. (2009) estimated solid-liquid partitioning coefficient (K_d) for polynuclear aromatic hydrocarbons (PAHs) in wastewater treatment by carrying out batch experiments. Both primary sludge and AS were used. The K_d for AS was higher than K_d for primary sludge. They also studied the biodegradation of the selected PAHs and found temperature had an influence on biodegradation rate. The sensitivity analysis in full-scale WWTPs showed that the removal of PAHs was more sensitive to K_d than to biodegradation rate constants. They concluded that approximately 60% of the PAHs were removed due to sorption.

Stevens-Garmon et al. (2011) studied the sorption behavior of 19 PPCPs onto WWTP sludge. Based on K_d values they found for both primary sludge and AS, there was no significant difference between these two solids. Among the chemicals they studied, positively-charged chemicals, of which the log K_d value was between 2.8-3.8, have higher potential to be sorbed onto sludge compared with neutral or negatively charged chemicals.

Studies focusing on MCs sorbed onto AS are often studied together with biodegradation. Yu et al. (2011) studied four antibiotics and four non-steroidal anti-inflammatory drugs absorbed onto "immobilized cells" using batch reactors. Immobilized cells were prepared by paralyzing AS with sodium azide. MCs were spiked into the AS mixture and the liquid concentrations were tested. K_d values reported for 8 chemicals studied were between 7.3-42 L/kg (log K_d 0.9 to 1.6). They also conducted batch experiments with AS which was not deactivated. The difference in liquid phase concentration between deactivated and non-deactivated AS was attributed to biodegradation. They found out that the biodegradation over 8 days reaction results in 25 to 40% of total removal .Another study conducted by Yang et al. (2012) tested MCs concentration in both liquid and solid phases over periods of 2 and 14 days. The sludge was not deactivated. The results showed that sorption equilibrium was reached within several hours after they spiked selected MCs into a lab-scale AS system. Solid phase concentrations kept increasing in the first two days. Afterwards, both liquid and solid phases started to drop until selected MCs were completely removed. Although they claimed that the sorption equilibrium was reached within two hours, it is not totally convincing because they did not eliminate the possibility that biodegradation could also happen in the first two hours.

2.7 Sorption Kinetics Models

The sorption process is time-dependent; it is necessary to know the rate of sorption process to deal with a dynamic system. Sorption isotherms only provide information about equilibrium concentrations of a system, but kinetics are concerned with rates of change (Azizian, 2004).

Numerous kinetics models have been used to describe the process of sorption. In this thesis, only pseudo fist-order rate and pseudo second-order rate models are discussed and used to fit experimental data.

$$\frac{d_q}{d_t} = k_1(Q_e - Q_t) \qquad \text{Eq. 2.17}$$

where Q_e is solid phase concentration under equilibrium condition, g/g;

Q_t is the solid phase concentration at different time sequence, g/g;

k_1 is the rate constant of pseudo first-order sorption, h^{-1}.

Given the boundary conditions t = 0 to t =t and q = 0 to q =q, Eq. 2.17 can be derived in the form of Eq. 2.18,

$$\ln\left(\frac{Q_e - Q_t}{Q_e}\right) = -k_1 t \qquad \text{Eq. 2.18}$$

According to Azizian (2004), the constant rate for pseudo first-order sorption is "a combination of adsorption and desorption rate".

The pseudo second-order rate model is expressed by Eq. 2.19,

$$\frac{1}{(Q_e - Q_t)} = \frac{1}{Q_e} - k_2 t \qquad \text{Eq. 2.19}$$

Eq. 2.19 can be rearranged to a linear form,

$$\frac{t}{Q_t} = \frac{1}{k_2 {Q_e}^2} + \frac{1}{Q_e} t \qquad \text{Eq. 2.20}$$

where k_2 is the rate constant of pseudo second-order sorption

According to Azizian (2004), pseudo second-order sorption works when initial liquid concentrations for solutes are not too high**.**

2.8 Linear, Freundlich and Langmuir Sorption Isotherms

In this study, kinetics and isotherms of MCs sorption onto primary sludge AS were determined. Under an equilibrium condition, solid phase concentration was also referred to as solid phase saturation concentration. Solid phase saturation concentration is calculated by Eq. 2.21:

$$Q_e = Q_0 + \frac{(C_o - C_e)\cdot V}{m} \qquad \text{Eq. 2.21}$$

where Q_e is solid phase concentration under equilibrium condition, μg/kg;

Q_o is initial solid phase concentration, μg/kg;

C_e is liquid phase concentration under equilibrium condition, μg/L;

C_o is initial liquid phase concentration, μg/L;

V is volume of solution, L;

m is mass of solids, kg.

Solid phase saturation concentration is often estimated by a solids-liquid partitioning coefficient, K_d (Droste et al., 2010, Goldberg et al. 2005),

$$Q_e = K_d \cdot C_e \qquad \text{Eq. 2.22}$$

where K_d is the solid-liquid partitioning coefficient, L/kg;

The solids-liquid partitioning coefficient K_d is either determined by experiment or estimated from the octanol-water partition coefficient, K_{ow} (Dobbs et al., 1989; Droste et al., 2010; Nakada et al., 2006; Stevens-Garmon et al., 2011).

$$K_d = f_{oc} \cdot K_{oc}$$ Eq. 2.23

$$logK_{oc} = a \cdot logK_{ow} + b$$ Eq. 2.24

where f_{oc} is the fraction of organic carbon present on the solid, g/g;

K_{oc} is the organic-carbon distribution coefficient, L/kg;

a and b are constants estimated from empirical data.

Freundlich and Langmuir isotherms are also widely used in most studies. The Langmuir adsorption isotherm model was first developed to describe gas adsorbing to the surface of metals (Foo et al., 2010; Chan et al., 2012). The Langmuir isotherm is based on three assumptions: (1) the adsorption involves the attachment of only one layer of absorbate molecule, i.e., monolayer adsorption; (2) the number of adsorption sites is limited at the surface of the adsorbents; (3) the possibility of absorption to an empty site is independent of the surface coverage, i.e., the attraction or repulsive forces between adjacent absorbate molecules are negligible (Foo et al., 2010).

The Langmuir isotherm model is represented by Eq. 2.25.

$$Q_e = \frac{Q_m \cdot K_l \cdot C_e}{(1+K_l \cdot C_e)}$$ Eq. 2.25

where Q_m is monolayer adsorption capacity, μg/kg;

K_l is a Langmuir constant, which is related to the adsorption energy, L/μg.

The following equations are the two commonly used linear forms for the Langmuir isotherm, the linear form expressed by Eq. 2.26 is also called the reciprocal Langmuir plot:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{K_l Q_m}$$ Eq. 2.26

The linear form expressed by Eq. 2.27 is called the Scatchard plot:

$$\frac{1}{Q_e} = \left(\frac{1}{K_l Q_m}\right)\frac{1}{C_e} + \frac{1}{Q_m} \qquad \text{Eq. 2.27}$$

The Freundlich model was found to be suitable to describe sorption of most contaminants from water. Unlike the Langmuir isotherm, the Freundlich isotherm was created to describe adsorption to non-ideal absorbent surfaces (Chan et al., 2012; Goldberg et al., 2005). The Freundlich isotherm can be used to describe multilayer absorption, with a non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Foo et al., 2010).

$$Q_e = K_f \cdot {C_e}^{1/n} \qquad \text{Eq. 2.28}$$

where K_f is Freundlich constant, unit is determined by n;

1/n is Freundlich exponent, unitless.

The linear form of the Freundlich isotherm model is given by Eq. 2.29:

$$\log Q_e = \frac{1}{n}\, log C_e + \log K_f \qquad \text{Eq. 2.29}$$

The three empirical models introduced in this section are widely used to describe sorption processes; however, all of them have certain limitations. The linear sorption isotherm, which is the easiest approach among all the sorption isotherms, cannot describe a scenario where the solid reaches saturation. The linear forms of Langmuir or Freundlich sorption isotherm are generated from the original model by simply applying mathematic transformation; however, they cannot imply any information about the chemical reaction mechanism. Linear forms for the Langmuir sorption isotherm "produce changes in the original error distribution by giving greater weight to low adsorption values than to high adsorption values" (Kinniburgh, 1986). The linear form for the Freundlich sorption isotherm uses log-log plots, which are well known for their insensitivity. The frequent good fit for Freundlich sorption isotherm is largely due to its insensitive linear form (Goldberg et al., 2005).

Nonlinear regression is used for some sorption isotherm models which contains more than two parameters and linear regressions are not able to be used. Nonlinear regression is usually achieved by defining an error function of experimental data and calculated data. By minimizing the value of the defined error function, the model can fit the experimental data directly and avoid the problem of changing error distribution associate with linear forms (Goldberg et al., 2005).

The most commonly used error function is called the least square error function (Chan et al., 2012). The formula of the error function is shown by Eq. 2.30.

$$\sum_{i-1}^{n}\left(Q_{e,Calc} - Q_{e,Meas}\right)^2 \qquad \text{Eq. 2.30}$$

where $Q_{e,\,Calc}$ is the calculated solid-phase concentrations,

$Q_{e,\,Meas}$ is the tested solid-phase concentrations.

2.9 Selected MCs in this Study

Three chemicals were chosen in this study: BPA, EE2 and TCS.

BPA is a synthetic compound belonging to the group of diphenylmethane derivatives and bisphenols (Bauer et al., 2014). BPA has been widely used in industry since 1957. One application is to use BPA as the monomer to make polycarbonate plastic or epoxy resins. BPA based plastic is clear and tough so it is widely used to make water bottles, sports equipment, CDs, DVDs, while epoxy resin is the material for can lining. BPA can also be used as a plasticizer that added to polyvinyl chloride plastic makes it softer and more flexible (Bauer et al., 2014). The third application according to the literature is to use BPA as a reactive agent in the production of temperature-sensitive paper with color developing layer (Mohapatra et al., 2010).

BPA received much attention since it is “the one of the most produced chemicals worldwide with known endocrine disrupting effects” (Clara et al., 2004). BPA is now identified as an EDC by the US Environmental Protection Agency and World Wide

Fund for Nature. According to the EPA, ‘‘BPA is an exogenous agent that interfaces with synthesis, secretion, transport, binding, action or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction or behavior” (Zhao et al., 2003). BPA is a classic estrogen mimicking compound which binds as an agonist to estrogen receptor β, albeit with a much lower affinity than estradiol (Kuiper et al., 1998). The endocrine disrupting effects of BPA are well documented. From a study based on the adult US population, exposure to BPA at very low dose would “increase the incidence of prostate cancer, cardiovascular disease, type 2 diabetes and liver-enzyme abnormalities (Wetherill et al., 2002). Recent evidence proves that BPA can also cause organizational changes in brain structure and chemistry, and behavior of laboratory animals (vom Saal et al., 2007).

EE2 is a semisynthetic steroidal estrogen used in orally active contraceptives (Manickum et al., 2014). It is one of the most frequently detected EDCs in effluents of WWTPs and in surface water (Lima et al., 2012; Zhang et al., 2012). EE2 is now a great environmental concern because it is “toxic to aquatic organisms and may cause long-term effects in the aquatic environment” (Carlsson et al., 2006). All humans and animals will excrete natural estrogens through urine or feces, which will end up in the environment through sewage discharge and animal waste disposal (Ying et al., 2002). However, compared with natural estrogens, EE2 is proved to be more effective to induce feminization. EE2 can cause feminization to several species such as fish, molluscs, amphibians, birds and mammals, at concentrations as low as 0.1 ηg/L (Clouzot et al., 2010), while the value for natural estrogen is 10 times higher. Lee et al. (2008) proved that EE2 is 11-27 times more estrogenic potent than 17β-estradiol (E2) through in vivo tests. In addition, EE2 is more resistant than E2 to biodegradation (Manikum, 2014).

TCS is a synthetic chlorinated phenylether bisphenol with broad-spectrum antimicrobial and antifungal properties. It is extensively used in household cleaners,

soaps, toothpaste, mouthwash and cosmetics (Bester, 2003). It is also used in some plastic products, toys and underwear because it can inhibit microbial growth (Gao et al., 2014; Chen et al., 2012). TCS can be absorbed dermally and has been detected in human plasma, urine and breast milk (Chen et al., 2012; Allmyr et al., 2006). Currently concern about TCS is mainly focused on its possible effect on antibiotic resistance. Triclosan-resistant strains have been isolated in laboratories and hospitals; furthermore, mutated genes have been identified by several studies (Schweizer, 2001; Fan et al., 2002; Brenwald et al., 2003). In addition, TCS has been identified as an EDC. Foran et al. (2000) suggest that TCS shows weak androgenic effects while Ishibashi et al. (2004) claimed that its metabolites can act as estrogen receptor antagonists.

According to the literature, approximately 1500 t of TCS are produced yearly and more than 95% of them will end up in sewer systems (Singer et al., 2002). The concentration of TCS measured in WWTPs influents is in the range of 1-10 μg/L (Chen et al., 2011). More than 90% of TCS can be removed by biodegradation or sorption to AS; however, it can still be detected in the effluents of WWTPs and surface waters (Gao et al., 2014). Researchers now also focus on the photolysis of TCS in the natural environment. Martínez-Zapata et al. (2013) found that the photodegradation reaction for TCS followed first-order kinetics and exhibited a lifetime of 2.3 h.

The removal efficiency of the three selected MCs is affected by their physical-chemical properties. Table 2.2 has literature reported physical-chemical properties of BPA, EE2 and TCS. All chosen chemicals have relatively low vapor pressures and Henry's law constants which makes vaporization not likely a major removal mechanism.

Except for TCS, there is no photodegradation reported for BPA and EE2. Sorption is a possible removal pathway for these compounds since all of them have low water solubility. The octanol-water partition coefficient (K_{ow}) is related to water solubility (Silva et al., 2012). Chemicals with high K_{ow} are considered to be hydrophobic and have a strong tendency to sorb to sludge. In the previous section, K_d can be predicted

by K_{ow} based on Eqs. 2.23 and 2.24. According to the literature, chemicals with log K_{ow} less than 2 have negligible sorption, while if log K_{ow} is more than 4, sorption could be a very significant removal mechanism. Table 2.2 indicates the relationship between log K_{ow} and adsorption potential of hydrophobic compounds. While Table 2.3 represents the reported log K_{ow} and log K_{oc} values for the chosen chemicals.

Table 2.2 Sorption Potential Dependence on Log K_{ow} [a]

Log $K_{ow} \leq$ 2.5	Low sorption potential
2.5< Log K_{ow} < 4.0	Medium sorption potential
Log $K_{ow} \geq$ 4.0	High sorption potential

a. (RIWA, 2007)

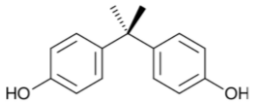
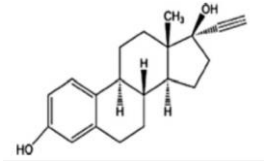
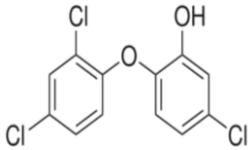
Table 2.3 Log K_{ow} and log K_{oc} of BPA, EE2 and TCS Reported in the Literature

Chemicals	Log K_{ow}	Log K_{oc}
BPA	-	0.51-3.04 [a]
EE2	3.03 [b]	3.31 [b]
	4.15 [c]	3.00-3.86 [a]
TCS	4.8 at 25 ˚C [d]	-

b. a. Sun et al. (2012) b. Clara et al. (2004) c. Silva et al. (2012) d. Bester (2003)

Judging by log K_{ow}, EE2 has medium sorption potential while TCS has high sorption potential. Compared with log K_{ow}, log K_d is more intuitive and more widely studied. The reported log K_d for BPA, EE2 and TCS are listed in Section 4.4 for the purpose of making comparison with the log K_d found in this study.

Table 2.4 Physical-chemical Properties of BPA, EE2 and TCS

Chemicals	Structure	Molecular Formula	Molecular Weight (g/mol)	Water Solubility (mg/L)	Vapor Pressure （mm Hg）	Henry's Constant (atm m^3/mol)
BPA		$C_{15}H_{16}O_2$	228.3	120-200 at 20-25 ˚C [a]	0.65 at 190 ˚C [a]	2.1×10^{-10} [b]
EE2		$C_{20}H_{24}O_2$	296.4	4.8 at 20 ˚C [c]	4.5×10^{-11} [c]	7.9×10^{-12} [c]
TCS		$C_{12}H_7Cl_3O_2$	289.5	1-4 at 20-50 ˚C [d]	5.2×10^{-6} at 25˚C, 2.2×10^{-6} at 20˚C [d]	2.1×10^{-8} (estimated) [e]

a. Mohapatra et al., (2010), b. GSI. Environment, (2013), c. Silva et al., (2012) , d. SCCS, (2010), e. NCBI, (2013).

Chapter 3 Experimental Setup

In this study, sorption kinetics and isotherms of the selected MCs absorbed onto primary sludge were determined by carrying out a series of batch experiments. Primary sludge was taken from a local WWTP. Sorption isotherms for AS were also determined. AS was produced in the lab by a bench-scale continuous flow AS system.

In this chapter, the procedure for sorption kinetics and isotherms batch experiments will be presented as well as the setup of the bench-scale AS system and a brief introduction to the detection method for MCs.

3.1 Porous Pot Bioreactors and Bench-scale Continuous Flow Wastewater Treatment System

Three 3 L-porous pot bioreactors were used to simulate a continuous flow AS system. A porous pot bioreactor is approved by the USEPA to provide laboratory simulation of an AS wastewater treatment system (USEPA, 2008).

As shown in Fig. 3.1, the porous pot bioreactor consists of an inner porous cylinder made of membrane, and a slightly larger vessel made of proper material, usually plastic, that can hold the inner cylinder. The membrane used for the inner cylinder in this study is a polytetrafluoroethylene membrane, which has a pore size of 90 μm. The porous pot reactor has a working volume of 3 L. The difference between a porous pot bioreactor and other simulation systems is the retention of AS by the inner membrane cylinder, which eliminates the need for a secondary clarifier. SRT is then achieved by removing a certain amount of mixed liquor from the bioreactor every day. The thickened waste AS used to seed the reactor was obtained from the Robert O. Pickard Environmental Center (ROPEC) wastewater treatment facility in Ottawa, ON.

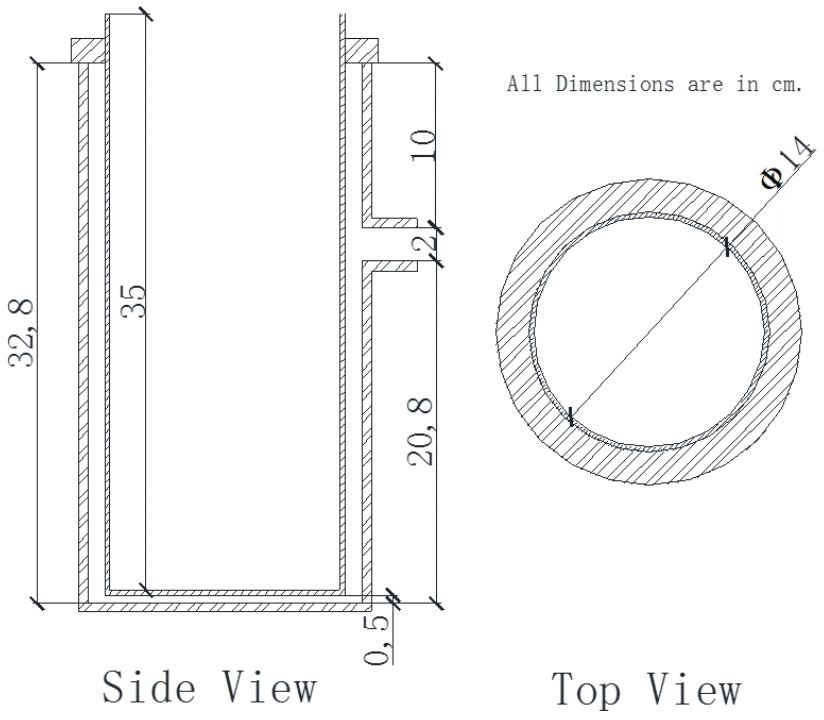


Figure 3.1 Detailed Diagram of the Porous Pot Aeration Bioreactor

SRT is defined as the average time particles are retained in the reactor, which can be calculated by Eq. 3.1.

$$\theta_X = \frac{X_v \cdot V}{Q_W \cdot X_{vr} + (Q - Q_W) X_{ve}} \qquad \text{Eq. 3.1}$$

where θ_X is SRT, d,

X_v is volatile suspended solids (VSS) concentration in bioreactor, mg/L;

V is the volume of the bioreactor, L;

Q_w is the flowrate of wasted AS, L/d;

X_{vr} is the VSS concentration of wasted AS, mg/L;

Q is the flowrate of influent, L/d;

X_{ve} the VSS concentration of effluent, mg/L.

Since there is no settling of AS in a porous pot bioreactor system, the VSS concentration of wasted sludge is the same as the AS inside the reactor, also assuming the effluent VSS is negligible, Eq. 3.1 can be simplified as follows:

$$\theta_X = \frac{V}{Q_w}$$ Eq. 3.2

Fig. 3.2 is a schematic of the bench-scale continuous flow wastewater treatment system. The influent, which was a synthetic wastewater made in the lab, is pumped into the porous pot bioreactors at the determined flow rate.

A: Influent Tank, B: Influent Pump, C: Porous Pot Bioreactor, D: Effluent Tank, E: Air Diffuser

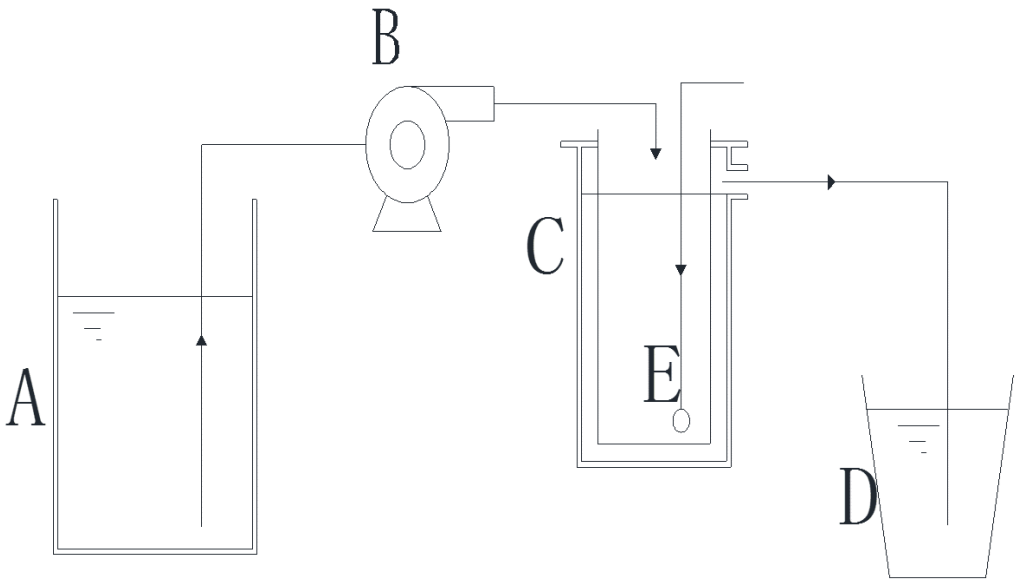


Figure 3.2 Scheme of Bench-Scale Continuous Flow Wastewater Treatment System

The synthetic wastewater stock solution was prepared every 10 d and stored in the refrigerator. Every day 100 mL of stock solutions was mixed with 40 L distilled water to make the influent. Alum stock solutions were also made and added into the influent (100 mL/d). No continuous stirring was applied to the influent and it was maintained at room temperature. After 24 h running, all synthetic wastewater was pumped into the bioreactors. There were some precipitates retained in the walls of the influent tank. Containers were cleaned every day before new synthetic wastewater was made. During the cleaning, aluminum precipitates will be wasted. To determine the mass of aluminum precipitates remaining in the influent container, three samples at each aluminum dosage

were collected by adding 2 L distilled water into the influent tank and washing all the precipitates into the water. Total aluminum concentration was tested for the mixture.

The composition of the synthetic wastewater is listed in Table 3.1. This formula was modified according to Zhao et al. (2008). It contains a carbon source, nutrients, trace elements and buffering compounds. The average influent COD is around 380 mg/L.

Table 3.1 Composition of the Synthetic Wastewater

Compounds		Concentration (mg/L)
Dextrose	$C_6H_{12}O_6$	150
Peptone		150
Sodium Acetate	NaCOOH	80
Ferric Chloride	$FeCl_3 \cdot 6H_2O$	0.45
Ammonia Chloride	NH_4Cl	40
Potassium Phosphate Monobasic	$KH_2PO_4 \cdot 2H2O$	44.1
EDTA	$C_{10}H_{16}N_2O_8$	3
Sodium Bicarbonate	$NaHCO_3$	150
Magnesium Sulfate	$MgSO_4 \cdot 7H_2O$	20
Calcium Chloride	$CaCl_2$	10.6
Boric Acid	H_3BO_3	0.045
Copper Sulfate	$CuSO_4 \cdot 5H_2O$	0.01
Potassium Iodide	KI	0.054
Manganese Chloride	$MnCl_2 \cdot 4H_2O$	0.036
Zinc Sulfate	$ZnSO_4 \cdot 7H_2O$	0.036
Sodium Molybdate	$Na_2MoO_4 \cdot 2H_2O$	0.1
Cobalt Chloride	$CoCl_2 \cdot 6H_2O$	0.01

Treated water is filtered by the inner membrane cylinder and AS is retained inside the reactors. SRT of the three bioreactors was maintained at 15, 10 and 5 d, respectively. According to (Metcalf & Eddy, 2003), SRT ranges from 3 to 18 d chosen for WWTP design if complete nitrification is one of treatment goals.

The F/M ratio required for AS systems varies from 0.04 to 1 g substrate /g biomass d (Metcalf & Eddy 2003). Given the COD of synthetic wastewater being 380 mg/L and TSS concentrations of bioreactors ranges from 1500 to 4500 mg/L, HRT of 6 h results in F/M ratio range from 0.4 to 1 g substrate /g biomass d, which is within the range of F/M ratios recommended by Metcalf & Eddy, (2003).

Since there is no settlement or circulation of sludge, SRTs were achieved by removing 200, 300 and 600 mL of sludge from each reactor every day according to Eq. 3.2.

The reactors were continuously aerated which also provided a mechanical force to stir the mixed liquor inside the inner membrane cylinder. The temperature of the reactor was room temperature (20-25^{o}C). In winter, temperature dropped to slightly below 20^{o}C since cooler air was supplied to the reactors; but no significant change in reactor performance was observed. The operation parameters of the AS system are summarized in Table 3.2.

Table 3.2 Operation Parameters for Bench-Scale Continuous Flow Wastewater Treatment System

	R1	R2	R3
SRT (d)	15	10	5
Wasted Sludge (mL/d)	200	300	600
HRT (h)		6	
Flow Rate (mL/min)		8.3	
DO (mg/L)	4.82-5.06	5.98-6.12	6.02-6.10
Temperature (^{o}C)		20-25	

To minimize effects of fixed film growth and retard fouling, the membrane walls were scraped daily. Even though, membrane fouling, a universal problem that happens to all types of membranes, happened during the operation. Physical backwashing and chemical cleaning were applied to the membrane ex situ whenever fouling happened. Physical backwashing can effectively remove the loosely attached cake layer (Kola et al., 2014). However, physical backwashing cannot solve irreversible fouling; thus chemical cleaning is needed. Chemical cleaning was done by immersing the whole membrane cylinder into a solution containing $Ca(OCl)_2$ and EDTA at pH of 12. OCl^- is a strong oxidant used in chemical cleaning. $Ca(OCl)_2$ was chosen because it is a strong oxidant which can be purchased at a low price. EDTA is an effective cleaner for scale compounds and metal oxides through chelating. NaOH was added to adjust the pH to 12. According to the literature, pH of 12 can increase the efficiency of OCl^- by reducing the concentration of Cl_2 in gaseous form (Liu et al., 2001). Usually, immersion for 24 h was sufficient time to clean the entire membrane.

Lin et al. (2014) studied the influence of membrane fouling on removal efficiency of six PPCPs. Three types of membrane, one reverse osmosis (XLE) and two nanofiltration (NF90 and NF270) were fouled by silica. The results shows that NF90 and XLE, described by the researchers as “tight membrane”, reduced the transportation of PPCPs across the membrane with size exclusion being the dominating mechanism. While for NF270, the “loose membrane”, increased PPCPs diffusion across the membrane. Among the six PPCPs tested, only ibuprofen, TCS and sulfamethazine were observed to adsorb to the membrane. In this study, the membrane was fouled by silica, while in wastewater treatment, membrane is usually fouled by extracellular polymer substances (Dvořák et al., 2011). Studies regarding to the influence of membrane fouled by extracellular polymer substances on MCs removal is scarce.

3.2 Alum Dosage

Aluminum sulfate hexadecahydrate ($Al_2(SO_4)_3 \cdot 18H_2O$) (J.T Baker Chemical Co, NJ,) was dosed into the influent according to a determined amount. According to Metcalf & Eddy (2003) the dosage of aluminum and its corresponding phosphorus removal is summarized in Table 3.3.

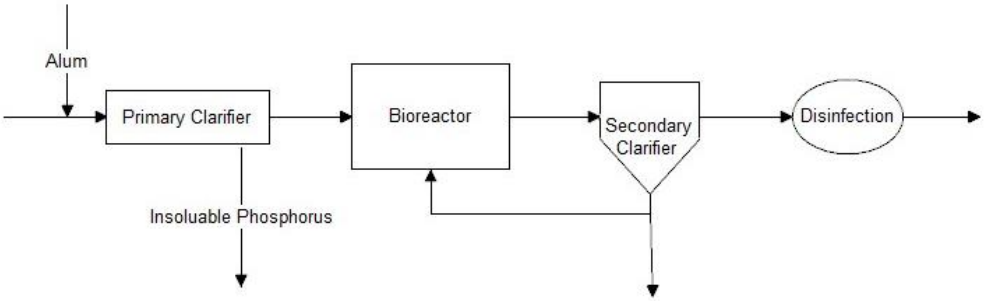
Table 3.3 Aluminum Dosages and Corresponding Phosphorus Removal

Al : P (mol:mol)		Phosphorus Removal
Range	Typical	(%)
1.25:1-1.5:1	1.4:1	95
1.6:1-1.9:1	1.7:1	85
2.1:1-2.6:1	2.3:1	75

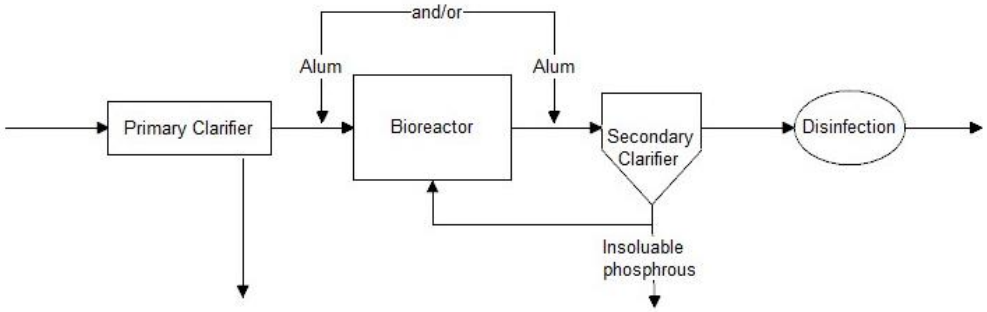
In practice, alum can be dosed in WWTPs at several sites (Fig. 3.3). Pre-precipitation refers to dosing alum into raw wastewater or directly in the primary clarifier; coprecipitation refers to alum added in the bioreactor or secondary clarifier; thus, the precipitants are removed together with wasted sludge; post-precipitation involves the addition of alum to the effluent of the secondary clarifier. In the latter case additional sedimentation is needed to remove the precipitates (Metcalf & Eddy, 2003).

Pre-precipitation and coprecipitation schemes are shown in Figs. 3.3a and 3b.

According to the formula of the synthetic wastewater, the concentration of potassium phosphate monobasic ($KH_2PO_4 \cdot 2H_2O$) is 44.1 mg/L, which makes phosphorus concentration around 8 mg/L (0.23×10^{-3} mol/L). However, peptone may also contain a certain amount of phosphorus. Since the chemical formula of peptone is not determined, it makes the concentration of influent phosphorus concentration hard to predict. In the study of Banihashemi (2012), the measured total phosphorus concentration was 11mg/L (0.35×10^{-3} mol/L). So in this study, the influent phosphorus concentration is assumed to range from 8 to 11 mg/L (0.23 to 0.35×10^{-3} mol/L).



a. Pre-precipitation



c. Coprecipitation

Figure 3.3 Schemes of Pre-precipitation (a) and Coprecipitation (b), Modified from (Metcalf & Eddy, 2003)

Assuming that the efficiency of a primary clarifier is 60% (Metcalf & Eddy, 2003) and all dosed aluminum will precipitate eventually, then when pre-precipitation is used, only 40% of the aluminum will be delivered to the bioreactor.

Taking the estimated phosphorus concentration (0.23 to 0.35 $\times 10^{-3}$ mol/L) and alum dosage requirements (Table 3.3) into consideration, the alum dosage ranges from 0.12 to 0.36 $\times 10^{-3}$ mol/L Al for pre-precipitation, and 0.29 to 0.91 $\times 10^{-3}$ mol/L Al for coprecipitation.

Three doses were chosen to be used in this study corresponding to three different scenarios and listed in Table 3.4.

Table 3.4 Alum Dosage Used for Three Different Scenarios

	Dosing Site	Alum Dosage Ranges $\times 10^{-3}$ mol/L as Al	Alum Dosage as Al $\times 10^{-3}$mol/L	mg/L
Dosage 1	Pre-precipitation	0.12 to 0.36	0.28	7.6
Dosage 2	Coprecipitation	0.29 to 0.91	0.48	13.0
Dosage 3			0.72	19.4

As introduced in Section 2.4, the purpose of this study is to investigate the effect of alum on MCs sorption on AS, so that phosphorus removal is not important. The molar ratios between phosphorus and alum presented in Table 3.4 are considered for the purpose of determining the proper alum dosages, not for improving phosphorus removal. As a result, the pH of the synthetic wastewater was also not maintained at the optimum pH range for phosphorus removal. After adding alum, the pH of the synthetic wastewater dropped to around 5.6-5.8. Sodium hydroxide was added to the influent to adjust the pH back to 6.5-7.5. This pH range falls into the zone where $Al(OH)_3$ controls C_{TP} and C_{TAl} (details presented in Section 2.4), the added aluminum will mainly form $Al(OH)_3$ precipitates. C_{TP} is at the range of 10^{-4} to $10^{-2.5}$ mol/L while C_{TAl} is at range of 10^{-6} to 10^{-5} mol/L. Above pH of 6.8, no phosphorus precipitates will form. So under most of the operation conditions in this study, most of the phosphorus will remain soluble. The ratio of influent degradable matter expressed on a COD basis to nitrogen and phosphorus should be COD: N: P=100: 5: 1 (Droste., 1997). Given that the influent COD was 380 mg/L, 3.8 mg/L is the minimum amount of phosphorus required for biomass growth. Based on the previous analysis, the amount of phosphorus remaining is sufficient for biomass growth.

As mentioned in Section 3.1, aluminum precipitates remained in the influent tank were washed and diluted in 2 L distill water for aluminum concentrations analysis. Based on the results, 23 to 25% of the aluminum passed to the bioreactors, resulting in an actual aluminum dosages of 1.95, 3.02, 4.73 mg/L for dosages 1, 2 and 3, respectively.

The insoluble aluminum in the influent will contribute to TSS of the bioreactor. Assuming VSS is not influenced by alum addition, the VSS/TSS ratios at three different alum dosages can be estimated by Eq. 3.3:

$$\text{VSS/TSS Ratio} = \frac{VSS}{\left(TSS + \frac{C_{Al} \times V_{inf} \times SRT}{V}\right)} \times 100\% \qquad \text{Eq. 3.3}$$

where VSS is VSS concentration of the bioreactor without alum addition, mg/L;

TSS is TSS concentration of the bioreactor without alum addition, mg/L;

C_{Al} is the aluminum dosage, mg/L;

V_{inf} is the volume of the influent daily, L/d;

V is the volume of the bioreactors, L;

SRT is the solid retention time of each bioreactor, d

In Section 4.3, the estimated TSS/VSS ratios are calculated and compared with the measured TSS/VSS ratios.

3.3 Analytical Method for the Selected Microconstituents

A proper extraction procedure, of which the purpose is to concentrate and clean up the sample, is necessary before using high performance liquid chromatography coupled with UV (HPLC-UV) detection system to measure the MCs concentration.

3.3.1 Solid Phase Extraction Separation Procedure

Solid phase extraction (SPE), according to the literature, is a cost effective alternative to replace liquid-liquid extraction (Aligent Tech, 2014). These two methods are very similar in basic concept. Instead of using a liquid solvent, SPE uses a solid matrix, usually silica, to extract solutes dissolved or suspended in a liquid. The silica matrix is known as the stationary phase, while the treated liquid is known as the mobile phase. Passing the mobile phase through the stationary phase is the loading procedure. The extracted solutes are either wanted or unwanted components. If the retained solutes are

the wanted components, elution is further needed to wash out the desired analytes. SPE has some obvious advantages compared with the traditional liquid-liquid extraction:

1) Less solvent is used in SPE.
2) It has a higher recovery rate than liquid-liquid extraction.
3) There is less contamination from extraction solvent.
4) Easy to operate for analyzer.

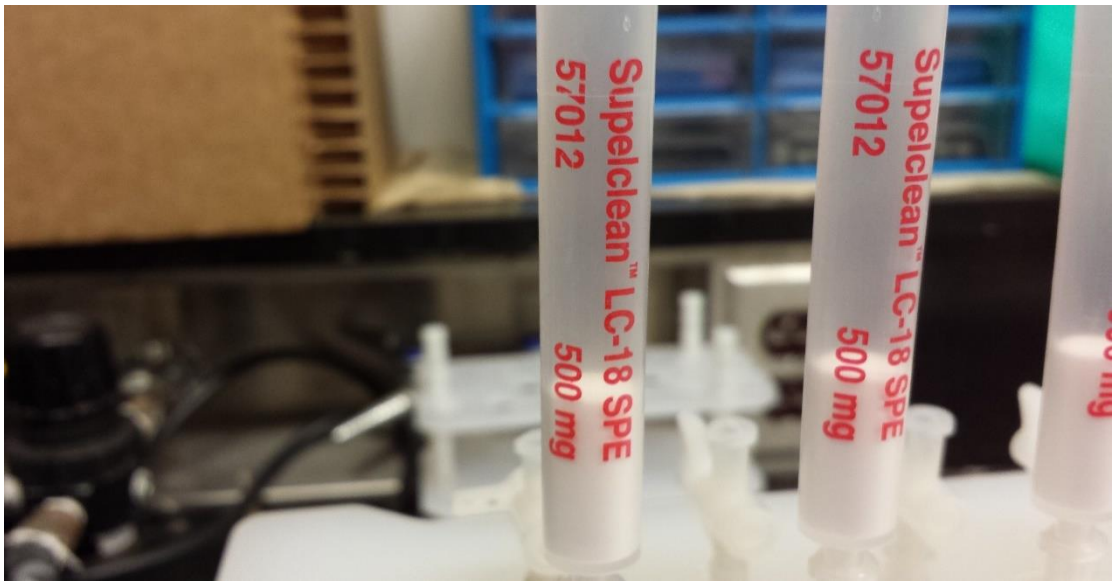
Based on the polarity of material in the stationary phase, SPE can be categorized as reversed and normal phase SPE. Reversed phase refers to a nonpolar stationary phase used while the sample matrix (mobile phase) is polar or mediate polar (Żwir-Ferenc et al., 2006). The analytes of interest are usually nonpolar to mediate polar. The primary removal mechanism for reverse phase SPE is a hydrophobic interaction which is strong in water and weak in organic solutions.

The detailed procedure for extraction is presented in Table 3.5. Commercial made cartridges, Supelclean LC-18 (Sigma-Aldrich, Ca), were chosen to perform SPE in this study (Fig. 3.4). A sample volume of 100 mL proved to be sufficient to result in obvious peaks with no breakthrough from the HPLC detection system.

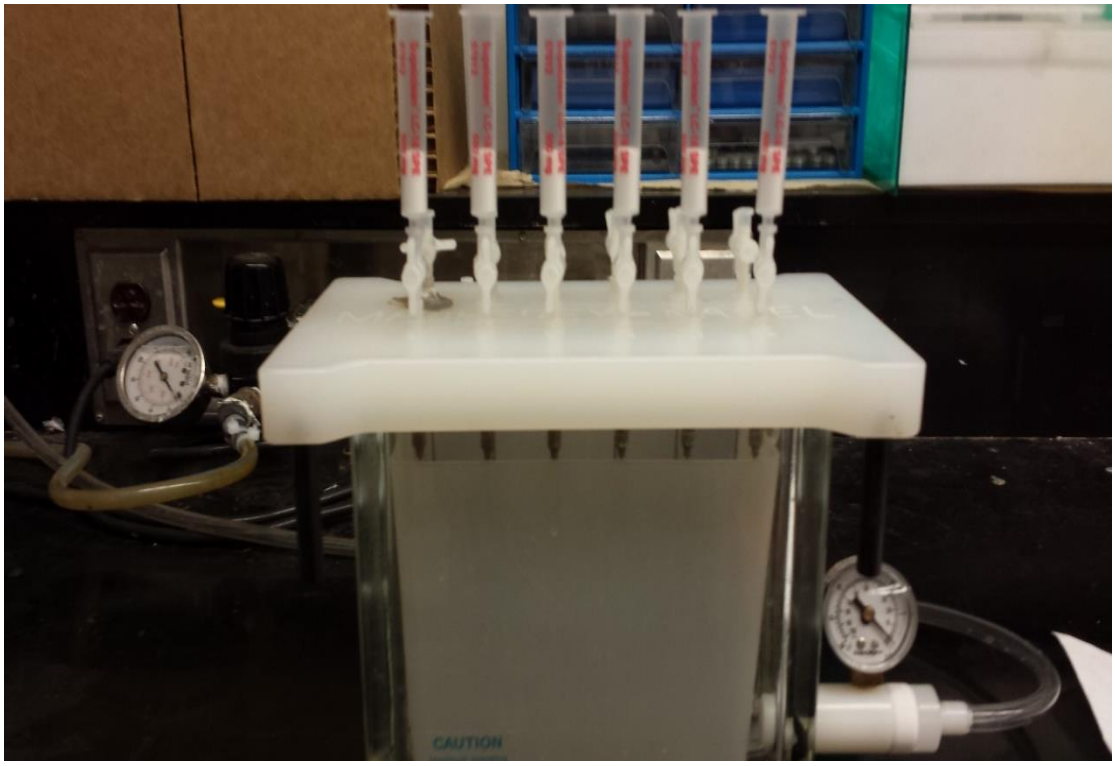
An activation step is usually needed before loading to activate the silica and clean up impurities in the cartridges. The flow rate of samples at loading step is about 10 mL/min. A high flow rate cannot be applied since breakthrough might happen. The washing step is accomplished by passing 10 mL methanol/water solution (30:70, V:V） to wash out non-target compounds. Finally, 10 mL of methanol is used to elute all MCs retained in the cartridges.

Methanol was chosen because it is strong enough to wash out the selected MCs from the cartridges; however, methanol is not suitable for the following HPLC detection procedure. As a result, the 10 mL of methanol solution, containing the selected MCs, is further dried by gently blowing nitrogen gas over the solution. 1 mL acetonitrile/water solution (45:55, V:V) is used to redissolve the MCs. Overall, the contents of the 100

mL sample are concentrated to 1 mL before being sent to the HPLC detection system, so that the concentration factor is 100. Sample volume of 50 mL was also used in this study, in that case, the concentration factor is 50.



a. Supelclean ™ LC-18 SPE cartridge



b. vacuum manifold device for large volume samples loading

Figure 3.4 Supelclean ™ LC-18 SPE Cartridge and Vacuum Manifold Device

Table 3.5 Details for SPE Procedure Developed by Banihashemi (2012)

SPE Cartridge	Supelclean LC-18
Sample Volume	100 mL
pH	7
Activation Step	10 mL methanol followed by 10 mL MilliQ water
Loading Step	Approximately 10 mL/min
Washing Step	10 mL methanol/water solution (30:70, V:V）
Elution Step	10 mL methanol

3.3.2 HPLC-UV Detection System

The origin of the idea of HPLC comes from an experiment conducted by a Russian botanist, Mikhail S. Tswett in the early 1900s. His studies focused on separating leaf pigments in a column packed with particles. The leaf pigments were extracted form plant using a solvent. When the solvent passed through the column by gravity, different color bands were seen to separate in the column because some of the pigments moves faster than others (Waters, 2014).

An HPLC uses a similar idea to separate different compounds and then using proper detection method to quantify the amount of each compound. HPLC is an improved form of column chromatography because the solvent is being passed through the column under high pressure up to 400 atm (Clark, 2007). Fig. 3.5 shows the flow scheme of the HPLC-UV detection system. The detection limit of the HPLC-UV system is 200 ηg/L according to Banihashemi (2012).

The results from the HPLC-UV system are similar to the graph shown in Fig. 3.6. A standard solution is required to be made before any test. The same chemical will always show its peak at the same time.

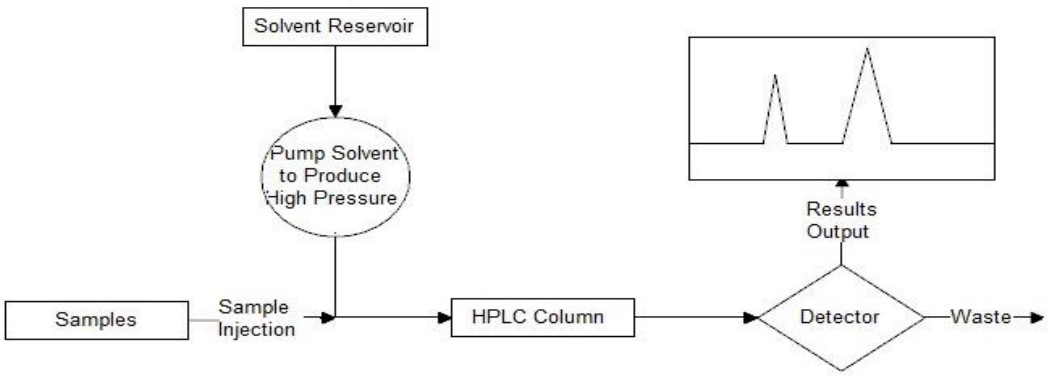


Figure 3.5 Flow Scheme for HPLC-UV Detection System

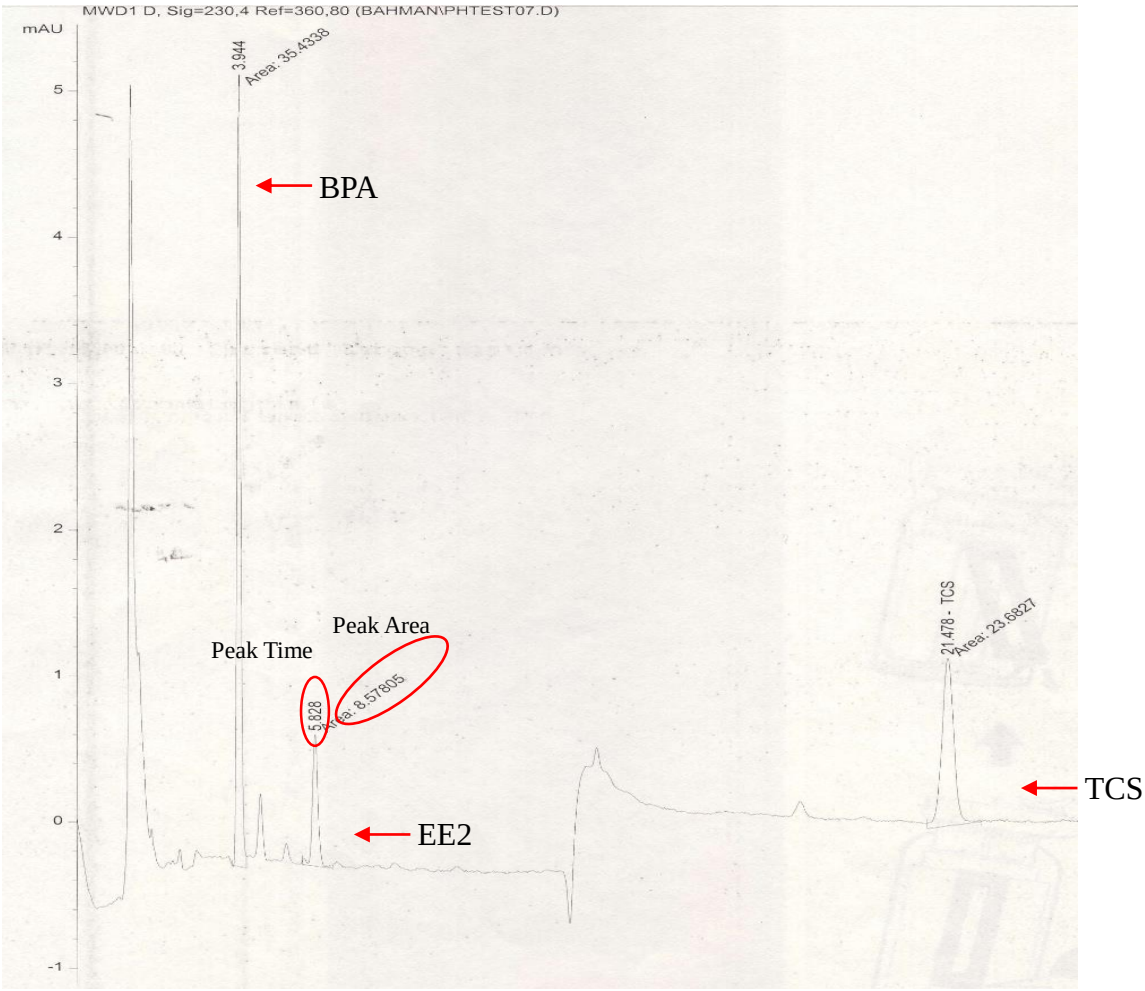


Figure 3.6 Chromatogram of 1mg/L Standard Solution Detected by HPLC-UV System

3.3.3 Standard Curve and Recovery Rate for Selected MCs

In analytical chemistry, a standard curve is a general method to determine the properties of unknown samples by measuring and graphing multiple samples with known

properties. Since HPLC-UV will not give the concentrations of selected MCs directly, a standard curve of selected MCs ranging from 0.5 to 100 µg/L was made. Standard curves are shown in Fig. 3.7.

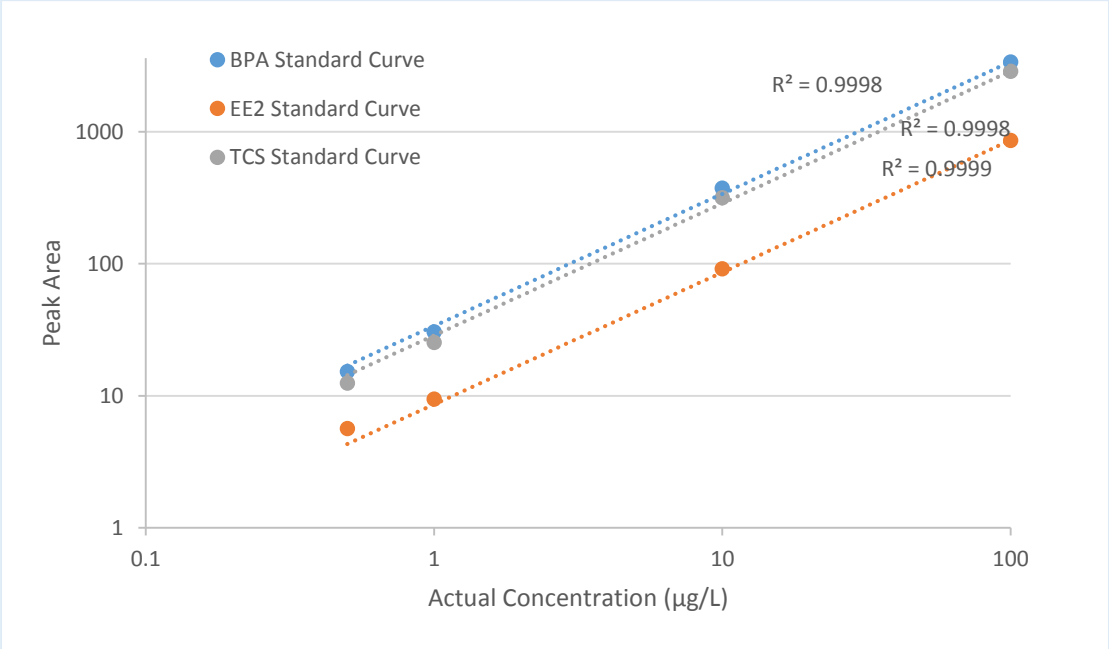


Figure 3.7 Standard Curves for BPA, EE2 and TCS Ranging from 0.5 to 100 µg/L (n=2)

The peak area is linear with respect to the concentrations of MCs; the R^2 values given on the graph were very high.

Table 3.6 Recoveries for the Selected MCs

	Peak Area			Average Recovery（%）		
	BPA	EE2	TCS	BPA	EE2	TCS
1 mg/L Standard Solution	36.2	8.2	28.1			
Recovered Sample 1	32.1	7.4	20.0	91.8	96.3	77.3
Recovered Sample 2	35.4	8.6	23.7			
Recovered Sample 3	32.2	7.7	21.5			

The relative recoveries were tested to find the reliability of SPE coupled with HPLC-UV system for the selected MCs. 1 mL of standard MCs (1 mg/L) solution was spiked into 100 mL milliQ water. Then SPE was applied to each sample before the samples were tested in HPLC-UV detection system. The recovery was calculated by Eq. 3.4:

$$\text{Recovery } \% = \frac{A_{found}}{A_{standard}} \times 100\% \qquad \text{Eq. 3.4}$$

where A_{found} is the peak area of selected MCs in recovered samples;

$A_{standard}$ is the peak area of corresponding MCs in standard solution.

3.4 Sorption Kinetics Experiment

Sorption kinetics were studied for the chosen MCs and primary sludge, while sorption kinetics between the chosen MCs and AS were conducted by Banihashemi (2012). Primary sludge was collected from the local WWTP, ROPEC (Ottawa, ON, Canada). ROPEC provides secondary treatment to about 720,000 people. There are several water treatment plants in its service area. As water treatment plants use alum for coagulation process, alum will appear in the sewer after backwash the filtration reactors. As a result, ROPEC receives alum in its influent.

Concentrated primary sludge was collected at the bottom of primary clarifier from ROPEC and stored in four 1 L-glass bottles before further treatment. Sludge was filtered with a P8 filter (Fisher Scientific Co, USA). The solids retained, the dewatered sludge, was dried in a fume hood for at least 4 h before storage. The dewatered primary sludge was stored at 4^{o}C in glass bottles filled with nitrogen gas. The water content of dewatered sludge was 78% (W:W).

The sorption kinetics experiment was conducted with a mixture containing 2.5 g dewatered primary sludge and 500 mL milliQ water. Sodium azide at a dosage of 0.2% (W:V) was added to the mixture to inhibit bioactivation 24 h before the sorption kinetics tests were begun. The mixture was kept at a shaker at the speed of 200 rpm to keep sludge from settling. Since the primary sludge was generated from a local WWTP, it was contaminated with MCs already. Background MCs concentrations were tested by taking 50 mL samples after mixing the sludge for 24 h.

BPA, EE2 and TCS were purchased from Sigma-Aldrich Co., Canada. Their purity reported by the manufacture was over 98%. Acetonitrile/water solution (45:55; V:V) was used as the solvent for MCs stock solutions. 1, 10 and 100 mg/L stock solutions were stored in glass flasks and kept in the refrigerator.

MCs were spiked into the mixture at the concentration of 200 μg/L. 50 mL samples were taken from the mixture at 0.25, 1, 2, 3.5, 5, 7, 20, 24 h after the MCs were spiked. During this process, the mixture was also kept in the shaker to prevent sludge from settling and provide a good mixture for MCs and sludge.

The 50 mL samples were filtered using 0.22 μm membrane filters (Durapore, EMD Millipore Co, CA) immediately after collection. The filtrates were collected and cleaned up by the SPE procedure. Triplicate samples were run.

3.5 Sorption Isotherm Experiment

Both primary sludge and AS were used to test the MCs sorption isotherms.

The primary sludge used for the sorption isotherm test was collected and pretreated as described in Section 3.4. Four 100 mL sludge water mixtures were used for sorption isotherm experiments each containing 1.25, 0.75, 0.5 and 0.1 g dewatered primary sludge, respectively. VSS and TSS concentrations were also tested for each mixture. The same chemical, sodium azide was used to inhibit biodegradation.

Since solid phase concentration is necessary for determination of a sorption isotherm, the MCs background concentrations in dewatered primary sludge were determined by the microwave assisted solid extraction procedure. Details about the microwave assisted solid extraction procedure are presented in Banihashemi (2012).

MCs were spiked into the primary sludge mixture at the initial concentration of 200 μg/L. Constant mixing was provided by putting samples on a shaker (200 rpm). The

solution was mixed for 24 h to allow for sorption to reach equilibrium based on the results of sorption kinetics study.

Only liquid phase concentrations were tested, solid phase concentrations were determined according to Eq. 2.21. As shown in Section 3.3 the recovery rate for the liquid phase is high, while the recovery rate for the solid phase is comparably low. This is reason why only liquid phase concentrations were measured and used in calculations in this study.

AS was produced in the lab. The mixed liquor removed from each bioreactor every day was collected in a glass bottle and stored at 4^{o}C. For each sample, 100 mL of mixed liquor is needed. Sodium azide was added at a dosage of 0.2% (W:V) to AS to inhibit bioactivity.

Since the mixed liquor generated from each reactor has relatively constant VSS and TSS concentrations, in order obtain different points in a sorption isotherm, the initial liquid MCs concentrations were chosen to range from 10 to 200 ug/L (10, 30, 50, 70, 100, 150 and 200 μg/L).

A volume of 100 mL was used for each sample. A time of 24 h is considered to be a sufficient reaction time for MCs to reach sorption equilibrium with AS.

Centrifugation was applied for AS samples (except for SRTs of 5 and 10 d at the first alum dosage, samples were filtered). A centrifuge was used instead of a membrane because a lower recovery rate for all three MC was obtained for samples using a membrane to separate liquid from solids. Liquid phase concentrations were measured while the solid phase concentrations were calculated.

3.6 Removal of Selected MCs in Continuous Flow Activated Sludge System

MCs were dosed at 50 μg/L into the influent tank of the continuous flow AS system in order to study the removal of MCs under lab scale conditions. The system was running at the first alum dosage for more than 2 months. Both influent and effluent concentrations were tested at different times. At the same time, TSS and VSS of influent, effluent and inside bioreactors were recorded as well as effluent soluble COD.

The samples for the influent MCs concentrations were taken at the outlet of the influent tubes. The MCs were dosed at a concentration of 50 μg/L; however, there were some losses when the influent was pumped through the tubes. The samples for the effluent MCs concentrations were taken at the effluent tanks. For all the samples, a volume of 100 mL was used.

TSS, VSS and soluble COD were recorded in order to indicate the performance of the bioreactors and whether steady states was reached. TSS is also used to calculate the removal rates of MCs by sorption.

The total removal is calculated by the following equation:

$$\text{Total Removal} = \frac{C_{inf} - C_{eff}}{C_{inf}} \times 100\% \qquad \text{Eq. 3.5}$$

where C_{inf} is the influent liquid phase concentration, μg/L;

C_{eff} is the effluent liquid phase concentration, μg/L.

The removal by sorption was calculated by Eq. 3.6:

$$\text{Removal by sorption} = \frac{Q_e \times TSS \times V_{wasted}}{C_{inf} \times V_{inf} \times 10^9} \times 100\% \qquad \text{Eq. 3.6}$$

where Q_e is the MCs concentration in the solid phase, μg/kg;

TSS is the total suspended solids inside the bioreactors, mg/L;

V_{wasted} is the volume of sludge removed from bioreactor every day, mL/d;

V_{inf} is the volume of the influent every day, L/d;

The removal by biodegradation is calculated by Eq. 3.7:

Removal by Biodegradation = Total Removal – Removal by Sorption

Eq. 3.7

Chapter 4 Results and Discussion

4.1 Sorption Equilibrium and Kinetics for MCs Sorbed onto Primary Sludge

Table 4.1 has the background liquid phase MCs concentrations as well as the liquid phase concentrations at different times after MCs were added. The liquid phase concentrations at 0 h were calculated by adding 200 μg/L to the background concentrations. Triplicate samples were run, average value and standard deviation were calculated.

Table 4.1 MCs Concentrations at Different Times

	BPA				
Time (h)	Sample 1 (μg/L)	Sample 2 (μg/L)	Sample 3 (μg/L)	Average (μg/L)	Standard Deviation (μg/L)
Background [a]	13.7	22.4	1.7	12.6	8.5
0 [b]	213.7	222.4	201.7	212.6	8.5
0.25	184.3	81.1	203.3	156.3	53.7
1	175.5	139.8	199.6	171.6	24.6
2	177.5	138.7	192.7	169.6	22.7
3.5	152.5	148.0	190.6	163.7	19.1
5	149.3	140.8	180.0	156.7	16.8
7	162.2	130.5	179.0	157.2	20.1
20	134.2	141.8	179.3	151.8	19.7
24	137.7	127.7	174.7	146.7	20.2

Table 4.1 continued

Time (h)	EE2 Sample 1 (μg/L)	Sample 2 (μg/L)	Sample 3 (μg/L)	Average (μg/L)	Standard Deviation (μg/L)
Background	5.6	1.3	2.0	3.0	1.9
0	205.6	201.3	202.0	203.0	1.9
0.25	133.3	73.6	131.7	112.9	27.8
1	103.3	101.6	127.4	110.8	11.8
2	105.6	139.4	151.8	132.3	19.5
3.5	94.8	123.4	175.0	131.1	33.2
5	94.2	135.6	150.0	126.6	23.7
7	93.7	149.6	153.0	132.1	27.2
20	73.3	144.2	144.3	120.6	33.4
24	83.8	99.5	149.4	110.9	28.0
Time (h)	TCS Sample 1 (μg/L)	Sample 2 (μg/L)	Sample 3 (μg/L)	Average (μg/L)	Standard Deviation (μg/L)
Background	4.1	2.8	1.2	2.7	1.2
0	204.1	202.8	201.2	202.7	1.2
0.25	24.1	8.9	8.0	13.7	7.4
1	20.3	6.2	7.7	11.4	6.4
2	19.6	20.0	20.3	20.0	0.3
3.5	18.3	18.7	25.3	20.8	3.2
5	17.9	18.0	16.5	17.5	0.7
7	14.7	15.2	22.2	17.4	3.4
20	10.1	15.4	24.1	16.5	5.8
24	10.5	15.9	21.7	16.0	4.6

a. The concentration in liquid phase before MCs stock solutions were added to the sample.

b. The concentration immediately after adding MCs stock solution.

Fig. 4.1 shows the liquid phase MCs concentrations at different times after MCs were added. From Fig. 4.1, it can be seen that the liquid phase concentrations of the three

chosen compounds dropped rapidly at the first 0.25 h, then the concentration slowly dropped to 150, 120 and 20 μg/L for BPA, EE2 and TCS, respectively, and then fluctuated. The equilibrium time for three chosen MCs is around 7 h. The equilibrium time found in this study is close to other reported studies.

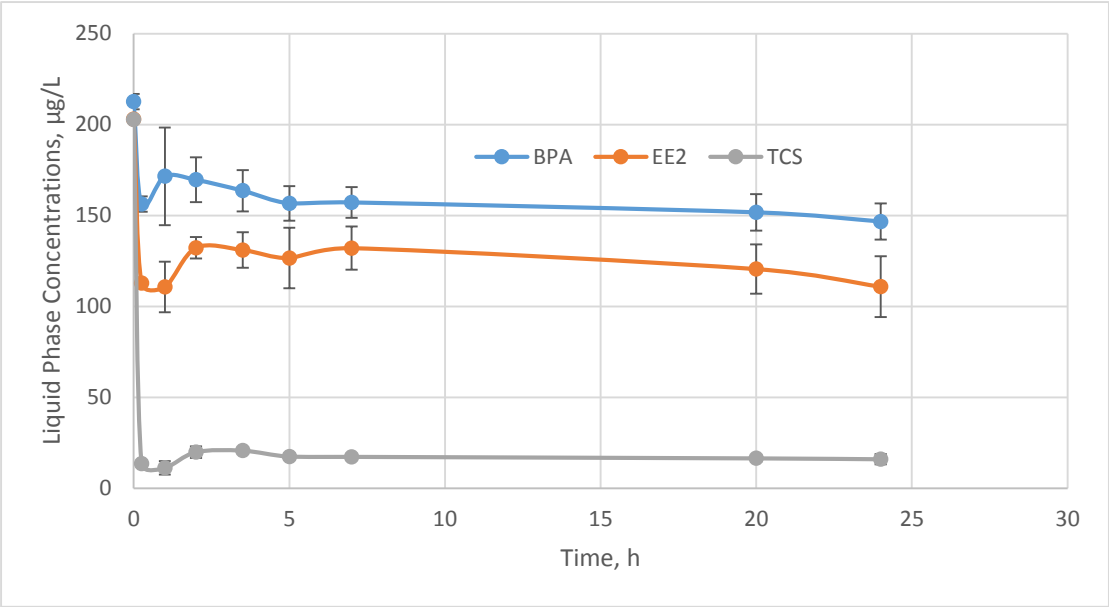


Figure 4.1 Liquid Phase MCs Concentration over 24 h Mixing with Primary Sludge Mixture (n=3)

A similar experiment was conducted by Banihashemi et al. (2014). The same MCs were added into deactivated AS generated at SRTs of 5, 10 and 15 days. The sorption equilibrium times were found to be 2, 4 and 6 h for BPA, TCS and EE2, respectively. Another study conducted by Clara et al. (2004) performed sorption kinetics experiments between BPA, E2, EE2 and inactivated AS. The equilibrium times for BPA and EE2 were found to be 2 and 8-10 h, respectively.

The experimental data were further analyzed for sorption kinetics models. Q_t, the solid phase concentrations at different times were calculated according to Eq. 2.21. Q_e, the solid phase concentration under equilibrium time was the average solid phase concentration after 7 h reaction (after 7 h, the system is considered to reach steady state).

For the pseudo first-order rate model, the term $\ln\left(\frac{Q_e-Q_t}{Q_e}\right)$ was calculated and then plotted against time according to Eq. 2.18. Linear regression was applied to obtain the

constant rate k_1. Since the unit of time here is h, k_1 has a corresponding unit of h^{-1}. Fig. 4.2 shows the linear regression results for the pseudo first-order rate model. Some points at the certain time series were eliminated since $\ln\left(\frac{Q_e - Q_t}{Q_e}\right)$ was mathematically impossible to calculate. This happens when Q_t equals to or is larger than Q_e.

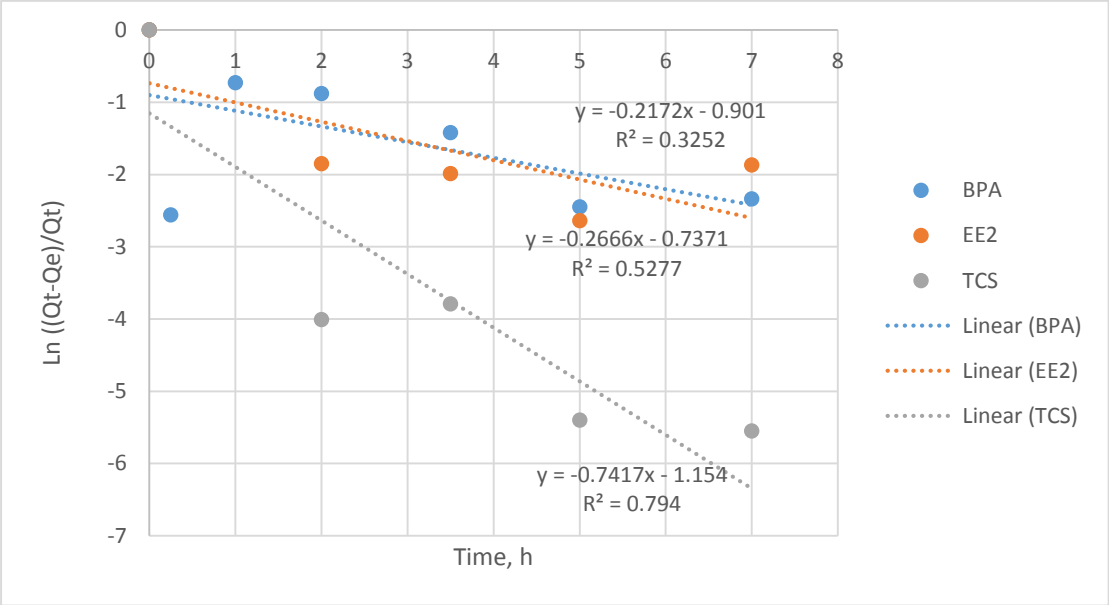


Figure 4.2 Linear Regression Results for the Pseudo First-order Rate Model [a]

a. The linear regression lines for BPA and EE2 are very close and overlap.

For the pseudo second -order rate model, the term t/Q_t is plotted against time according to Eq. 2.20, which is shown in Fig 4.3.

As seen by comparing Figs. 4.2 and 4.3, the pseudo second-order rate model describes experimental data much better than the pseudo first-order rate model. The rate constants, k_1 and k_2 were calculated and they are summarized in Table 4.2.

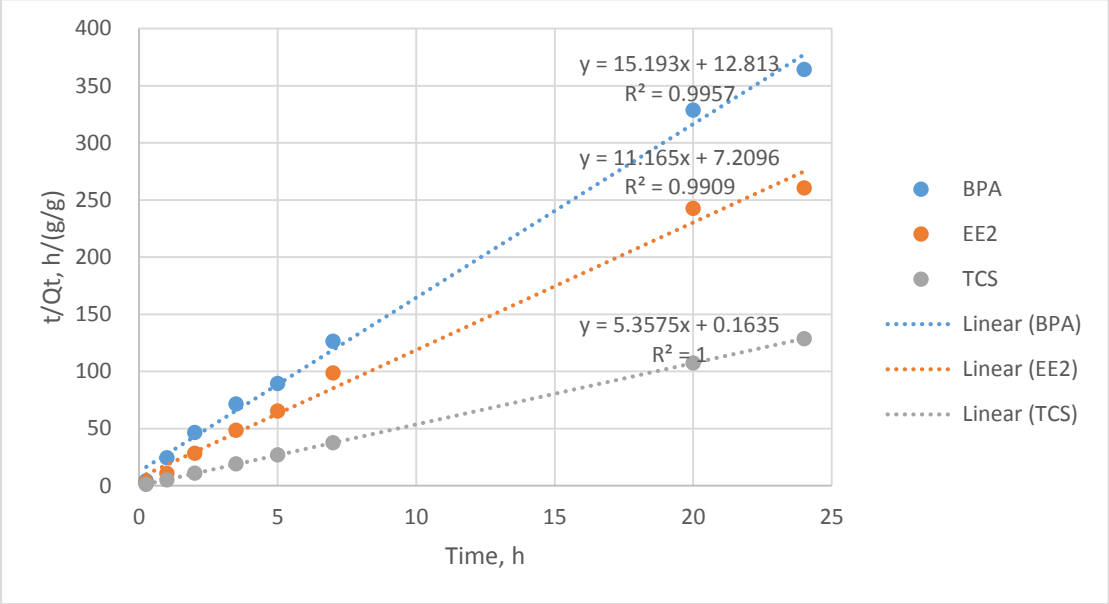


Figure 4.3 Linear Regression Results for the Pseudo Second-order Rate Model

Table 4.2 Rate Constants of Pseudo First-order and Second-order Rate Models for BPA, EE2 and TCS

Pseudo First-order	BPA		EE2		TCS	
	K_1 (h^{-1})	R^2	K_1 (h^{-1})	R^2	K_1 (h^{-1})	R^2
	0.22	0.33	0.27	0.53	0.74	0.79
Pseudo Second-order	BPA		EE2		TCS	
	K_2 (h^{-1})	R^2	K_2 (h^{-1})	R^2	K_2 (h^{-1})	R^2
	18.2	0.996	17.3	0.99	175.6	1

4.2 Sorption Isotherms for MCs Sorbed onto Primary Sludge

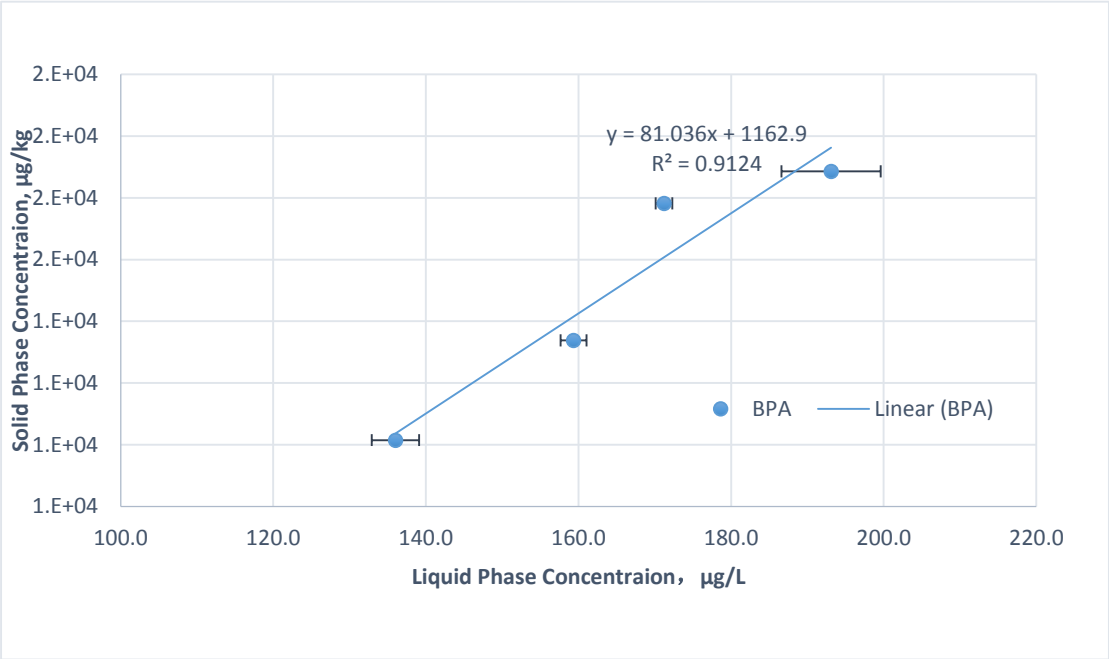
The sorption isotherm tests were conducted with primary sludge. Four 100 mL sludge mixtures containing 1.25, 0.75, 0.5 and 0.1 g dewatered primary sludge with TSS concentrations of 2650, 1485, 905 and 210 mg/L, respectively, were used.

Table 4.3 lists liquid concentrations, standard deviation and the calculated solid phase concentrations as well as log K_d and R^2.

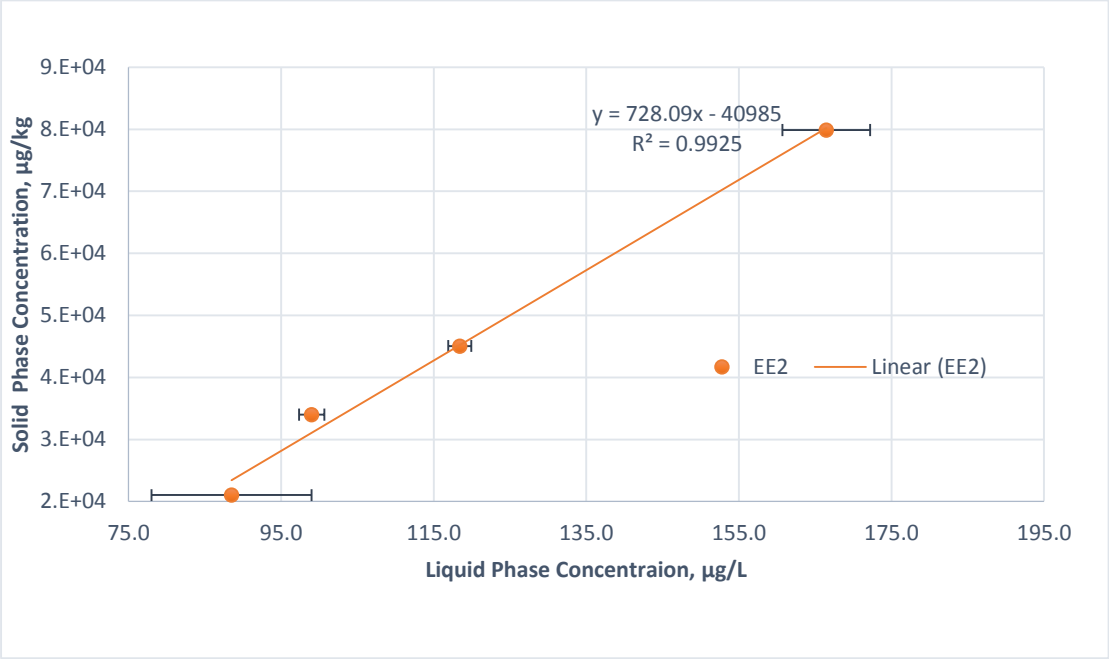
Table 4.3 K_d and R^2 Values for MCs Absorbed onto Primary Sludge

		Average Liquid Phase Concentration (n=3, μg/L)	Standard Deviation (μg/L)	Solid Phase Concentration (μg/g)	K_d	log K_d	R^2
BPA	Sample 1	136.0	6.8	44.0	81	1.9	0.91
	Sample 2	159.2	3.2	47.4			
	Sample 3	171.2	1.7	51.7			
	Sample 4	193.1	13.5	52.7			
EE2	Sample 1	88.5	21.2	155.1	728	2.9	0.99
	Sample 2	99.0	4.0	181.0			
	Sample 3	117.9	2.4	203.8			
	Sample 4	166.5	11.7	272.8			
TCS	Sample 1	5.0	0.3	78.4	6,407	3.8	1
	Sample 2	9.4	1.1	133.2			
	Sample 3	15.0	1.5	209.2			
	Sample 4	53.6	5.9	701.7			

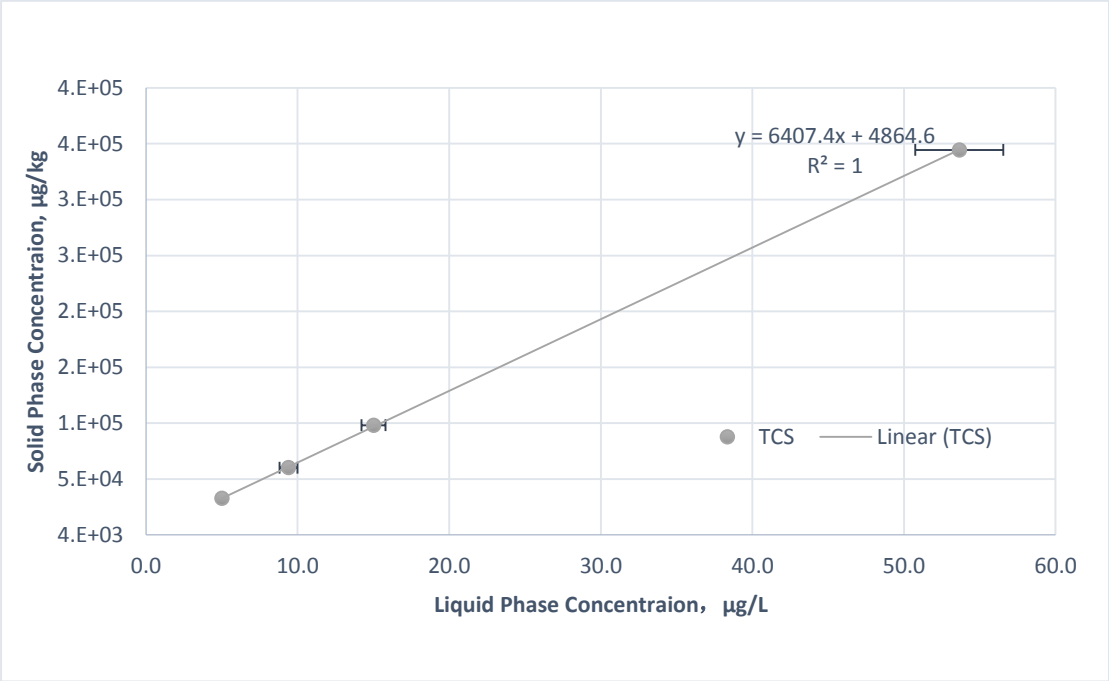
Results for the initial solid phase concentrations in primary sludge show that among the three MCs, EE2 has the highest concentration of 113 ηg/g, followed by BPA, 20 ηg/g, and TCS, 5 ηg/g. The initial solid phase concentrations were taken into consideration when calculating the equilibrium solid phase concentrations. The aluminum concentration in the sludge obtained from ROPEC was measured by inductively coupled plasma – mass spectrometry. The aluminum concentration was found to be about 3 μg/g in the dried sludge.



a. Sorption Isotherm of BPA



b. Sorption Isotherm of EE2



c. Sorption Isotherm of TCS

Figure 4.4 Sorption Isotherms and Linear Regression for MCs Sorbed onto Primary Sludge

As shown in Fig. 4.4, good fits were found between the linear model and experimental data for EE2 and TCS. The R^2 values for EE2 and TCS are 0.99 and 1, respectively. The linear solids-liquid partitioning coefficient (K_d) found for EE2 is 728 L/kg (log K_d = 2.9), while for TCS it is almost 10 times higher, 6,407 L/kg (log K_d = 3.8). The experimental data for BPA have a poorer fit for the linear sorption model indicating with an R^2 value of 0.91. The K_d value for BPA is 81 L/kg (log K_d =1.9).

Studies focusing on MCs adsorbing onto primary sludge are rare. The log K_d of EE2, reported in the literature, ranges from 2.1 to 2.9 (Carballa et al., 2008; Ternes et al., 2004). The log K_d of EE2 found in this study is at the higher end of the range of reported data. No similar studies were found for BPA and TCS.

4.3 Performance of Bench-scale Continuous Flow Bioreactor

As stated in the previous chapter, three 3 L-porous pot bioreactors were used to simulate a continuous flow AS system. The SRTs for the three reactors were 15, 10 and 5 d with

the HRT being 6 h for all reactors. Before dosing alum, the reactors were run for one month (from Jun. 24 to Jul. 23, 2013). Alum was then dosed at the concentration of 7.6 (from Jul. 24 to Sep. 5, 2013), 13 (from Sep. 6 to Oct. 31st, 2013) and 19.4 mg/L as Al (from Nov. 1 to Dec. 16, 2013), but as shown in Section 3.2, only approximately 25% of the alum was actually pumped into reactors.

The sorption isotherm tests were conducted for the AS collected from the bioreactors when they were operating at steady state. Effluent chemical oxygen demand (COD) and TSS, VSS were monitored on a daily basis. When the effluent COD and TSS, VSS fluctuate within ±10%, steady state is considered reached.

AS was collected after the reactors reached steady state. Usually it took 20 to 30 days to reach steady state. Average TSS, VSS and VSS/TSS ratio at steady state were calculated and are summarized in Table 4.4 .

Table 4.4 Average TSS, VSS and VSS/TSS Ratio at Steady State (n=10)

		No Alum Added	Alum Dosage 1	Alum Dosage 2	Alum Dosage 3
Reactor 1 SRT=15 d	TSS (mg/L)	3520	3286	4110	3341
	VSS (mg/L)	3274	2668	3344	2924
	VSS/TSS Ratio (%)	93	81	81	88
Reactor 2 SRT=10 d	TSS (mg/L)	2634	2551	3013	2417
	VSS (mg/L)	2471	2111	2509	2143
	VSS/TSS Ratio (%)	94	83	83	89
Reactor 3 SRT=5 d	TSS (mg/L)	1729	1726	1695	1299
	VSS (mg/L)	1617	1549	1413	1180
	VSS/TSS Ratio (%)	94	90	83	91

From Table 4.4 and Fig. 4.5, it is obvious that the reactor with the highest SRT has the highest TSS, VSS concentrations but a lower VSS/TSS ratio. At the aluminum dosage 2, reactors 1 and 2 have the highest TSS and VSS concentrations. However, for reactor 3, increasing aluminum dosage resulted in a decline in both TSS and VSS concentrations.

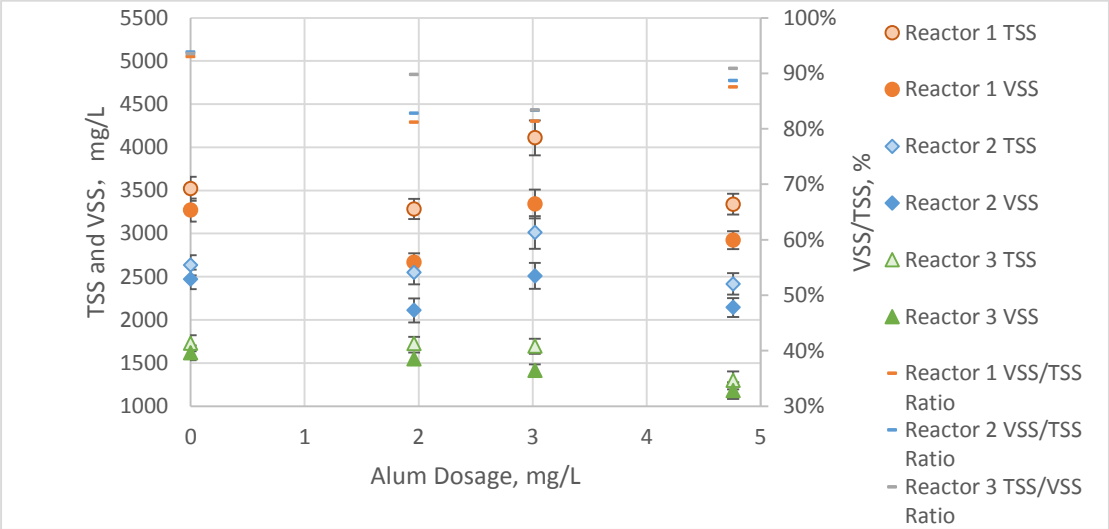


Figure 4.5 Average TSS, VSS and VSS/TSS at Different Alum Doses (n=10)

The VSS/TSS ratios when no alum was added into the influent were 93 to 94% and this ratio decreased after alum addition. The theoretical VSS/TSS ratios were calculated according to Eq. 3.3 and compared with measured results. The alum concentrations used were the adjusted aluminum concentration, i.e., 1.95, 3.02 and 4.73 mg/L. The comparison is shown in Fig. 4.6. The theoretical VSS/TSS ratios are shown in triangles and the measured results are shown in short bars.

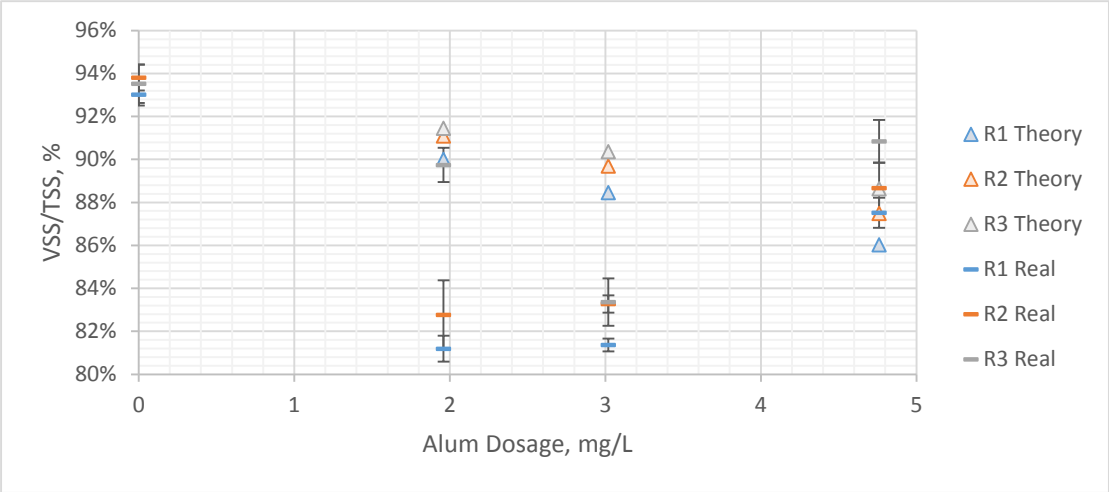


Figure 4.6 Comparison of Theoretical and Measured VSS/TSS Ratios (n=10)

In theory, when aluminum dosage increases, VSS/TSS ratios decrease. The measured values are lower than the predicted ones at the aluminum dosages 1 and 2. One of the assumptions for Eq. 3.3 is that aluminum does not influence the VSS of each reactors,

however, it is not necessarily the case. Although aluminum is inorganic and therefore is not part of VSS, it may have an influence on the components contributing to VSS, in this case, biomass. After adding aluminum, a decrease in VSS of all reactors was observed (except for reactor 2 at the second aluminum dosage).

The effluent COD measured daily at the first alum dosage is total COD, while at the other two alum dosages, soluble effluent COD was measured daily. Although, at the end of each phase, both effluent total COD and soluble COD were tested twice for the record. Since the number of samples is too low to be statistically significant, Table 4.5 lists the total COD concentration and the estimated soluble COD for first phase while soluble COD for other two phases. Table 4.6 shows the results of effluent total and soluble COD at the end of each phase.

From Table 4.6, the soluble COD concentrations were 78 to 103% of the total COD in the effluent. If calculated soluble COD for the first phase is based on such ratio range (78-103%), the soluble COD for reactors 1, 2 and 3 are in the range of 20.4- 26.3, 22.6-29.1, and 18.8-24.2 mg/L, respectively.

In the study conducted by Banihashemi (2012), the mean total COD concentrations in the effluent of reactors 1, 2 and 3 (corresponding SRTs are 15, 10 and 5 d) were 21.5, 22.7, and 23.15 mg/L, respectively. In comparison, adding alum does not show a significant effect on COD removal.

Table 4.5 Average Effluent COD (mg/L) at Steady State (n=10)

	Alum Dosage 1[a]	Alum Dosage 1[b]	Alum Dosage 2	Alum Dosage 3
Reactor 1	25.5	20.4- 26.3	15.0	14.5
Reactor 2	28.2	22.6-29.1	16.0	15.5
Reactor 3	23.5	18.8-24.2	18.1	16.4

a. The COD value tested under first aluminum dosage is total COD, the other COD values are soluble COD for which the sample was filtered by membrane filter (0.22 μm). b. This column shows the estimated soluble COD for first phase assuming soluble COD is 78 to 103% of the total COD.

The results above are further presented in Fig. 4.4:

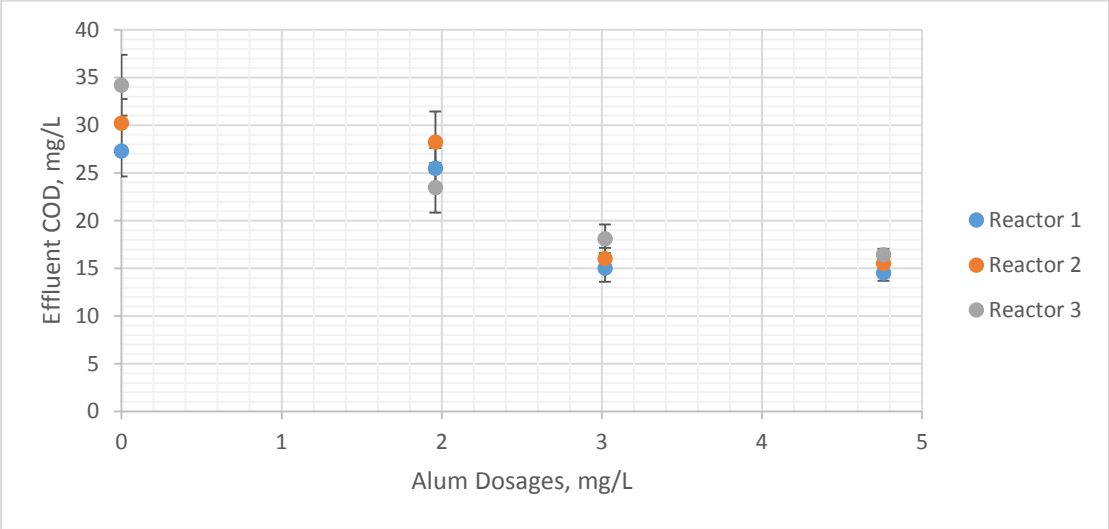


Figure 4.7 Effluent CODs for Three Reactors at Different Alum Doses (n=10)

Figs. A.1 to A.4 in Appendix A present the daily effluent COD and TSS, VSS of three bioreactors for the three alum dosages.

Table 4.6 Total and Soluble COD at the End of Each Phase (n=2)

			R1	R2	R3
Phase 1	Total COD	Sample 1	37.0	45.4	30.6
		Sample 2	40.1	47.1	31.2
		Average	38.6	46.3	30.9
	Soluble COD	Sample 1	39.7	43.4	31.2
		Sample 2		41.5	30.6
		Average	39.7	42.5	30.9
	Soluble COD/Total COD		103%	92%	100%
Phase 2	Total COD	Sample 1	21.0	14.0	26.0
		Sample 2	15.0	15.0	13.0
		Average	18.0	14.5	19.5
	Soluble COD	Sample 1	15.0	14.0	21.0
		Sample 2	13.0	14.0	11.0
		Average	14.0	14.0	16.0
	Soluble COD/Total COD		78%	97%	82%
Phase 3	Total COD	Sample 1	30.0	25.0	21.0
		Sample 2	18.0	22.0	23.0
		Average	24.0	23.5	22.0
	Soluble COD	Sample 1	24.0	22.0	23.0
		Sample 2	24.0	19.0	20.0
		Average	24.0	20.5	21.5
	Soluble COD/Total COD		100%	87%	98%

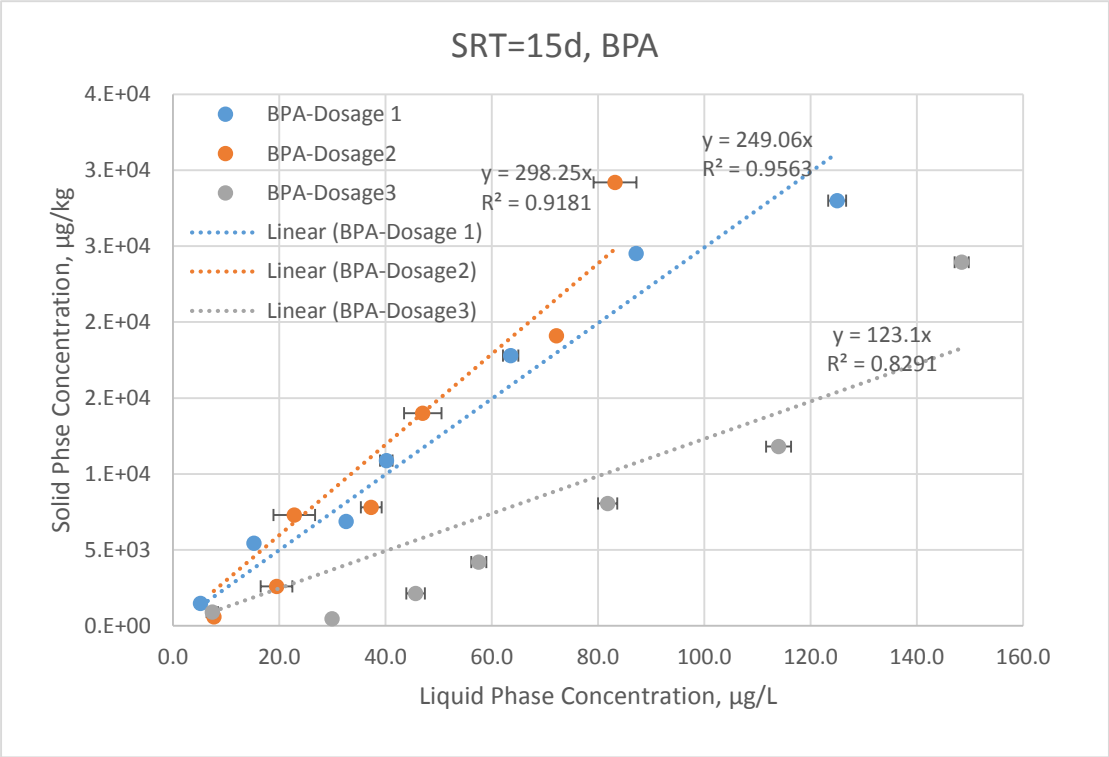
Zahid et al. (2012) investigated the effects of alum addition on the treatment performance of cloth-media membrane bioreactor. The results shows that at alum dosage of 7.5 and 15 mg/L enhanced phosphorus removal while it did not influence the effluent turbidity, ammonia, TKN and COD. They also found that dosing alum above 60 mg/L to AS in batch experiments has an effect on autotrophic bacteria with significant reduction in nitrification. Thus they suggested that "using alum doses below 60 mg/L is required to avoid any inhibitory effects on the sludge microbiological activity". In other literature (Guo et al., 2010; Rogalla et al., 1990), nitrification inhibition was reported while no influence of COD removal was observed after alum addition.

4.4 Sorption Isotherms for MCs Sorbed onto Activated Sludge

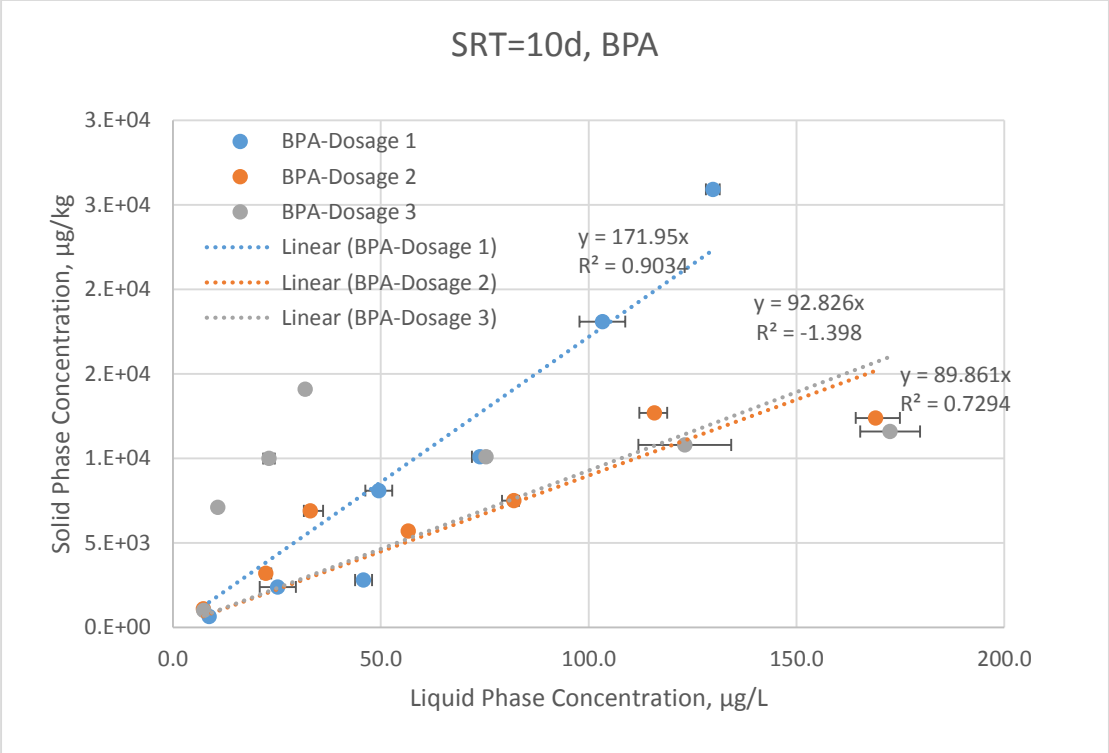
AS was generated from the bench-scale continuous flow wastewater treatment system in the lab. One month was allowed for the microorganisms to adapt to lab conditions in the bioreactors. The characteristics of the biomass were presented in the previous section. After 1 month operation, background MC concentrations were measured in the effluent from each reactor. Results show that concentrations for BPA, EE2 and TCS were below detection limits.

MCs were injected into each sample (100 mL mixed liquor) according to the determined initial liquid concentrations. Only the liquid phase concentrations were tested; solid phase concentrations were calculated by Eq. 2.21. All samples were carried out in triplicate.

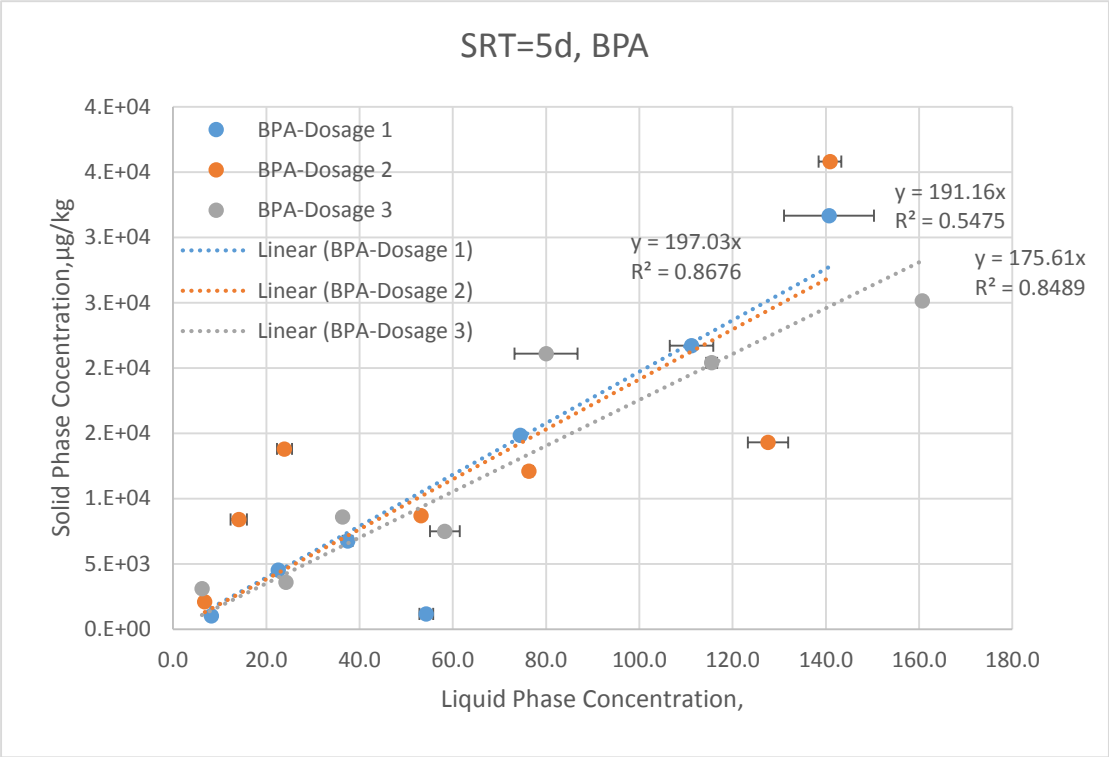
Figures for the sorption isotherms are presented below:



a. Sorption Isotherms of BPA onto Activated Sludge at SRT of 15 d.

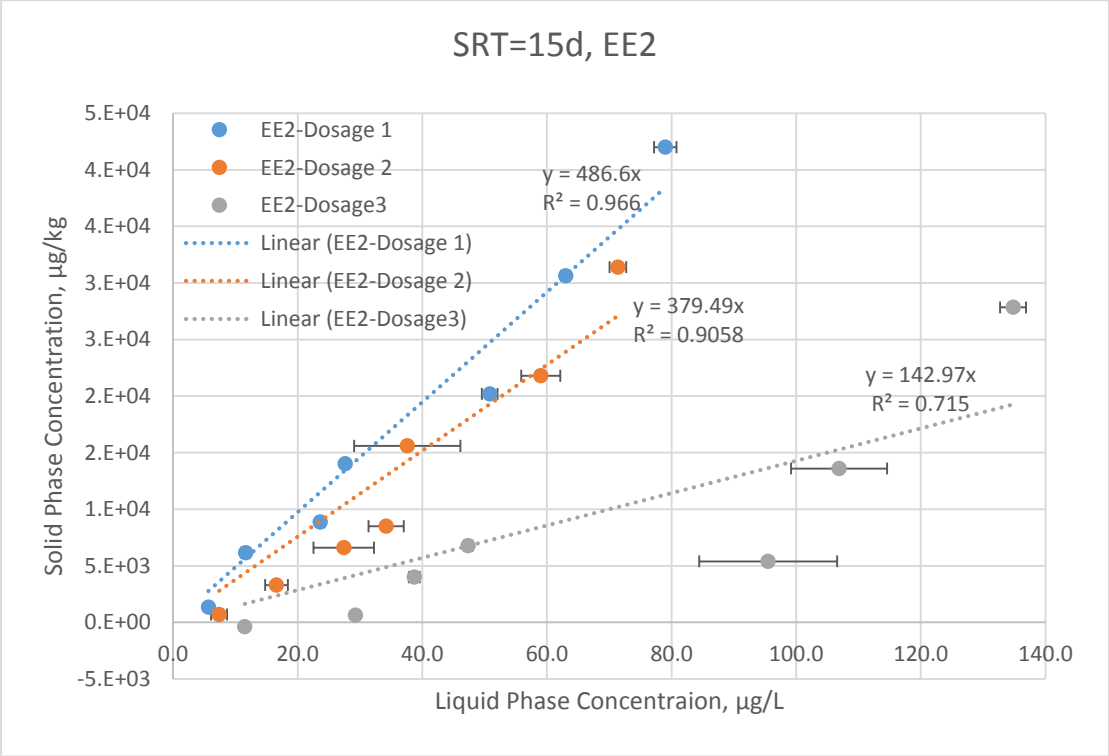


b. Sorption Isotherms of BPA onto Activated Sludge at SRT of 10 d.

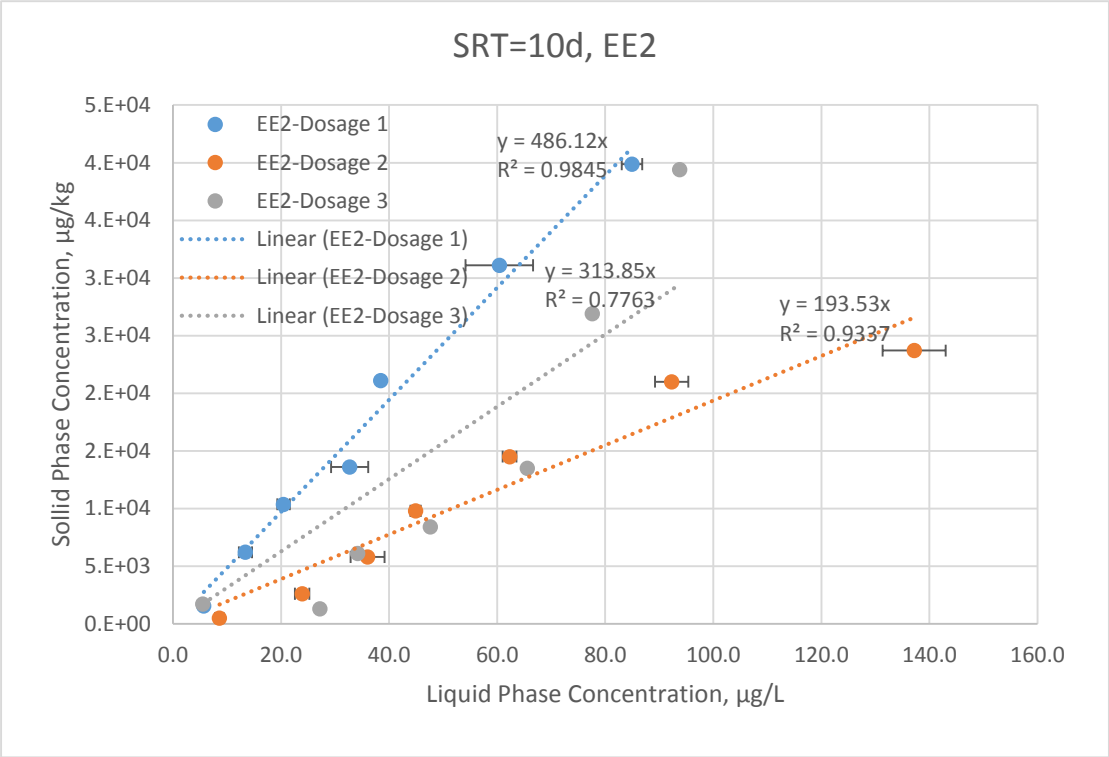


c. Sorption Isotherms of BPA onto Activated Sludge at SRT of 5 d.

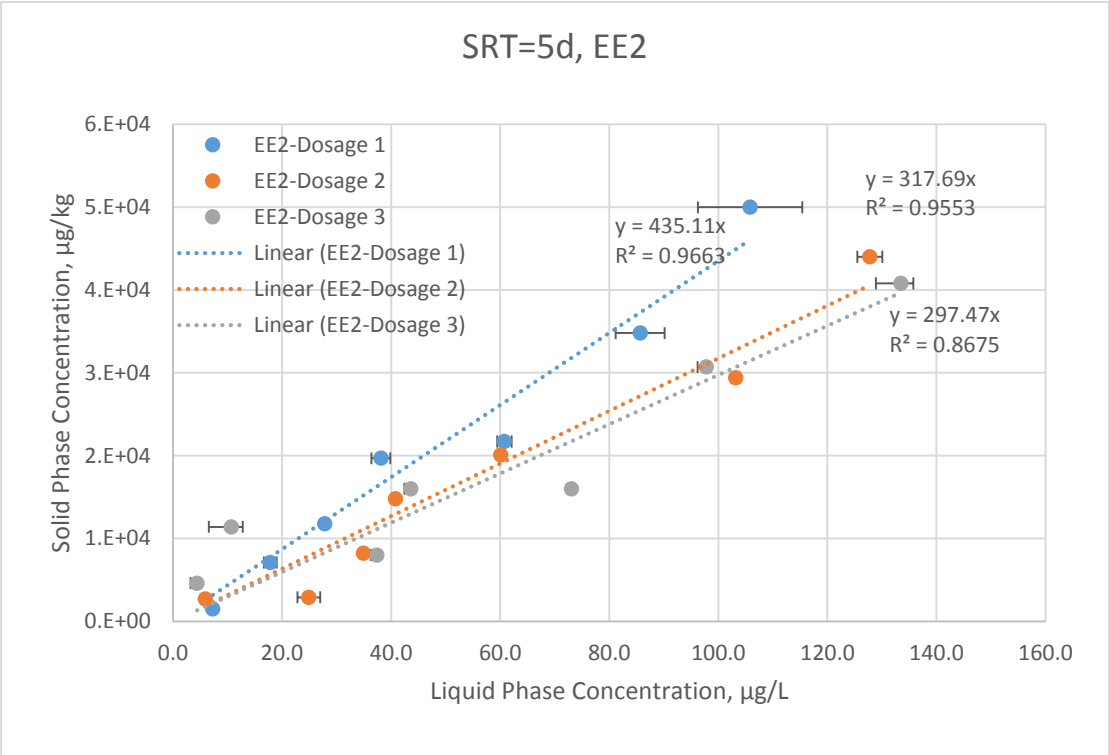
Figure 4.8 Sorption Isotherms of BPA for Activated Sludge



a. Sorption Isotherms of EE2 onto Activated Sludge at SRT of 15 d

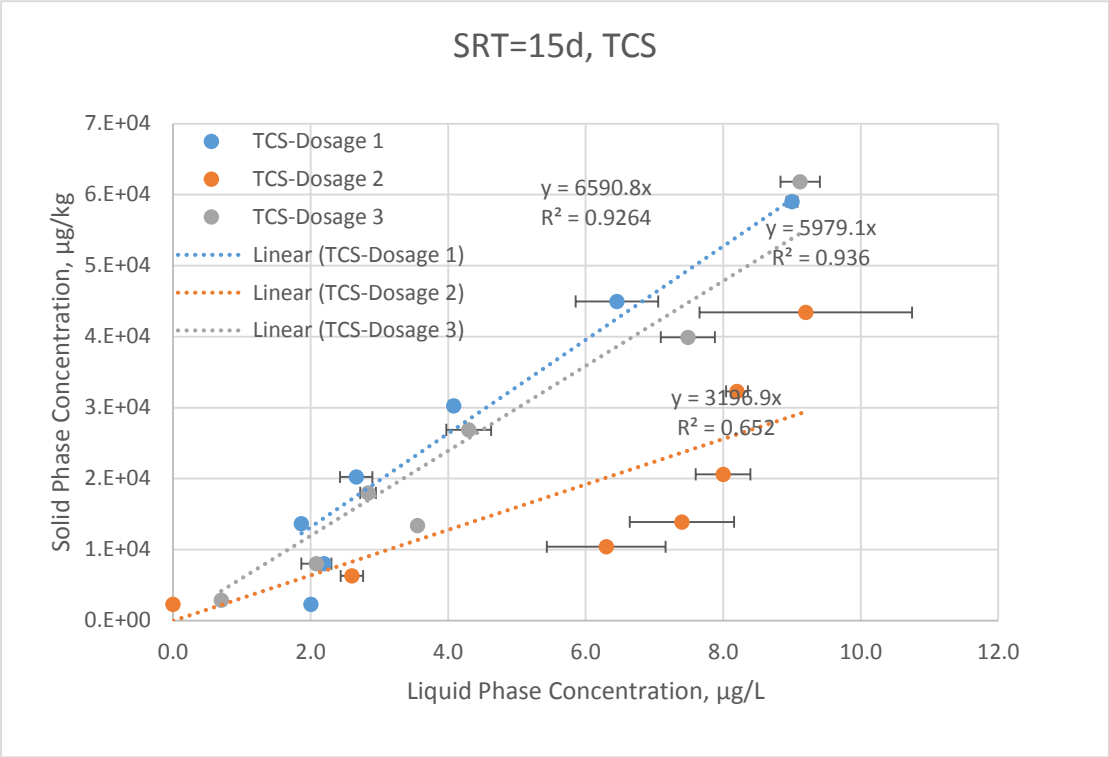


b. Sorption Isotherms of EE2 onto Activated Sludge at SRT of 10 d.

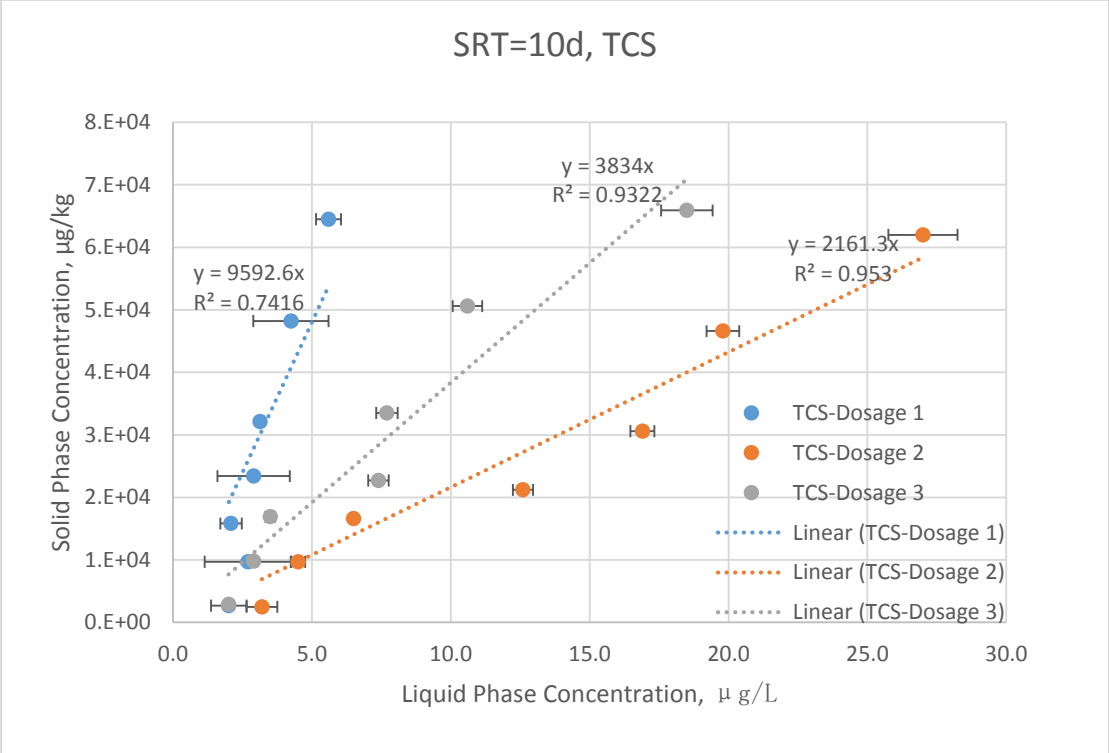


c. Sorption Isotherms of EE2 onto Activated Sludge at SRT of 5 d

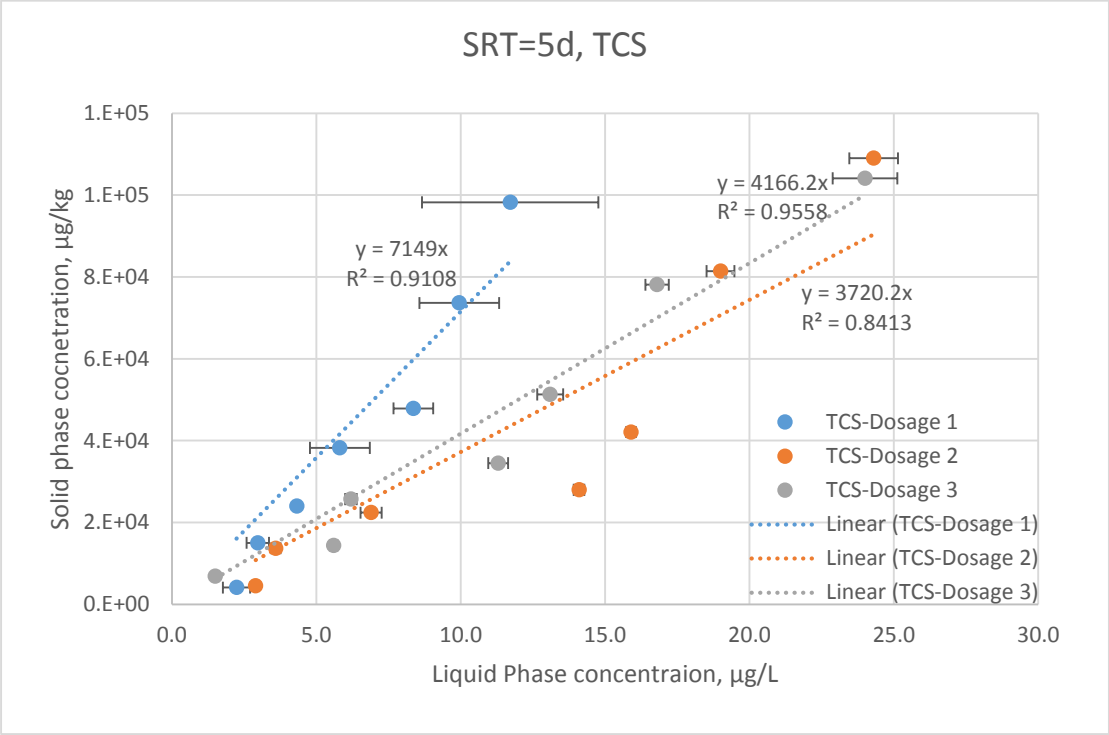
Figure 4.9 Sorption Isotherms of EE2 onto Activated Sludge



a. Sorption Isotherms of TCS onto Activated Sludge at SRT of 15 d.



b. Sorption Isotherms of TCS onto Activated Sludge at SRT of 10 d.



c. Sorption Isotherms of TCS onto Activated Sludge at SRT of 5 d

Figure 4.10 Sorption Isotherms of TCS onto Activated Sludge

The K_d values and corresponding R^2 values are summarized in the Table 4.7. BPA was found to be sorbed to AS at the lowest level (K_d : 90-300 L/kg, log K_d = 2.0-2.5). EE2 has a relatively higher K_d, ranging from 140 to 490 L/kg (log K_d = 2.2-2.7). TCS absorbed to AS the most with K_d value ranging from 2,160 to 7,110 L/kg (log K_d = 3.4-4.0), almost 10 times higher than the other two MCs.

Table 4.7 Sorption Coefficient K_d and R^2

		Alum Dosage 1			Alum Dosage 2			Alum Dosage 3		
		K_d (L/kg)	log K_d	R^2	K_d (L/kg)	log K_d	R^2	K_d (L/kg)	log K_d	R^2
BPA	R1	249	2.4	0.96	298	2.5	0.92	123	2.1	0.83
	R2	172	2.2	0.90	90	2.0	0.73	93	2.0	-1.40
	R3	211	2.3	0.99	191	2.3	0.55	176	2.2	0.85
EE2	R1	520	2.7	0.97	380	2.6	0.91	143	2.2	0.72
	R2	486	2.7	0.98	194	2.3	0.93	314	2.5	0.78
	R3	435	2.6	0.97	318	2.5	0.96	298	2.5	0.87
TCS	R1	6,591	3.8	0.97	3,197	3.5	0.91	5,979	3.8	0.72
	R2	9,593	4.0	0.74	2,338	3.4	0.95	3,834	3.6	0.93
	R3	7,113	3.9	0.91	3,720	3.6	0.84	4,166	3.6	0.96

Stasinakis et al. (2010) studied the fate of BPA and TCS in three continuous-flow AS systems, operating at SRTs of 3, 10 and 20 d. Batch experiments were carried out by adding BPA and TCS into sterilized AS, with the initial liquid phase concentration range from 10 to 500 μg/L. The results are presented in Table 4.8. They concluded that SRT seems to have no influence on K_d of BPA and TCS. However, they found log K_d for BPA ranges from 0.5-0.9, which is much lower than that found in this study. On the contrary, the log K_d (5.7-8.6) for TCS Stasinakis et al. (2010) found is much higher. Table 4.8 has the reported log K_d from several studies. The log K_d found in this study are close to the range of other studies except for Stasinakis' study discussed above.

The different log K_d found in different studies may result from several reasons. Firstly, the sludge used in different studies was generated in different ways. It may be cultivated from a lab-scale reactor or generated from local WWTPs. Sludge cultivated in the lab is more controllable than that generated from WWTPs since the feed water composition, SRT, HRT in the lab are more constant. In addition, lab-generated sludge can make sure that no background MCs will be presented. Secondly, the initial liquid MCs concentrations vary from studies. The K_d is only independent from initial liquid phase concentrations when it is in a low concentration range. However, in the studies shown in Table 4.8, the initial liquid phase concentrations go up to 5 mg/L; although no evidence shows that saturation of sludge occurs under this condition. Last but not least, an improper inhibition technique applied to inactivate the sludge may change the sludge structure, thus altering the sorption behavior of MCs. Hamon et al. (2014) evaluated common AS inhibition techniques including thermal, chemical and air purging. They concluded that "thermal techniques irreversibility damage the AS structure and are not suitable to assess sorption properties"; chemical inhibition, which is the technique used in this study, can also alter the structure of the sludge; air purging is the only techniques which will not cause any change in sludge structure; however, some of the compounds may react with the purging air. Sodium azide, the chemical chosen to inhibit sludge in this study, cannot fully deactivate AS after 20 h reaction at the dosing concentration of

200 mg NaN_3 g TSS^{-1}. In contrast, dosing 100 mg Hg_2SO_4 g TSS^{-1} and 30 mg $HgCl_2$ gTSS^{-1}, a complete deactivation would be achieved within 2 h of reaction.

Log K_d values for primary sludge are close to the log K_d value ranges. The log K_d for BPA sorbed to primary sludge is at the lower range of log K_d for BPA sorbed to AS, on the contrary, the log K_d for EE2 and TCS sorbed to primary sludge is at the higher range of log K_d based on AS. No significant differences were observed for these two different types of sludge.

From this study and in agreement with the literature, the effect of SRT is not consistent and varies with respect to the agent being sorbed.

Table 4.8 Literature Reported log K_d for BPA, EE2 and TCS

BPA				
log K_d [a]	Reference	Adsorbents	Inhibition Techniques	Initial Liquid Phase Concentrations
0.6	(Stasinakis et al., 2010)	Deactivated AS, SRT of 3 d	Pasteurization at 103ºC for 3 h.	10, 40, 80, 120, 200, 350 and
0.9		Deactivated AS, SRT of 10 d		500 μg/L
0.5		Deactivated AS, SRT of 20 d		
2.56	(Zhao et al., 2008)	Deactivated AS, 10ºC	Heating in an autoclave	2, 10, 20, 50, and 100 μg/L
2.53		Deactivated AS, 20 ºC	at 120ºC for 30 min.	
2.49		Deactivated AS, 30 ºC		
EE2				
log K_d	Reference	Adsorbents	Inhibition Techniques	Initial Liquid Phase Concentrations
2.84	(Clara et al., 2004)	Deactivated AS, pH 3 to 12.	Implemented with 0.5 mL mercury sulfate ($Hg_2 SO_4$, 200 g/L)	1, 3, 5 and 7 g TSS L^{-1} [b]
2.4	(Ternes et al., 2004)	Primary sludge get from local WWTPs	Blow argon into sludge to replace oxygen.	1.7 mg/L
2.5		AS get from local WWTPs		
2.7-2.9	(Andersen et al., 2005)	AS get from local WWTPs	Heating at 103ºC for minimum 3 h.	8 ηg/L and 44.3 μg/L
2.1-2.9	(Carballa et al., 2008)	Primary sludge digested under different operation conditions.	Not needed since sludge was already digested	4 μg/L

Table 4.8 continued

TCS				
log K_d	Reference	Adsorbents	Inhibition Techniques	Initial Liquid Phase Concentrations
2.6	(Heidler, 2007)	Digested sludge get from local WWTPs.	Not needed since sludge was already digested	0.1, 3, and 200 µg/L.
8.6	(Stasinakis et al., 2010)	Deactivated AS, SRT of 3 d	Pasteurization at 103ºC for 3 h.	10, 40, 80, 120, 200, 350 and
5.7		Deactivated AS, SRT of 10 d		500 µg/L
7.3		Deactivated AS, SRT of 20 d		

4.5 Comparison of Sorption Isotherms for AS with and without Alum Addition

To study the influence on sorption behavior of selected MCs by adding alum to AS is one of the objectives of this research. As introduced in Chapter 2, most of the study focused on the effect of coagulation to remove MCs; no research has studied the influence of adding alum to AS on MCs sorption. In this section, results from a study conducted by Banihashemi et al. (2014) will be used to make a comparison with the results generated in this study. Banihashemi et al. (2014) operated reactors at conditions identical to those used in this study except that no alum was added. The effect of alum addition on sorption isotherms will be analysed in this chapter.

4.5.1 Sorption Test Conducted with AS without Alum Addition

Experimental details for the other study are recorded in (Banihashemi et al., 2014). The experimental setup, including bioreactor type, synthetic wastewater formula and operation conditions, was the same as described in Chapter 3 except no alum was added to the influent. For the sorption studies, the same reagent, sodium azide was used to deactivate AS at the same dosage. As described in Banihashemi's study, the initial MCs concentrations were 5, 10, 20, 50, 100 and 200 μg/L. Six 1 L samples were put on a shaker and mixed for 24 h, and both liquid and solid phase concentrations were tested. The experimental data were subjected to linear regression analysis using linear, Langmuir and Freundlich models. Table 4.9 has the parameters and R^2 values for the three isotherm models

Table 4.9 Sorption Isotherm Parameters and R^2 Values for BPA, EE2 and TCS with the Absorbent being AS without Alum Addition (Banihashemi et al., 2014)

BPA		Linear Model		Freundlich Model			Langmuir Model	
	SRT (d)	K_d (L/kg)	R^2	K_f ($\mu g^{1-1/n} L^{1/n} g^{-1}$)	1/n	R^2	K_l (L/g)	R^2
	15	351	0.987	0.453	0.918	0.989	0.663	0.086
	10	477	0.980	0.48	1.025	0.984	0.504	0.001
	5	319	0.991	0.468	0.867	0.997	0.515	0.345
EE2		Linear Model		Freundlich Model			Langmuir Model	
	SRT (d)	K_d (L/kg)	R^2	K_f ($\mu g^{1-1/n} L^{1/n} g^{-1}$)	1/n	R^2	K_l (L/g)	R^2
	15	901	0.990	0.802	1.031	0.995	0.829	0.065
	10	1,368	0.993	1.389	0.98	0.997	1.332	0.00
	5	1,161	0.994	1.386	0.975	0.995	1.357	0.248
TCS		Linear Model		Freundlich Model			Langmuir Model	
	SRT (d)	K_d (L/kg)	R^2	K_f ($\mu g^{1-1/n} L^{1/n} g^{-1}$)	1/n	R^2	K_l (L/g)	R^2
	15	1,591	0.990	1.035	1.1	0.995	1.082	0.703
	10	2,266	0.998	2.092	1.027	0.998	2.119	0.259
	5	2,018	0.993	2.019	1.005	0.995	2.033	0.003

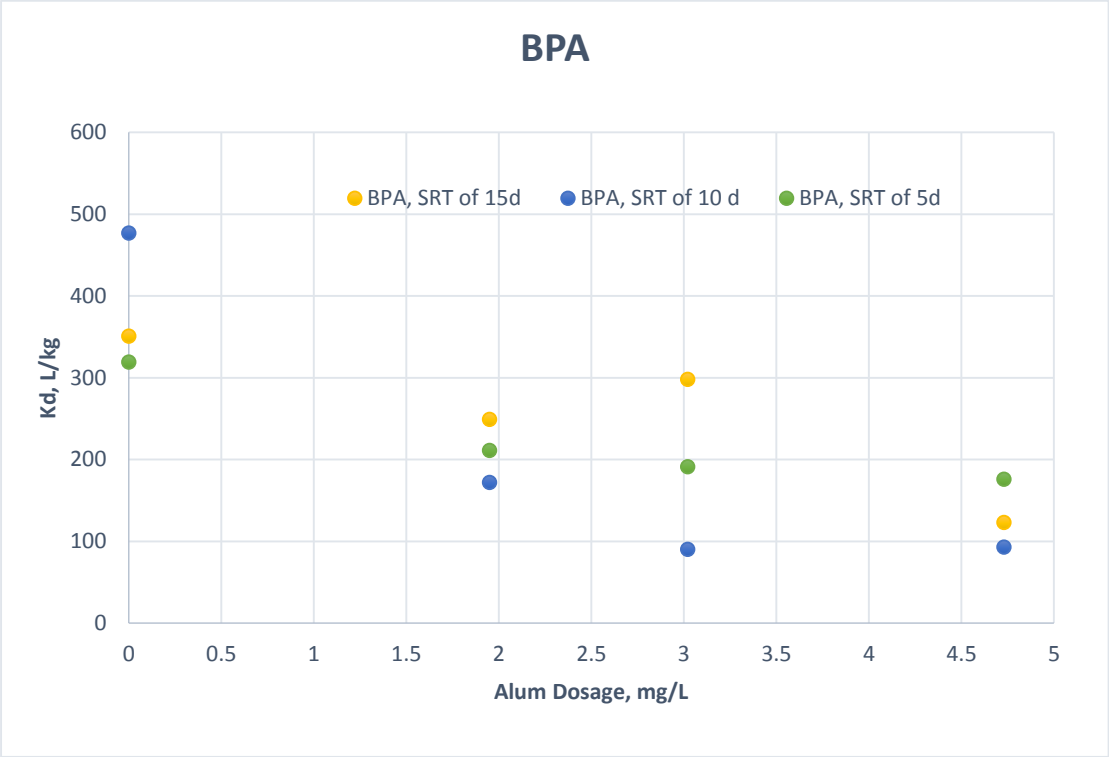
Linear and Freundlich models fit experimental data very well based on the R^2 values. However, Langmuir models had a poor fit. K_d for TCS are the highest between 1,591 to 2,266 L/kg, followed by EE2, 901 to 1,368 L/kg. BPA had the lowest affinity to AS with a K_d between 319 to 477 L/kg. Judging from the K_d values, AS with SRT of 10 d attracts all selected MCs the most, For EE2 and TCS, AS with SRT of 5 d attracts more chemicals than that with SRT of 15 d, while for BPA, the opposite trend existed.

4.5.2 Effects of Alum on Sorption Isotherm

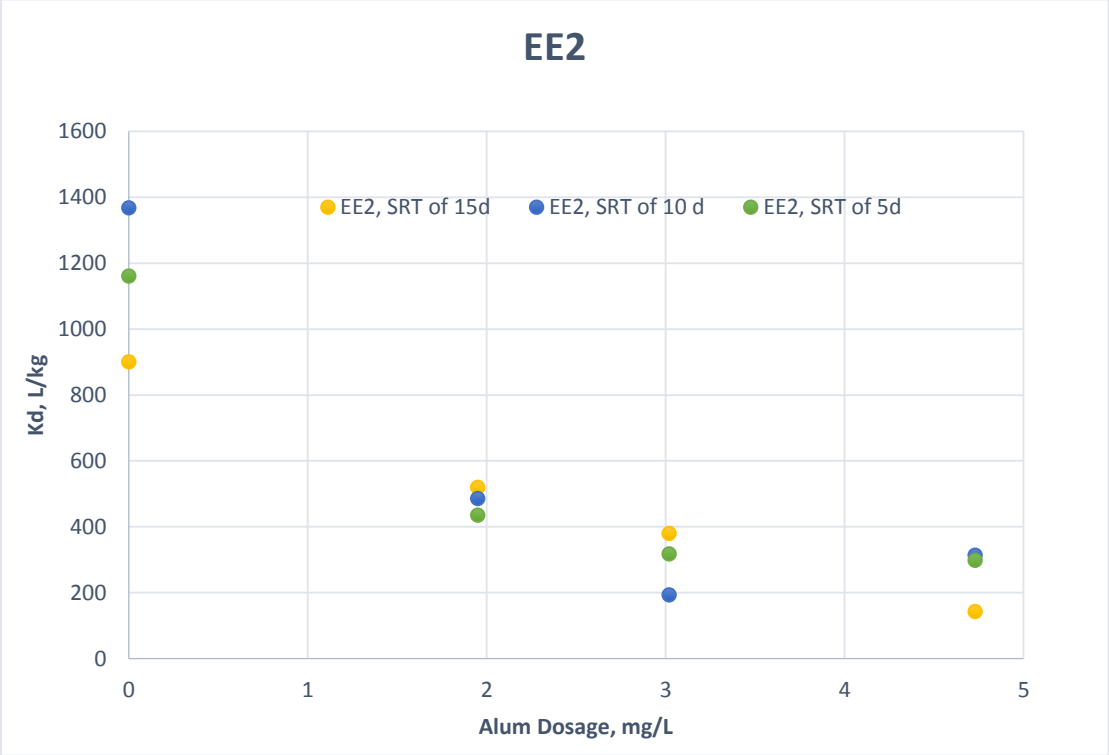
The MCs sorption isotherms with the absorbent being AS with alum addition are reported in Section 4.4. In both studies, TCS shows the strongest affinity to AS, followed by EE2 and BPA.

When compared with the results without alum addition, alum lowers the K_d values for both BPA and EE2, while much higher K_d values for TCS were observed for AS with alum addition (Fig. 4.11). Since there is no alum addition in the study of Banihashemi et al. (2014), in Fig 4.11, the results are shown at alum dosage of zero. For BPA and EE2 it is also clear that increasing alum dose resulted in decreasing K_d.

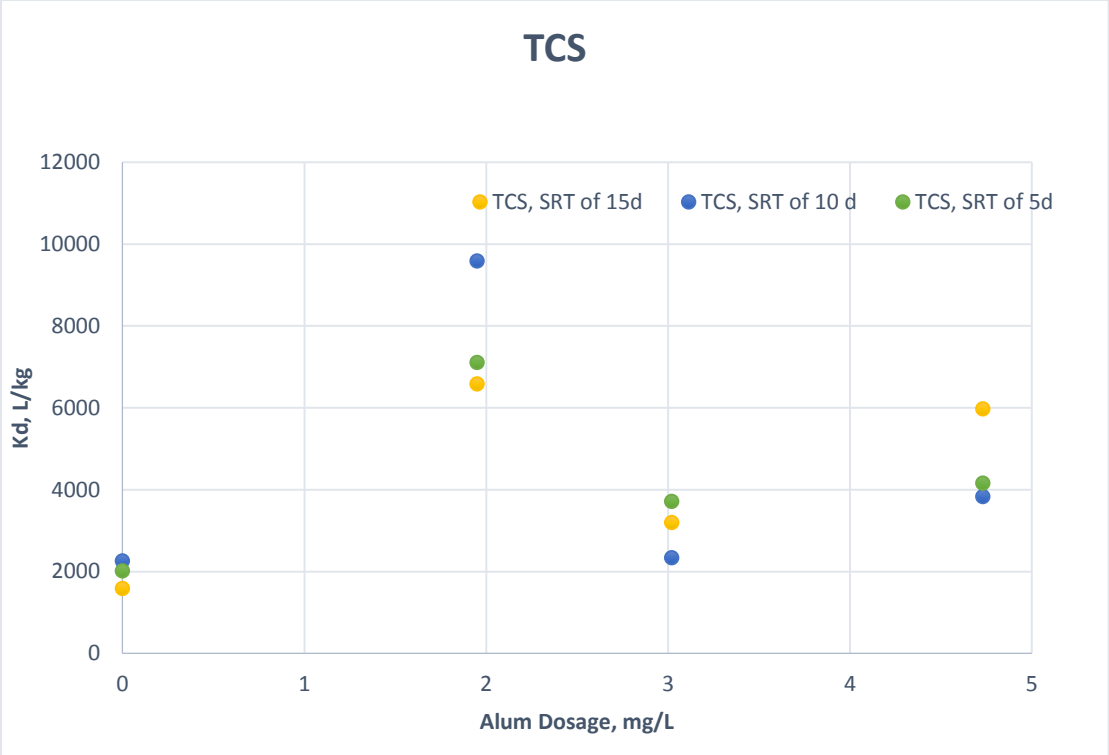
Generally speaking, SRT has no obvious influence on K_d. For sludge without alum addition, sludge under SRT of 10 d has the highest K_d for all three MCs. EE2 and TCS sorbed more to sludge under SRT of 5 d than to sludge under SRT of 15 d, while for BPA, the opposite results were found. As for with alum addition, no clear pattern was found. For BPA at the first and second aluminum dosages, K_d for sludge under SRT of 15 d with alum addition are the highest value, followed by SRT of 5 d and then SRT of 10 d.



a. K_d for BPA under different alum dosage.



b. K_d for EE2 under different alum dosage.



c. K_d for TCS under different alum dosage.

Figure 4.11 Sorption Coefficient, K_d, for BPA, EE2 and TCS under Different Alum Dosages

4.6 Langmuir and Freundlich Sorption Isotherms

In Section 4.4, the linear sorption isotherm model was used to fit the experimental data. However, there are certain sets of data that do not fit the linear model judging from the low R^2 values. In this section, Langmuir and Freundlich adsorption isotherm models were used to fit the experimental data. Linear forms of Freundlich and Langmuir sorption isotherm were applied to experimental data to generate parameters. Values of parameters and corresponding R^2 values are summarized in the following tables.

From Table 4.10, it can be seen that for some sorption isotherms, the Langmuir constants are negative. According to Ramakrishna et al. (1996), a negative Langmuir constant indicate the inadequacy of Langmuir model to explain the sorption process,

while Shah et al. (2011) state that a negative value means the sorption process is difficult to take place. Judging from the low R^2 values, Eq. 2.26 or the Langmuir plot do not provide a good description for the experimental data.

Langmuir isotherm parameters generated from Eq. 2.27 are presented in Table 4.11. Compared with Eq. 2.26, Eq. 2.27 provides a better description of experimental data. However, more negative parameters appear when using Eq. 2.27. In Section 4.5, results show that the Langmuir sorption isotherm is also not good to describe the experimental data when no alum is added to the AS. Table 4.12 shows the parameters for the Freundlich sorption isotherm. The Freundlich isotherm can describe the experimental data well judging from R^2. However, as explained in Section 2.7, the good fit for Freundlich isotherm may result from the insensitivity of the linear form. The same good fit happens to AS without alum addition as discussed in Section 4.5.

Figs. B.1 to B.9 in Appendix B show the experimental data and the regressed sorption isotherms. As indicated by the graphs, the regressed isotherm is more close to data at low sorption values. These phenomena match the literature mentioned in Section 2.8. By observing the figures in Appendix B, Freundlich isotherm models do fit the experimental data better. This is probably because the Freundlich isotherm describes non-ideal and multilayer adsorption, which is more realistic than the Langmuir isotherm. By observing the n values, it can be seen that in most cases, increasing the alum doses tends to increase the heterogeneity of the absorbent surface.

Table 4.10 Parameters for Langmuir Isotherm and Corresponding R^2 Values Generated by Linear Regression Using Eq. 2.26

BPA	SRT (d)	5			10			15		
		Q_m (μg/kg)	K_L (L/μg)	R^2	Q_m (μg/kg)	K_L (L/μg)	R^2	Q_m (μg/kg)	K_L (L/μg)	R^2
	Dosage 1	-6.5×10^{4}	-2.4×10^{-3}	0.38	-1.4×10^{4}	-5.3×10^{-3}	0.61	6.3×10^{4}	5.2×10^{-3}	0.18
	Dosage 2	3.1×10^{4}	1.3×10^{-2}	0.43	2.3×10^{4}	7.6×10^{-3}	0.72	-1.0×10^{4}	-1.1×10^{-2}	0.48
	Dosage 3	7.1×10^{4}	3.3×10^{-3}	0.15	1.4×10^{4}	3.3×10^{-2}	0.80	-5.4×10^{3}	-5.8×10^{-3}	0.19
EE2	SRT (d)	5			10			15		
		Q_m (μg/kg)	K_L (L/μg)	R^2	Q_m (μg/kg)	K_L (L/μg)	R^2	Q_m (μg/kg)	K_L (L/μg)	R^2
	Dosage 1	-7.1×10^{4}	-4.1×10^{-3}	0.26	-9.1×10^{4}	-4.1×10^{-3}	0.28	-9.2×10^{4}	-4.0×10^{-3}	0.24
	Dosage 2	-1.6×10^{4}	-5.7×10^{-3}	0.60	-1.6×10^{4}	-5.7×10^{-3}	0.35	-8.3×10^{4}	2.7×10^{-3}	0.06
	Dosage 3	5.8×10^{4}	9.0×10^{-3}	0.28	-1.2×10^{4}	-7.8×10^{-3}	0.16	1.9×10^{4}	9.3×10^{-3}	0.01
TCS	SRT (d)	5			10			15		
		Q_m (μg/kg)	K_L (L/μg)	R^2	Q_m (μg/kg)	K_L (L/μg)	R^2	Q_m (μg/kg)	K_L (L/μg)	R^2
	Dosage 1	-3.7×10^{4}	-7.0×10^{-3}	0.42	-1.0×10^{-4}	-1.8×10^{-1}	0.14	-2.7×10^{4}	-9.0×10^{-2}	0.28
	Dosage 2	1.1×10^{-5}	2.2×10^{-2}	0.23	-5.9×10^{-4}	-1.9×10^{-2}	0.22	-4.2×10^{4}	-1.2×10^{-1}	0.15
	Dosage 3	4.2×10^{-6}	8.1×10^{-4}	0.08	-8.8×10^{-4}	-2.8×10^{-2}	0.15	9.6×10^{4}	4.2×10^{-2}	0.37

Table 4.11 Parameters for Langmuir Isotherm and Corresponding R^2 values Generated by Linear Regression Using Eq. 2.27

BPA	SRT (d)	5			10			15		
		Q_m(μg/kg)	K_L(L/μg)	R^2	Q_m(μg/kg)	K_L(L/μg)	R^2	Q_m(μg/kg)	K_L(L/μg)	R^2
	Dosage 1	-1.7×10^{4}	-7.1×10^{-3}	0.98	-1.3×10^{4}	-5.7×10^{-3}	0.98	2.5×10^{5}	1.2×10^{-3}	0.99
	Dosage 2	6.2×10^{4}	5.8×10^{-3}	0.86	3.4×10^{4}	4.7×10^{-3}	0.98	-4.1×10^{3}	-1.8×10^{-2}	0.96
	Dosage 3	1.4×10^{4}	4.2×10^{-2}	0.68	-2.4×10^{4}	-7.3×10^{-3}	0.67	2.9×10^{3}	4.4×10^{-2}	0.21
EE2	SRT (d)	5			10			15		
		Q_m(μg/kg)	K_L(L/μg)	R^2	Q_m(μg/kg)	K_L(L/μg)	R^2	Q_m(μg/kg)	K_L(L/μg)	R^2
	Dosage 1	-1.6×10^{4}	-1.2×10^{-2}	0.96	-1.6×10^{4}	-1.5×10^{-2}	0.93	-1.9×10^{4}	-1.4×10^{-2}	0.97
	Dosage 2	1.7×10^{4}	2.8×10^{-2}	0.62	-4.1×10^{3}	-1.3×10^{-2}	0.98	-4.4×10^{3}	-1.9×10^{-2}	0.96
	Dosage 3	2.2×10^{4}	6.1×10^{-2}	0.79	8.0×10^{3}	4.3×10^{-2}	0.36	1.2×10^{3}	-2.7×10^{-2}	0.52
TCS	SRT (d)	5			10			15		
		Q_m(μg/kg)	K_L(L/μg)	R^2	Q_m(μg/kg)	K_L(L/μg)	R^2	Q_m(μg/kg)	K_L(L/μg)	R^2
	Dosage 1	-1.8×10^{4}	-1.0×10^{-1}	0.79	-6.0×10^{3}	-2.2×10^{-1}	0.48	-1.5×10^{4}	-1.3×10^{-1}	0.34
	Dosage 2	-5.7×10^{4}	-3.2×10^{-2}	0.79	-1.8×10^{4}	-4.7×10^{-2}	0.79	5.7×10^{3}	-4.9×10^{-1}	0.08
	Dosage 3	1.3×10^{4}	3.6×10^{-2}	0.95	-9.1×10^{1}	-4.4×10^{-2}	0.99	-1.8×10^{4}	-8.5×10^{-2}	0.80

Table 4.12 Parameters for Freundlich Isotherm and Corresponding R^2 Values Generated by Linear Regression Using Eq. 2.29

BPA	SRT （d)	5			10			15		
		1/n	K_F ($\mu g^{1-1/n}L^{1/n}kg^{-1}$)	R^2	1/n	K_F ($\mu g^{1-1/n}L^{1/n}kg^{-1}$)	R^2	1/n	K_F($\mu g^{1-1/n}L^{1/n}kg^{-1}$)	R^2
	Dosage 1	1.16	101	0.99	1.36	30	0.94	0.93	343	0.97
	Dosage 2	0.62	1067	0.92	0.76	296	0.69	1.56	31	0.95
	Dosage 3	0.51	617	0.45	0.72	1190	0.84	1.19	34	0.71
EE2	SRT （d)	5			10			15		
		1/n	K_F ($\mu g^{1-1/n}L^{1/n}kg^{-1}$)	R^2	1/n	K_F ($\mu g^{1-1/n}L^{1/n}kg^{-1}$)	R^2	1/n	K_F ($\mu g^{1-1/n}L^{1/n}kg^{-1}$)	R^2
	Dosage 1	1.22	172	0.97	1.18	246	0.98	1.20	222	0.96
	Dosage 2	0.97	28	0.84	1.47	26	0.96	1.66	28	0.99
	Dosage 3	0.53	2156	0.77	1.13	128	0.70	1.34	0.0011	0.75
TCS	SRT （d)	5			10			15		
		1/n	K_F ($\mu g^{1-1/n}L^{1/n}kg^{-1}$)	R^2	1/n	K_F ($\mu g^{1-1/n}L^{1/n}kg^{-1}$)	R^2	1/n	K_F ($\mu g^{1-1/n}L^{1/n}kg^{-1}$)	R^2
	Dosage 1	1.67	1670	0.94	2.48	1207	0.72	1.49	2741	0.69
	Dosage 2	1.22	1800	0.89	1.27	977	0.90	1.14	2081	0.87
	Dosage 3	1.01	3771	0.94	1.28	2086	0.89	1.18	4111	0.96

4.7 Error Function and Nonlinear Regression

The inherit bias of linear regression can sometimes lead to large differences between experimental data and calculated values. As shown in Fig. 4.12, the experimental data (TCS , SRT=10 d, the third Aluminum Dosage) seem to fit Langmuir isotherm at low liquid phase concentrations, but a large difference begins to appear when liquid phase concentrations rise above 10 μg/L. To solve this problem, non-linear regression was introduced to determine the isotherm parameters.

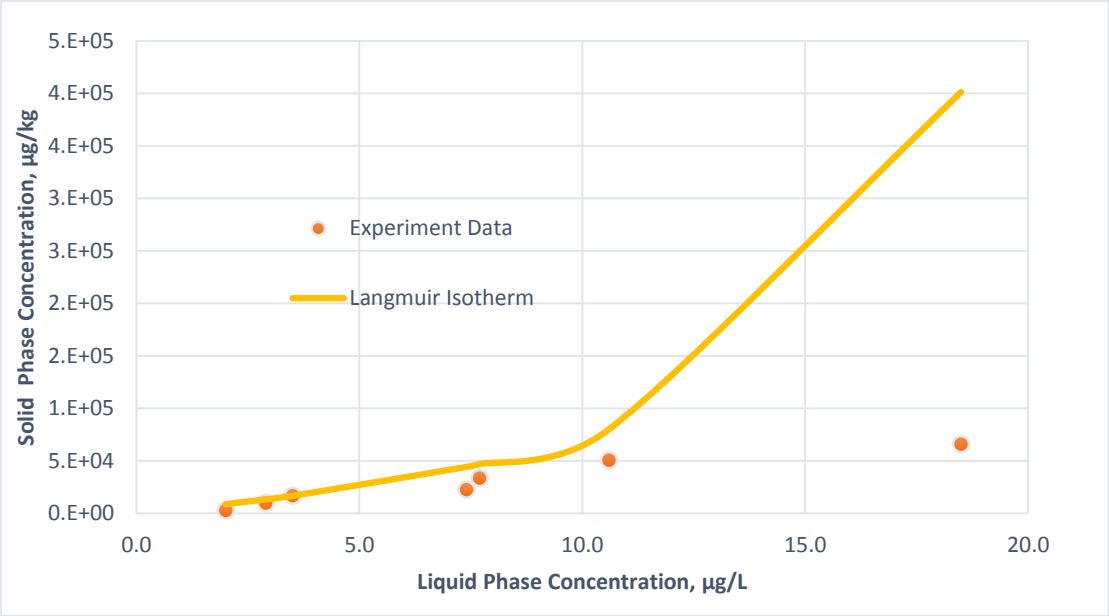


Figure 4.12 Sorption Isotherm Obtained by Using Linear Regression, Sorption Isotherm for TCS at SRT of 10d and the Third Aluminum Dosage

In order to do nonlinear regression, an error function was used in this study. The error function is expressed as Eq. 2.30. As mentioned in Section 2.8, when the value of Eq. 2.30 approaches zero, the sorption isotherm is closer to experimental data. The value of Eq. 2.30 can be minimized by using the *solver* add-in with, Microsoft Excel.

The following graph shows the results of Freundlich and Langmuir isotherms by using non-linear regression, compared with the results simply using linear regression.

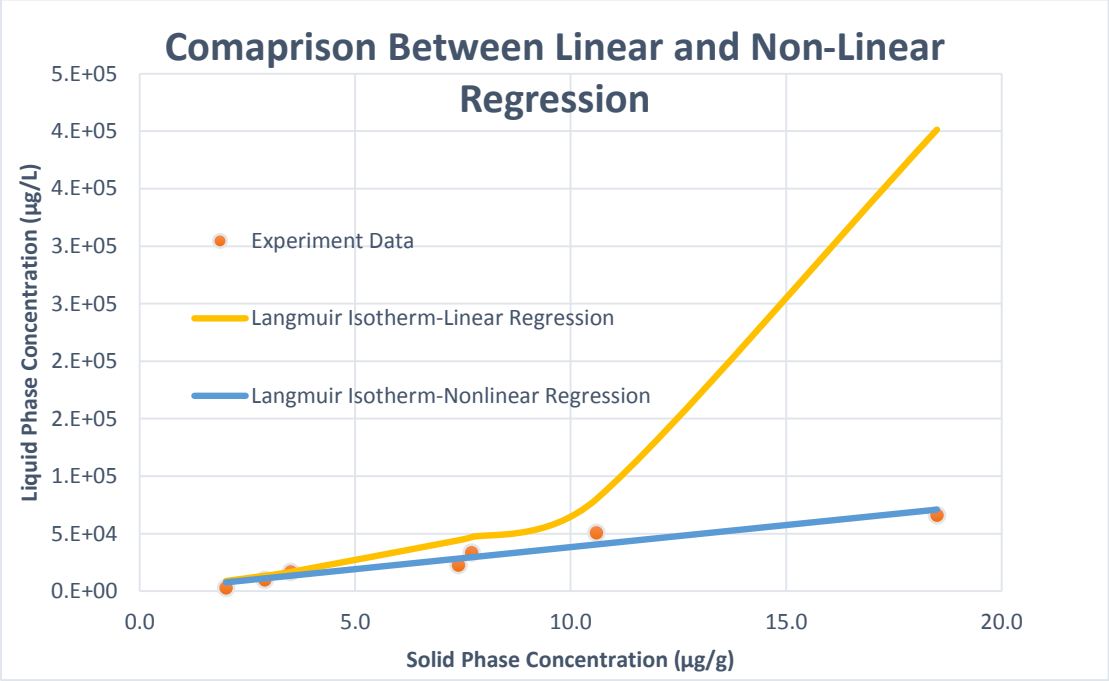


Figure 4.13 Comparison Between Linear and Non-linear Regression, Sorption Isotherms for TCS at SRT of 10 d and the Third Aluminum Dosage

From Fig. 4.13, it can be see that non-linear regression results in isotherms more close to experimental data. The isotherm parameters and value of error function are summarized in Tables 4.13 and 4.14. The graphs showing the experimental data and sorption isotherms regressed by using non-linear isotherm can be seen in Appendix C. Due to the limitation of *solver* add-in with Microsoft Excel, the error function cannot be minimized to zero.

Table 4.13 Parameters for Langmuir Isotherm and Corresponding Error Function Obtained by Non-Linear Regression

BPA	SRT (d)	5			10			15		
		Q_m(μg/kg)	K_L(L/μg)	Error Function	Q_m(μg/kg)	K_L(L/μg)	Error Function	Q_m(μg/kg)	K_L(L/μg)	Error Function
	Dosage 1	1.6×10^{7}	1.4×10^{-5}	1.7×10^{7}	1.0×10^{7}	1.7×10^{-5}	5.1×10^{7}	1.1×10^{5}	2.9×10^{-3}	8.5×10^{7}
	Dosage 2	4.1×10^{5}	4.9×10^{-4}	3.1×10^{8}	2.2×10^{4}	8.7×10^{-3}	1.3×10^{7}	3.1×10^{7}	9.6×10^{-6}	5.0×10^{7}
	Dosage 3	7.4×10^{4}	3.3×10^{-3}	5.8×10^{7}	1.3×10^{4}	9.1×10^{-2}	4.3×10^{7}	7.9×10^{6}	1.6×10^{-5}	7.3×10^{7}
EE2	SRT (d)	5			10			15		
		Q_m(μg/kg)	K_L(L/μg)	Error Function	Q_m(μg/kg)	K_L(L/μg)	Error Function	Q_m(μg/kg)	K_L(L/μg)	Error Function
	Dosage 1	1.8×10^{4}	2.4×10^{-5}	5.7×10^{7}	3.4×10^{7}	1.4×10^{-5}	1.9×10^{7}	1.7×10^{7}	-2.9×10^{-5}	9.4×10^{9}
	Dosage 2	4.1×10^{7}	7.7×10^{-6}	6.2×10^{7}	1.2×10^{5}	1.9×10^{-3}	2.7×10^{7}	4.3×10^{7}	8.9×10^{-6}	6.9×10^{7}
	Dosage 3	7.3×10^{6}	4.1×10^{-5}	1.3×10^{8}	1.6×10^{7}	1.9×10^{-5}	2.8×10^{8}	2.0×10^{6}	7.0×10^{-6}	1.6×10^{8}
TCS	SRT (d)	5			10			15		
		Q_m(μg/kg)	K_L(L/μg)	Error Function	Q_m(μg/kg)	K_L(L/μg)	Error Function	Q_m(μg/kg)	K_L(L/μg)	Error Function
	Dosage 1	1.8×10^{8}	5.4×10^{5}	6.0×10^{8}	3.2×10^{7}	4×10^{-4}	1.6×10^{9}	3.1×10^{7}	2.1×10^{-4}	3.9×10^{9}
	Dosage 2	4.2×10^{7}	8.8×10^{-5}	1.4×10^{9}	2.2×10^{7}	9.8×10^{-5}	1.3×10^{8}	2.0×10^{7}	1.6×10^{-4}	4.6×10^{8}
	Dosage 3	1.4×10^{8}	2.9×10^{-5}	3.5×10^{8}	5.9×10^{7}	6.5×10^{-5}	6.2×10^{8}	8.6×10^{7}	6.9×10^{-5}	1.6×10^{8}

Table 4.14 Parameters for Freundlich Isotherm and Corresponding Error Function Obtained by Non-Linear Regression

BPA	SRT (d)	5			10			15		
		K_F ($\mu g^{1-1/n} L^{1/n} kg^{-1}$)	1/n	Error Function	K_F ($\mu g^{1-1/n} L^{1/n} kg^{-1}$)	1/n	Error Function	K_F ($\mu g^{1-1/n} L^{1/n} kg^{-1}$)	1/n	Error Function
	Dosage 1	101	1.16	7.2×10^{6}	12	1.57	1.3×10^{7}	343	0.93	8.8×10^{7}
	Dosage 2	819	0.69	2.9×10^{8}	571	0.61	1.3×10^{7}	66	1.36	2.8×10^{7}
	Dosage 3	465	0.80	6.3×10^{7}	4,669	0.22	7.6×10^{7}	0.92	2.0	2.0×10^{7}
EE2	SRT (d)	5			10			15		
		K_F ($\mu g^{1-1/n} L^{1/n} kg^{-1}$)	1/n	Error Function	K_F ($\mu g^{1-1/n} L^{1/n} kg^{-1}$)	1/n	Error Function	K_F ($\mu g^{1-1/n} L^{1/n} kg^{-1}$)	1/n	Error Function
	Dosage 1	283	1.10	5.1×10^{7}	522	0.98	1.8×10^{7}	208	1.21	1.5×10^{8}
	Dosage 2	163	1.15	5.2×10^{7}	271	0.93	3.1×10^{7}	54	1.49	5.1×10^{7}
	Dosage 3	387	0.94	1.3×10^{8}	0.7	2.4	2.9×10^{7}	0.0026	3.3	6.0×10^{7}
TCS	SRT (d)	5			10			15		
		K_F ($\mu g^{1-1/n} L^{1/n} kg^{-1}$)	1/n	Error Function	K_F ($\mu g^{1-1/n} L^{1/n} kg^{-1}$)	1/n	Error Function	K_F ($\mu g^{1-1/n} L^{1/n} kg^{-1}$)	1/n	Error Function
	Dosage 1	2,326	1.51	1.6×10^{8}	3,477	1.72	2.9×10^{8}	5,457	1.10	4.3×10^{9}
	Dosage 2	298	1.86	6.1×10^{8}	1,206	1.20	9.2×10^{8}	4.29	3	4.6×10^{8}
	Dosage 3	2,306	1.21	2.1×10^{8}	4,547	0.93	2.0×10^{8}	3,659	1.3	1.7×10^{8}

4.8 Best Fit Isotherms

In the previous sections (Sections 4.4 to 4.7), the linear, Langmuir and Freundlich isotherm models were used to fit the experimental data. For models using a linear regression approach, R^2 is used to indicate the ability of the models to describe experimental data, while for models using a nonlinear regression approach, an error function was used instead of R^2. Based on the previous results, the nonlinear regression approach is more effective than the linear regression approach for Langmuir and Freundlich isotherms for fitting experimental data.

In this section, the error function of linear models was also calculated and compared with the error functions of Langmuir and Freundlich isotherm models. The lowest value of the error function indicates the best isotherm to describe the experimental data.

According to the values of the error function shown in Table 4.14, the Freundlich isotherm is the best fit isotherm for most of the scenarios. It describes half of the isotherms for BPA and most of the isotherms for EE2 and TCS. Only two isotherms are best described by the linear isotherm model. The remaining isotherms were best described by a Langmuir model. Although for those isotherm which is not "best described" by Frendlich isotherm, the error function of Freundlich isotherm is very close to the error function of the best fit isotherm. So generally speaking, Freundlich is the best fit isotherm for experimental data.

Table 4.15 summarized the types of isotherm that described the experimental data the best at different scenarios as well as providing the parameters determined for the models.

Table 4.15 Error Function for Linear, Freundlich and Langmuir Isotherm Models

Unit: $\mu g^2/kg^2$		5d			10			15d		
		Linear	Freundlich	Langmuir	Linear	Freundlich	Langmuir	Linear	Freundlich	Langmuir
BPA	Dosage 1	9.66×10^{6}	7.02×10^{6}	1.71×10^{7}	5.02×10^{7}	1.28×10^{7}	5.06×10^{7}	9.02×10^{7}	8.81×10^{7}	6.49×10^{7}
	Dosage 2	3.07×10^{8}	2.87×10^{8}	3.07×10^{8}	3.05×10^{7}	1.30×10^{7}	1.26×10^{7}	4.97×10^{7}	2.76×10^{7}	4.98×10^{7}
	Dosage 3	7.61×10^{7}	6.26×10^{7}	5.84×10^{7}	2.53×10^{8}	7.64×10^{7}	4.27×10^{7}	7.21×10^{7}	1.98×10^{7}	7.28×10^{7}
EE2	Dosage 1	5.70×10^{7}	5.13×10^{7}	5.76×10^{7}	1.78×10^{7}	1.80×10^{7}	1.93×10^{7}	3.10×10^{8}	1.53×10^{8}	9.41×10^{9}
	Dosage 2	6.15×10^{7}	5.15×10^{7}	6.18×10^{7}	3.20×10^{7}	3.06×10^{7}	2.66×10^{7}	6.86×10^{7}	2.05×10^{7}	6.88×10^{7}
	Dosage 3	1.34×10^{8}	1.33×10^{8}	1.34×10^{8}	2.73×10^{8}	2.87×10^{7}	2.76×10^{7}	1.63×10^{8}	6.04×10^{7}	1.64×10^{8}
TCS	Dosage 1	5.97×10^{8}	1.56×10^{8}	6.94×10^{8}	7.50×10^{8}	2.85×10^{8}	1.60×10^{9}	4.11×10^{9}	4.30×10^{9}	3.92×10^{9}
	Dosage 2	1.40×10^{9}	6.14×10^{8}	1.40×10^{9}	1.76×10^{8}	9.19×10^{7}	1.26×10^{8}	4.57×10^{8}	3.12×10^{9}	4.57×10^{8}
	Dosage 3	3.32×10^{8}	2.07×10^{8}	3.47×10^{8}	2.09×10^{8}	1.99×10^{8}	1.63×10^{8}	1.63×10^{8}	1.68×10^{8}	1.63×10^{8}

Table 4.16 Best Fit Isotherm Models for Different Scenarios

		5 d		10 d		15 d	
BPA	Dosage 1	Freundlich	$Q_e=101\ C_e^{1.16}$	Frendlich	$Q_e=12\ C_e^{1.57}$	Lanmguir	$Qe = \frac{2.5 \times 10^5 \times 1.2 \times 10^{-3} Ce}{1 + 1.2 \times 10^{-3} C_e}$
	Dosage 2	Freundlich	$Q_e=819\ C_e^{0.69}$	Langmuir	$Qe = \frac{2.2 \times 10^4 \times 8.7 \times 10^{-3} Ce}{1 + 8.7 \times 10^{-3} C_e}$	Freundlich	$Q_e=66\ C_e^{1.36}$
	Dosage 3	Langmuir	$Qe = \frac{7.4 \times 10^6 \times 3.3 \times 10^{-3} Ce}{1 + 3.3 \times 10^{-3} C_e}$	Langmuir	$Qe = \frac{1.3 \times 10^4 \times 9.1 \times 10^{-2} Ce}{1 + 9.1 \times 10^{-2} C_e}$	Freundlich	$Q_e=0.92\ C_e^{2}$
EE2	Dosage 1	Freundlich	$Q_e=283\ C_e^{1.10}$	Linear	$Q_e=486\ C_e$	Freundlich	$Q_e=208\ C_e^{1.21}$
	Dosage 2	Freundlich	$Q_e=163\ C_e^{1.15}$	Langmuir	$Qe = \frac{1.2 \times 10^5 \times 1.9 \times 10^{-3} Ce}{1 + 1.9 \times 10^{-3} C_e}$	Freundlich	$Q_e=54\ C_e^{1.49}$
	Dosage 3	Freundlich	$Q_e=387\ C_e^{0.94}$	Freundlich	$Q_e=0.7C_e^{2.4}$	Freundlich	$Q_e=0.0026\ C_e^{3.3}$
TCS	Dosage 1	Freundlich	$Q_e=2326\ C_e^{1.51}$	Freundlich	$Q_e=3477\ C_e^{1.72}$	Langmuir	$Qe = \frac{3.1 \times 10^7 \times 2.1 \times 10^{-4} Ce}{1 + 2.1 \times 10^{-4} C_e}$
	Dosage 2	Freundlich	$Q_e=298\ C_e^{1.86}$	Freundlich	$Q_e=6206\ C_e^{1.19}$	Linear	$Q_e=3197\ C_e$
	Dosage 3	Freundlich	$Q_e=2306\ C_e^{1.21}$	Freundlich	$Q_e=4547\ C_e^{0.93}$	Langmuir	$Qe = \frac{8.6 \times 10^7 \times 6.9 \times 10^{-5} Ce}{1 + 6.9 \times 10^{-5} C_e}$

4.9 Removal of Selected MCs in Continuous Flow Activated Sludge System

BPA, EE2 and TCS were dosed into the influent tanks at a concentration of 50 µg/L in order to study their removal rates in lab scale AS system. 12 samples were taken during 64 days' running.

In Figs. 4.14 and 4.15, TSS, VSS and soluble COD of the three bioreactors are presented.

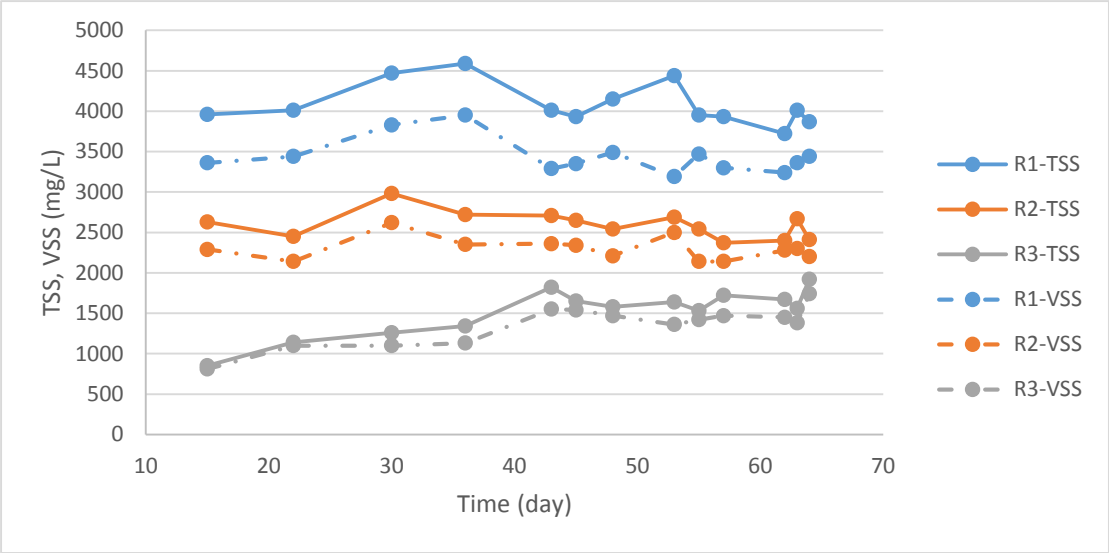


Figure 4.14 TSS, VSS of Bioreactors for MCs Removal Study

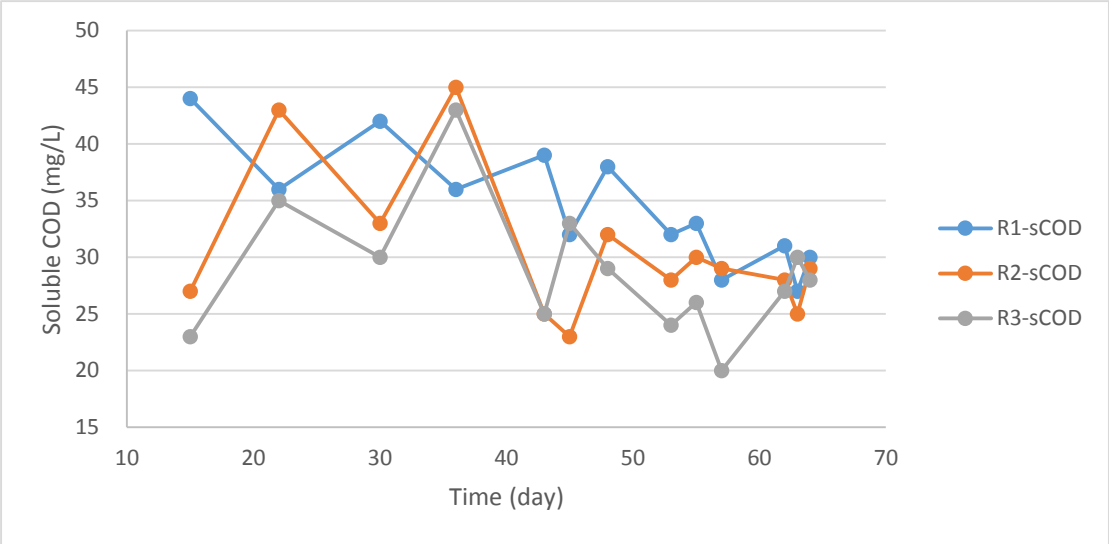


Figure 4.15 Soluble COD of Bioreactors Effluent for MCs Removal Study

According to Fig. 4.14, the TSS and VSS of reactor 1 and 2 did not flocculate too much during the whole process; however, reactor 3 did not reach steady state until 45 d of running. Effluent soluble COD shows a declined tendency during the whole process. Statistical analysis shows the standard deviation of soluble COD for reactors 1, 2, and 3after 45 d are 10.1, 9.4 and 13.6%, respectively. Reactors are considered to reach steady state after 45 d.

Table 4.17 contains the average TSS, VSS and soluble COD for the three reactors from day 45 to day 64.

Table 4.17 Average Values for TSS, VSS and Soluble COD and Corresponding Standard Deviation

	TSS		VSS		Soluble COD	
	Average (mg/L)	Standard Deviation (%)	Average (mg/L)	Standard Deviation (%)	Average (mg/L)	Standard Deviation (%)
Reactor 1	4000	5	3355	3	31.4	10.1
Reactor 2	2534	4.6	2264	5	28.0	9.4
Reactor 3	1659	6.9	1479	7.6	27.1	13.6

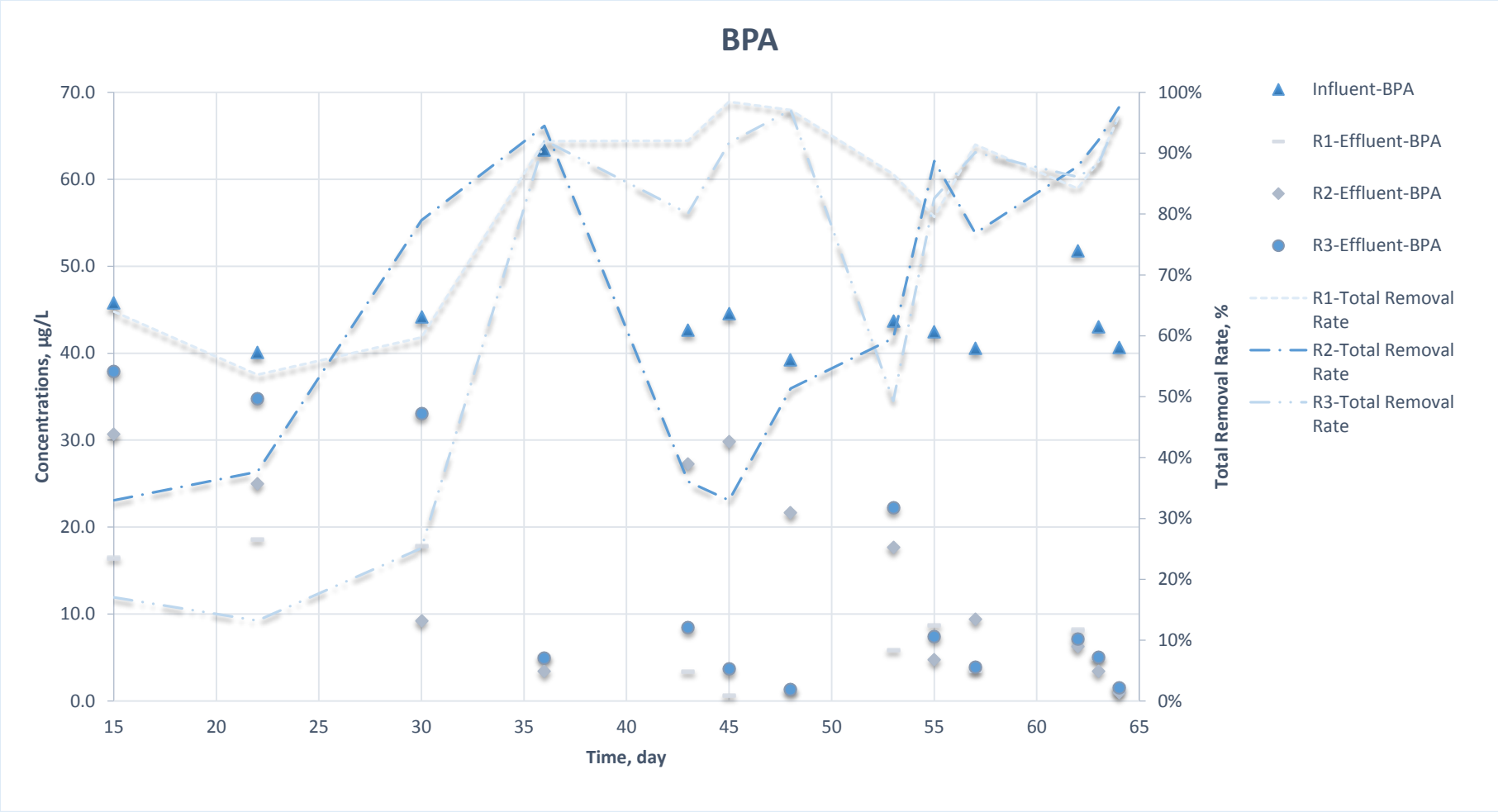
a. All values were based on 8 samples.

As mentioned in Section 3.9, the sampling location for influent MCs concentrations is at the outlet of the tubes since a certain amount loss will take place when the influent travels through them. The average influent concentration of BPA, EE2 and TCS were 45.2 (±6.0), 51.6 (±11.3) and 35.1 (±6.9) μg/L, respectively.

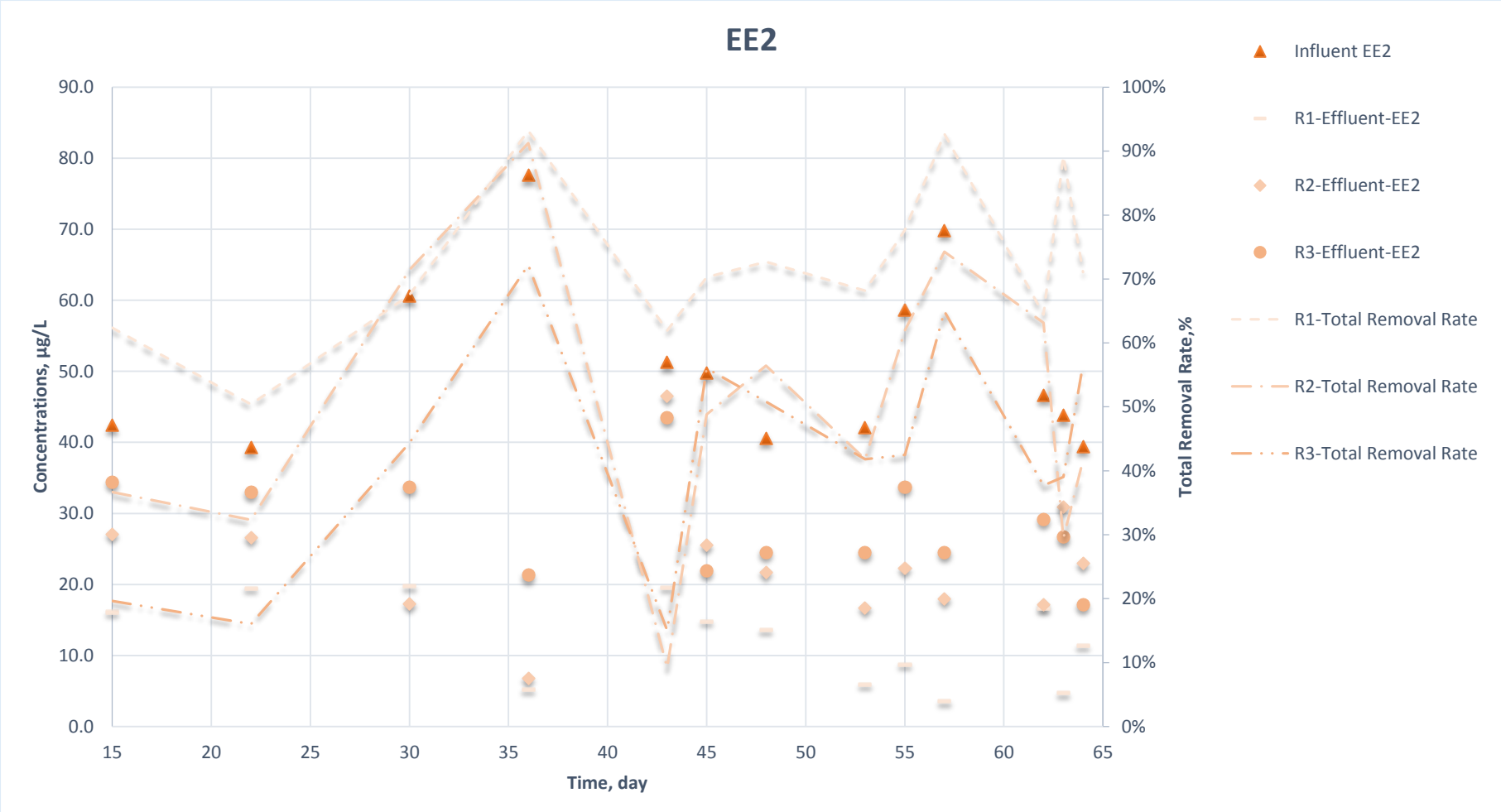
Effluent samples were taken at the effluent tanks of three bioreactors. The influent concentrations and effluent concentrations were shown in Fig. 4.16. Since the influent concentrations varies, it is difficult to determine the removal efficiency merely based on the effluent concentrations. Total removal rates were calculated according to Eq. 3.5 and shown by the dashed lines in Fig. 4.16.

The total removals for the selected MCs after 45 days running is summarized in Table 4.18. TCS has the highest removal rates (> 95%) followed by BPA (from 73 to 90%)

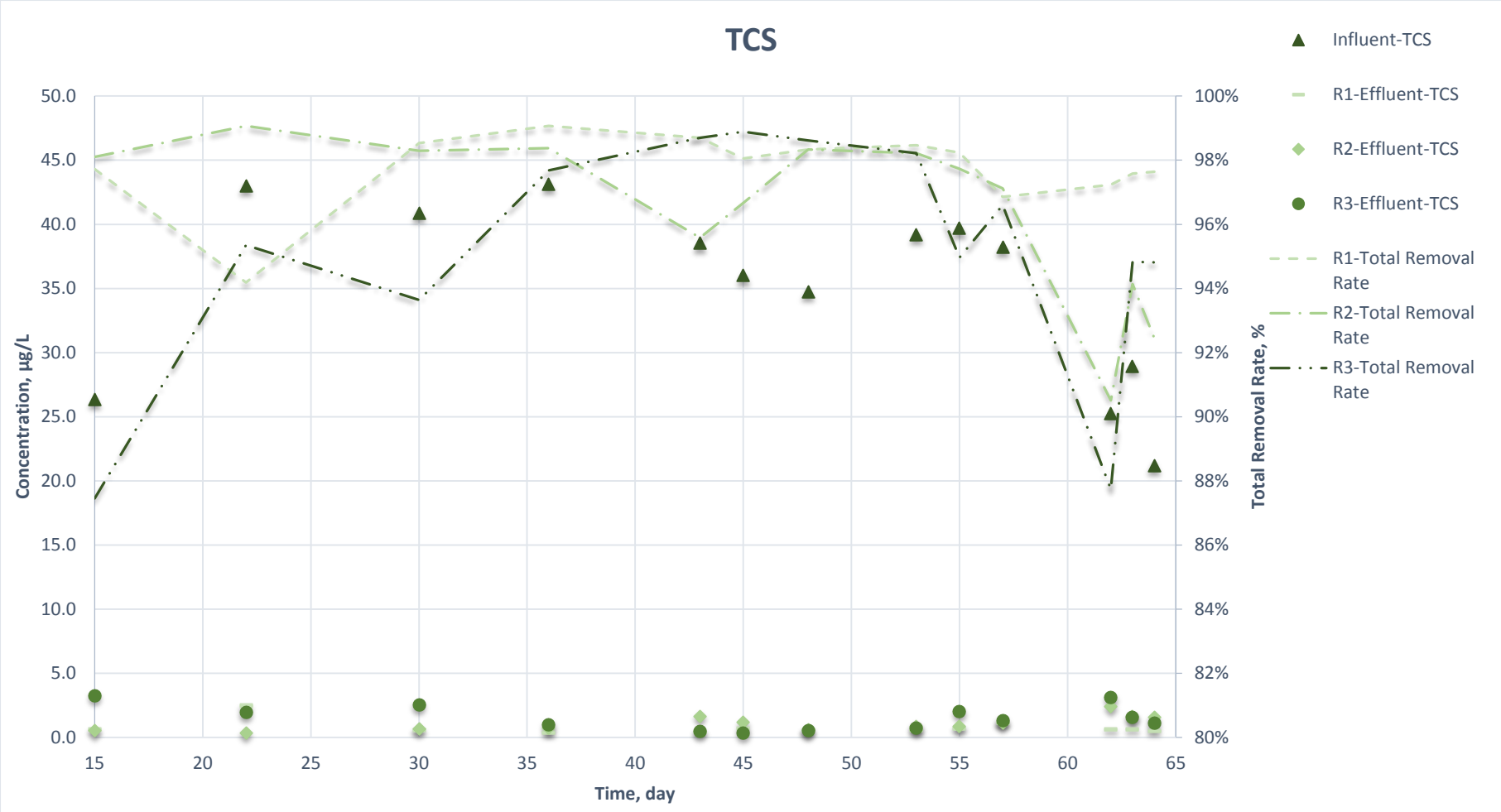
and EE2 (49 to 76%). Reactor 1, with a SRT of 15 days, has the highest removal rates among the three reactors.



a. Influent and Effluent Concentrations for BPA



b. Influent and Effluent Concentrations forEE2



c. Influent and Effluent Concentrations for TCS

Figure 4.16 Influent and Effluent Concentrations of Selected MCs

Table 4.18 Total Removal for Selected MCs after 45 Days Runing

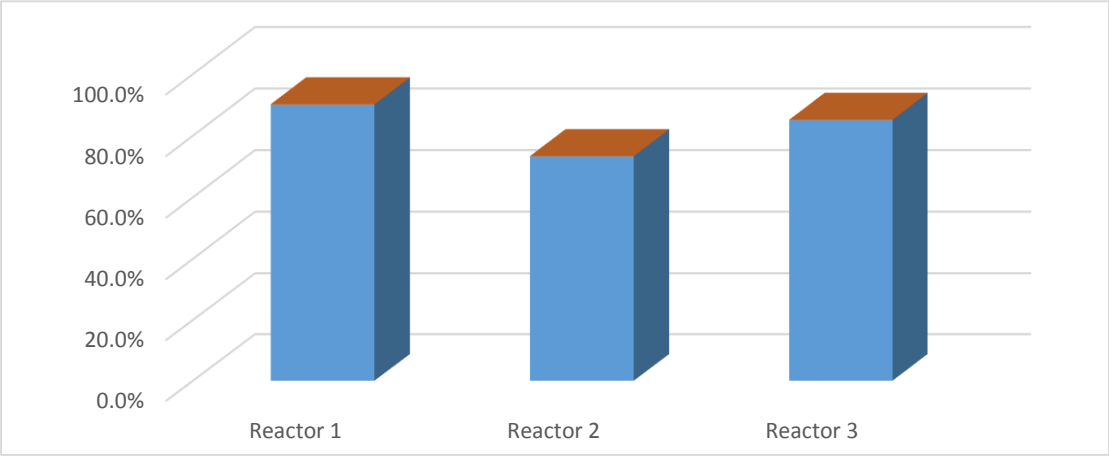
Total Removal (%)	BPA	EE2	TCS
Reactor 1	90.2 ±6.3	75.8 ±9.5	97.8 ±0.53
Reactor 2	73.4 ±21.5	52.2 ±13.6	95.7 ±2.74
Reactor 3	85.2 ±14.3	48.7 ±9.3	95.6 ±3.37

In order to determine the percentage of MCs removed by sorption, effluent concentrations and sorption isotherms were used to predict the solid phase (biomass) concentrations. Effluent MCs concentrations were used since in a complete mix reactor, liquid phase concentrations in the bioreactor is the same as the effluent concentrations. The sorption isotherms used to predict solid phase concentrations are the isotherms determined in Section 4.8. The removal rate by sorption is calculated by Eq. 3.6. Removal rate by biodegradation is calculated by Eq. 3.7. The average removal rates by sorption and biodegradation after 45 days' running is shown in Table 4.19. and Fig 4.17.

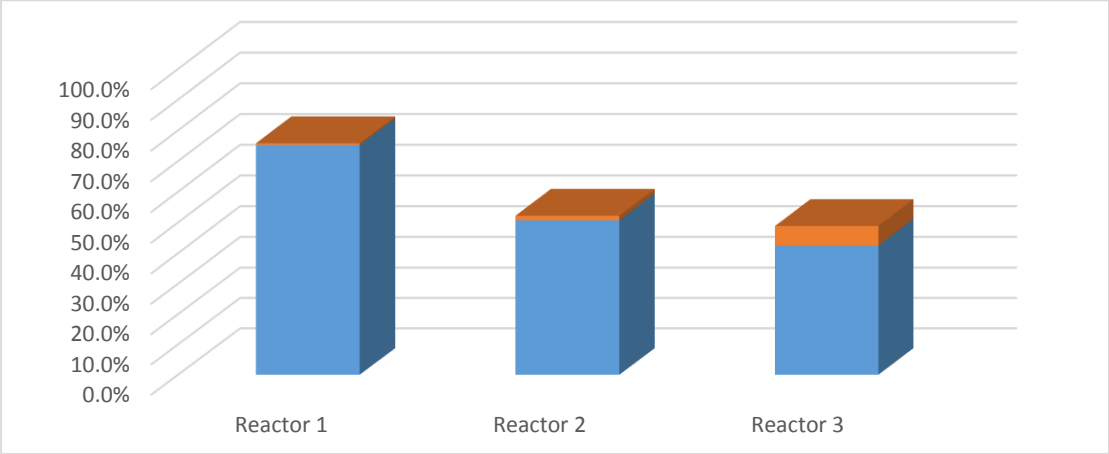
Table 4.19 Average Removal by Sorption and Biodegradation at Steady State

		Removal by Sorption (%)		Removal by Biodegradation (%)	
		Average	Deviation	Average	Deviation
Reactor 1	BPA	0.2	0.1	90.0	6.4
	EE2	0.6	0.2	75.2	9.7
	TCS	0.9	0.2	96.9	0.7
Reactor 2	BPA	0.1	0.1	73.3	21.6
	EE2	1.5	0.5	50.7	14.0
	TCS	1.3	1.1	94.3	3.9
Reactor 3	BPA	0.2	0.2	85.0	14.5
	EE2	6.4	1.5	42.5	10.5
	TCS	1.2	1.2	94.4	4.6

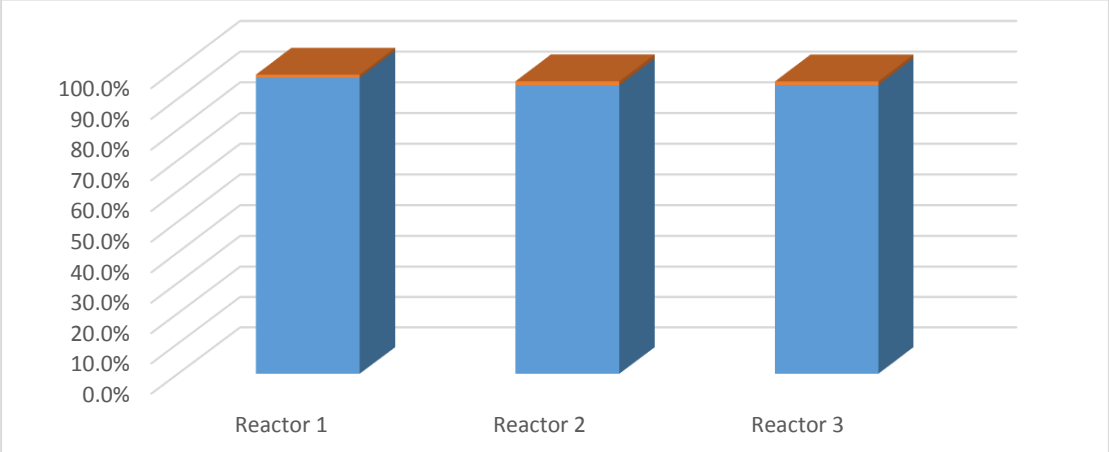
According to Fig 4.17, sorption did not contribute too much removal for all selected MCs in all three reactors. For EE2, the removal by sorption is the highest in reactor 3, followed by reactor 2 and 1, which coincides with the volume of sludge removed from reactor every day. This phenomenon is not significant for BPA and TCS.



a. Sorption and Biodegradation for BPA



b. Sorption and Biodegradation for EE2



c. Sorption and Biodegradation for TCS

Figure 4.17 Sorption and Biodegradation for MCs

EE2 also has a higher removal rate by sorption than BPA and TCS. BPA has a weaker sorption potential to biomass than EE2, in addition, the effluent concentrations for BPA are also lower than EE2. TCS has a stronger tendency to sorb to biomass, but the removal rate by sorption is not significant because the effluent concentrations for TCS are too low.

Biodegradation contributes to most of the removal for MCs. For EE2 and TCS, the removal by biodegradation is the highest in reactor 1, followed by reactor 2 and 3. No obvious pattern was discovered for BPA.

The extremely high removal rate for TCS may not because of the high removal efficiency for TCS in AS system. Judging by the influent concentrations, the TCS lost 30% of its concentration by simply being pumped through the influent tubes. There may be some unknown reasons to cause such loss, and this might by the reason why the effluent concentrations for TCS were extremely low.

Chapter 5 Conclusion and Recommendations

5.1 Summary and Conclusion

The sorption kinetics and isotherms between three chosen MCs (BPA, EE2 and TCS) and primary sludge and AS were determined by carrying out a series batch experiment. A lab-scale continuous flow bioreactor system, to which alum was added into the influent, was used to generate AS. The conclusions that can be made from current research are:

1) The equilibrium time for chosen MCs sorbed onto primary sludge is 7 h. Most of the sorption happened within the first 0.5 h of reaction. The sorption equilibrium time found in current study is close to the equilibrium time of other MCs sorbed to primary sludge and AS found by other studies.

2) Pseudo second-order kinetic models were suitable to describe sorption processes for all selected MCs.

3) Judging from K_d, TCS has the strongest tendency to sorb to primary sludge and AS, followed by EE2 and BPA. The same tendency was also found for AS without alum addition.

4) K_d found for BPA , EE2 and TCS sorbed onto primary sludge is 81 L/kg (log K_d 1.9), 728 L/kg (log K_d 2.9) and 6,407 L/kg (log K_d 3.8), respectively. K_d found for EE2 is close to results reported by other studies.

5) K_d found for BPA , EE2 and TCS sorbed onto AS under different SRTs (15, 10 and 5 d) and different alum dosages are 90 to 300 L/kg (log K_d 2.0-2.5), 140 to 490 L/kg (log K_d 2.2-2.7) and 2,160 to 7,110 L/kg (log K_d 3.4 -4.0) respectively. K_d reported from other studies for the selected MCs were in a different range. Different initial liquid concentrations, how AS were generated and how AS was inhibited may be the reasons for discrepancy in K_d reported in various studies. Among which,

the inhibition technique may be the most imported reason since improper technique has a high potential to change the structure of sludge.

6) The K_d found for AS in current study were compared to K_d found for AS without alum addition. Results shows that as alum dosage increased, the K_d for BPA and EE2 decreased. While K_d for TCS sorbed to AS with alum addition is much higher than K_d without alum addition.

7) SRT has no significant influent on K_d except for for BPA at first and second aluminum dosages. At these two aluminum dosages, K_d found under SRT of 15 d are the highest, followed by those for sludge with SRTs of 5 and 10 d. No obvious pattern was observed for TCS.

8) Langmuir and Freundlich sorption isotherm models were used to fit experiment data by linear regression and nonlinear regression approaches. When using a linear regression approach, the Langmuir model shows a poorer fitness than the Freundlich model. However, both models exhibit great discrepancy to experiment data at high adsorption concentrations. A nonlinear regression approach gives better fitness to experiment data. Freundlich isotherm was found to be the best isotherm to describe experimental data.

9) The TSS, VSS, influent and effluent COD were recorded for the lab-scale continuous flow bioreactor system. No significant differences in effluent COD were observed under three alum dosages. The TSS and VSS for reactor 3 (SRT of 5 d) decreased as alum dosage increased.

10) Biodegradation contributes to most of the removal of MCs in the lab-scale continuous flow bioreactor system based on the results found for first aluminum dosage. TCS was removed for more than 95%, followed by BPA (70-90%) and EE2 (50-75%), while sorption contributes to less than 6% of the total removal.

5.2 Recommendations for Future Work

This study mainly focused on the sorption behavior of between MCs and sludge in WWTPs. To fully understand the fate and behavior of MCs in WWTPs, works focusing on biodegradation of MCs in AS unit need to be done. In addition, the analytical method and experiment design also needs improvement.

1) Biodegradation studies of selected MCs in AS unit need to be done by adding MCs into the wastewater influent. By testing the effluent MCs concentrations, the biodegradation can be found by comparison with the results found in current study. Results of the first aluminum dosage have already shown in this study, two more aluminum dosages need to be tested in order to investigate the influence of alum on MCs removal in WWTPs.

2) Only liquid phase concentrations were tested for most of samples in the current study. Solid phase concentrations were simply calculated assuming no biodegradation or other transformation happens during the sorption process. Sodium azide was added to samples to suppress biodegradation; however, the efficiency of sodium azide to inhibit biodegradation is in question. To improve the reliability of current study, it is better develop a reliable and feasible way to test the solid phase concentrations of MCs.

3) Whether sodium azide can alter the structure of the biomass or not needs to be evaluated.

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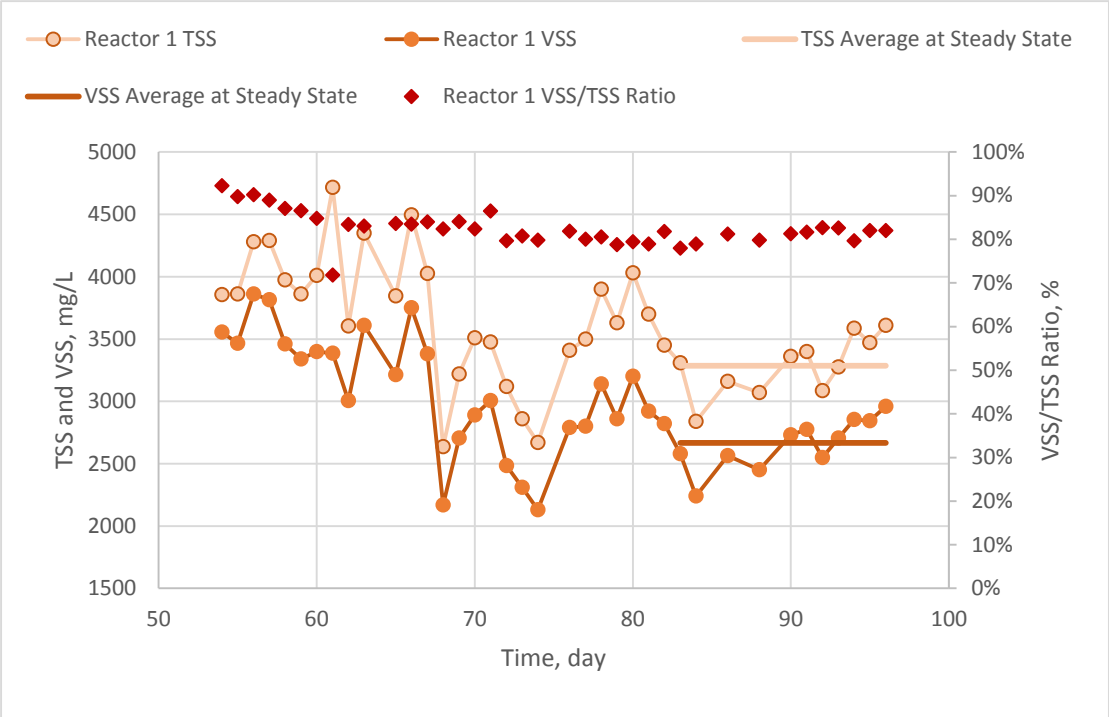
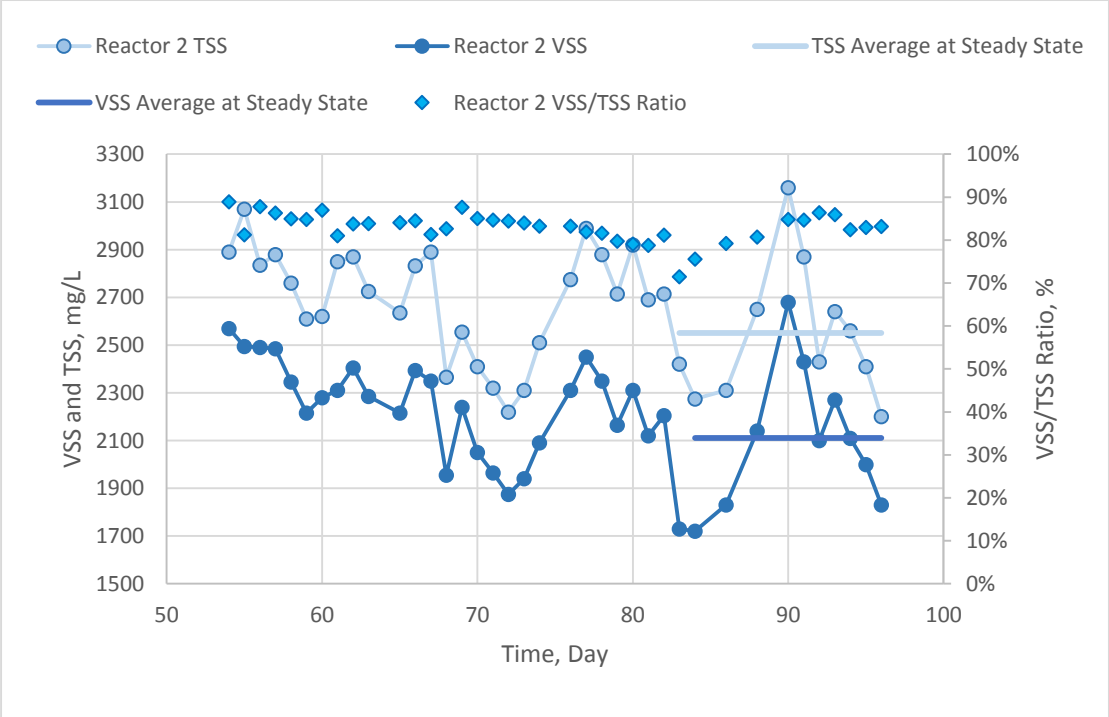
Appendix A



a. TSS, VSS and VSS/TSS Ratio of Reactor 1



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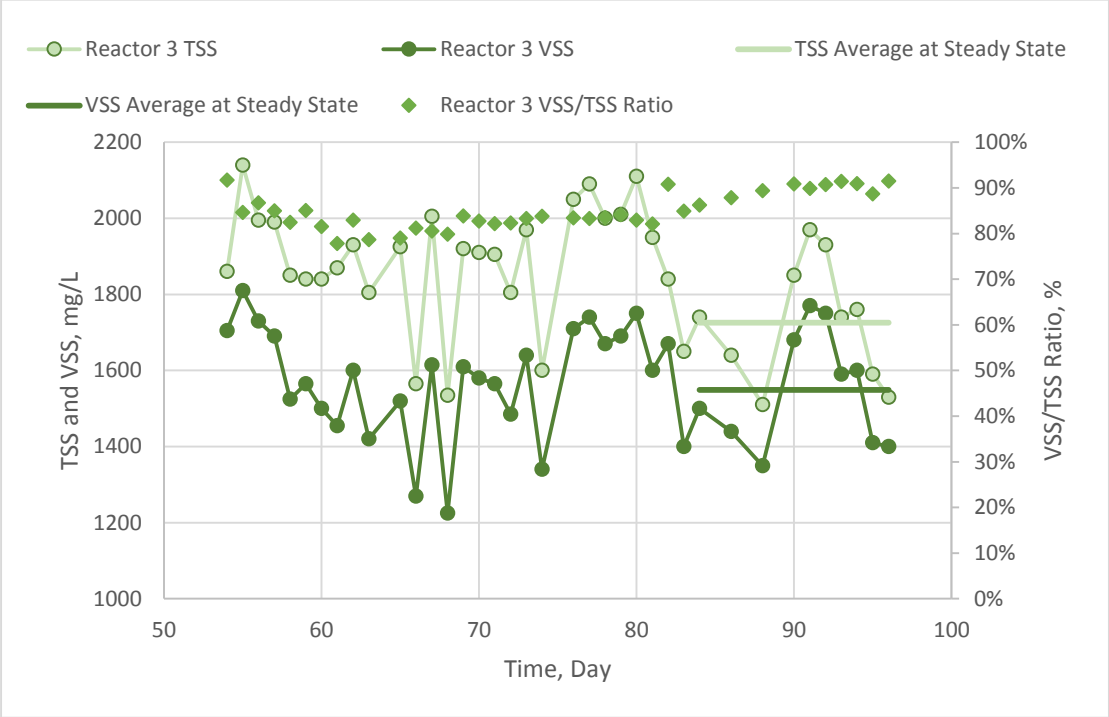
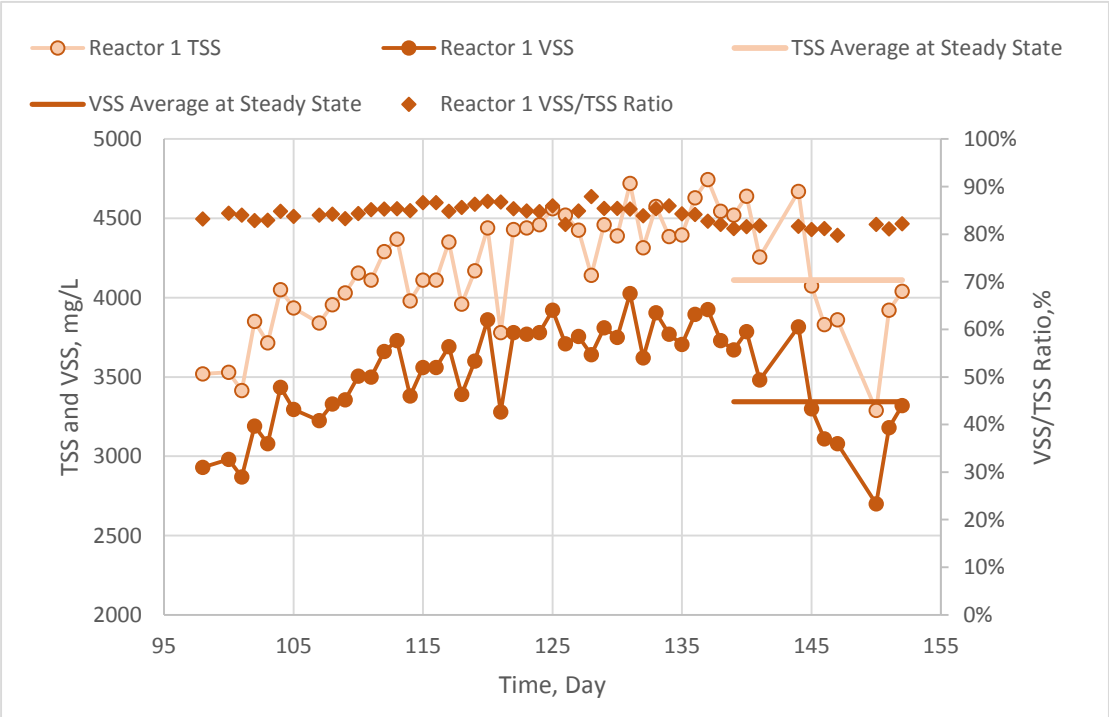


c. TSS, VSS and VSS/TSS Ratio of Reactor 3

Figure A. 1 TSS, VSS Concentrations and VSS/TSS Ratio at Aluminum Dosage 1



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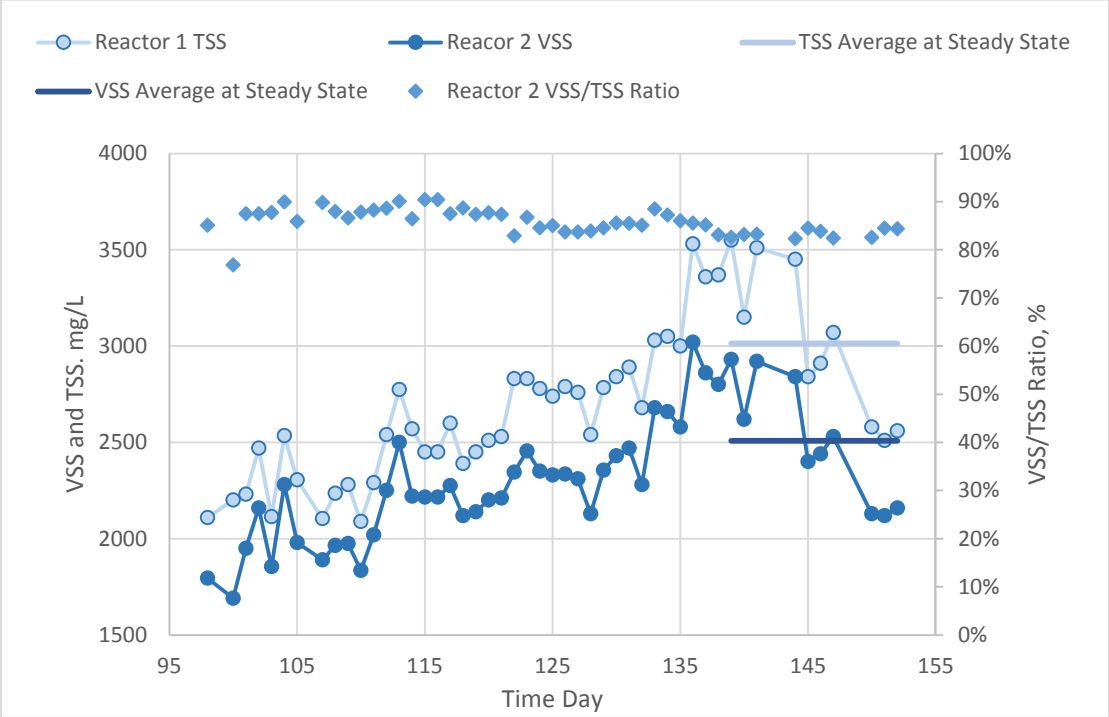

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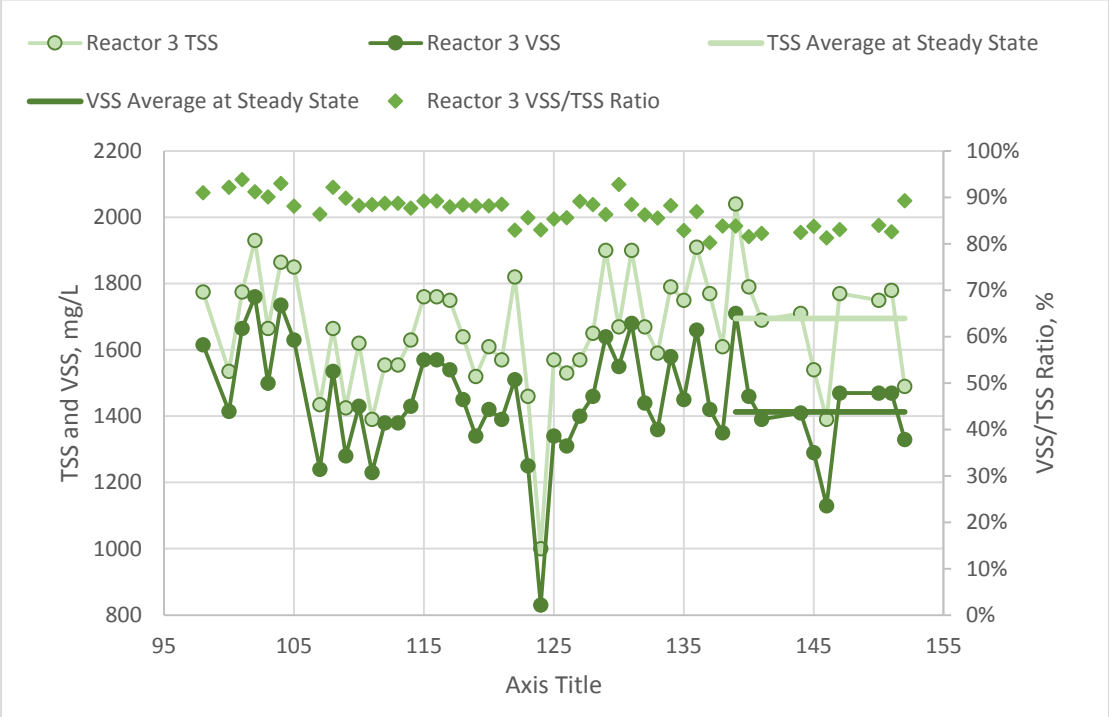
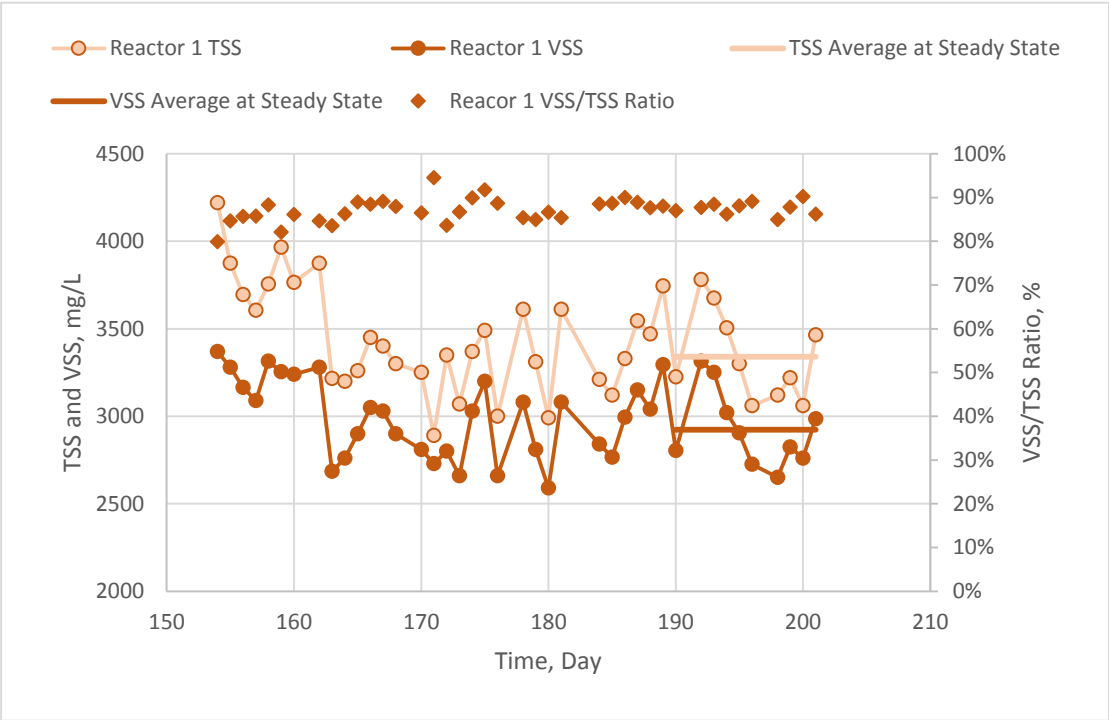


c. TSS, VSS and VSS/TSS Ratio of Reactor 3

Figure A. 2 TSS, VSS Concentrations and VSS/TSS Ratio at Aluminum Dosage 2



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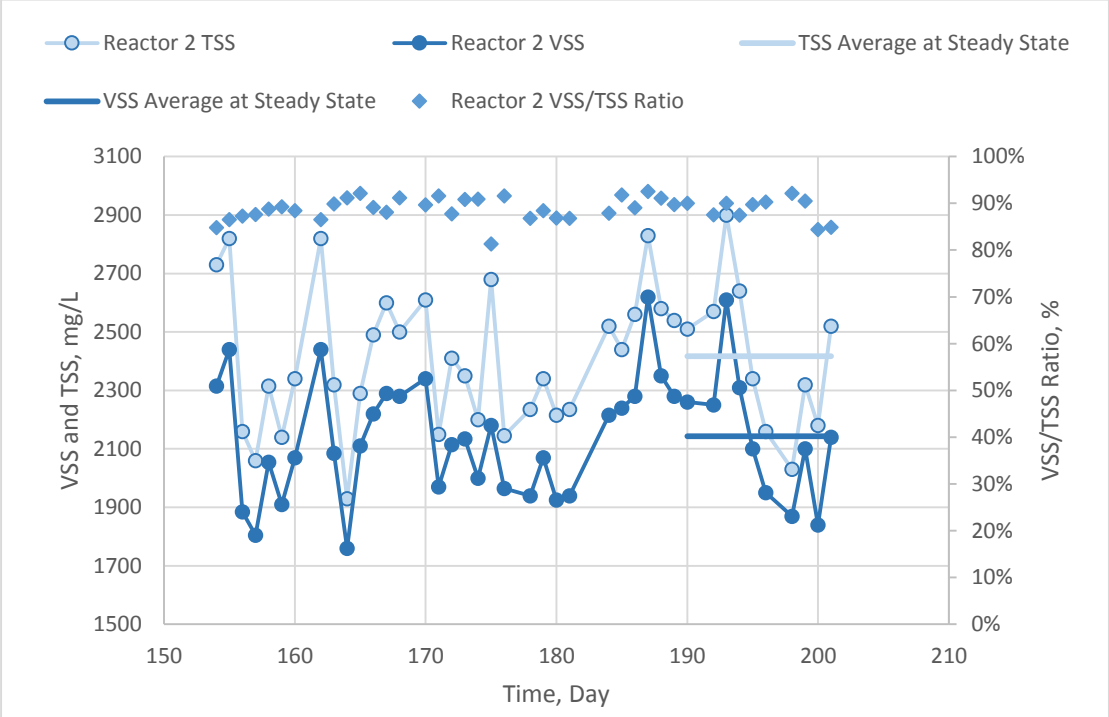

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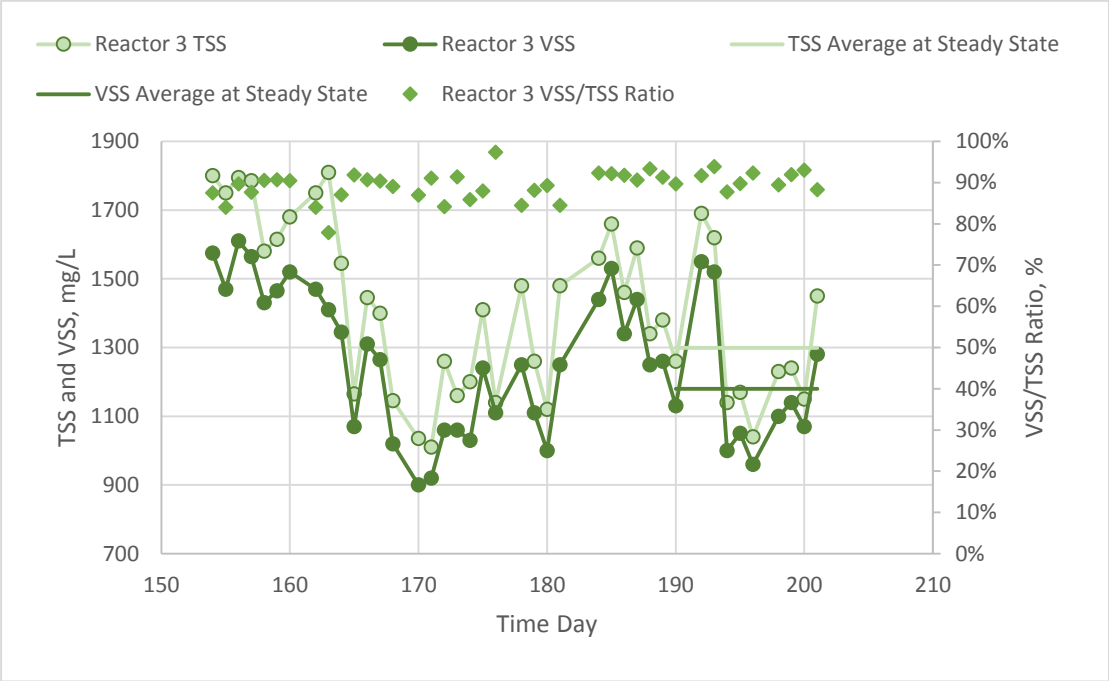
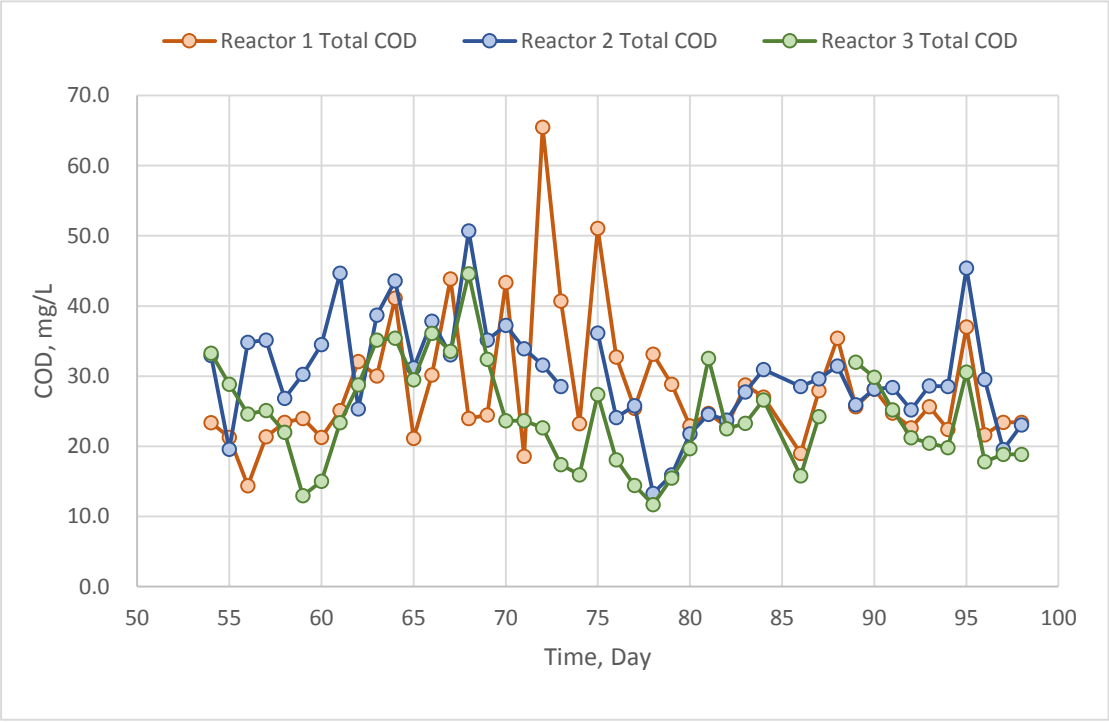
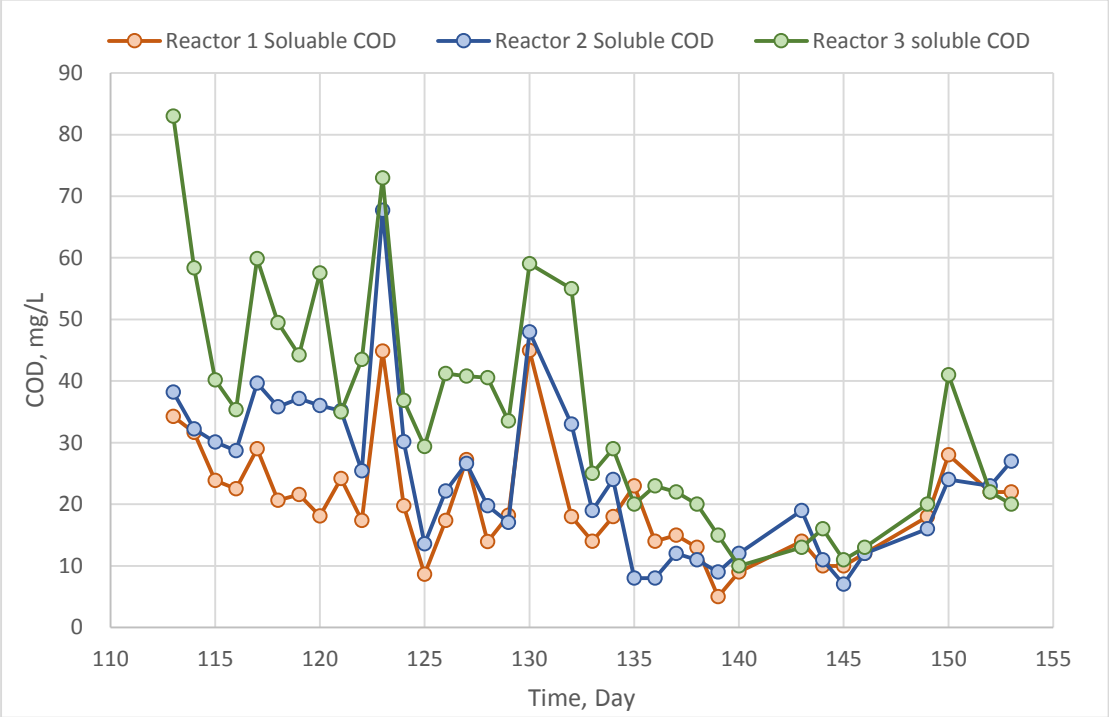


c. TSS, VSS and VSS/TSS Ratio of Reactor 3

Figure A. 3 TSS, VSS Concentrations and VSS/TSS Ratio at Aluminum Dosage 3



a. Effluent (Total) COD at Aluminum Dosage 1



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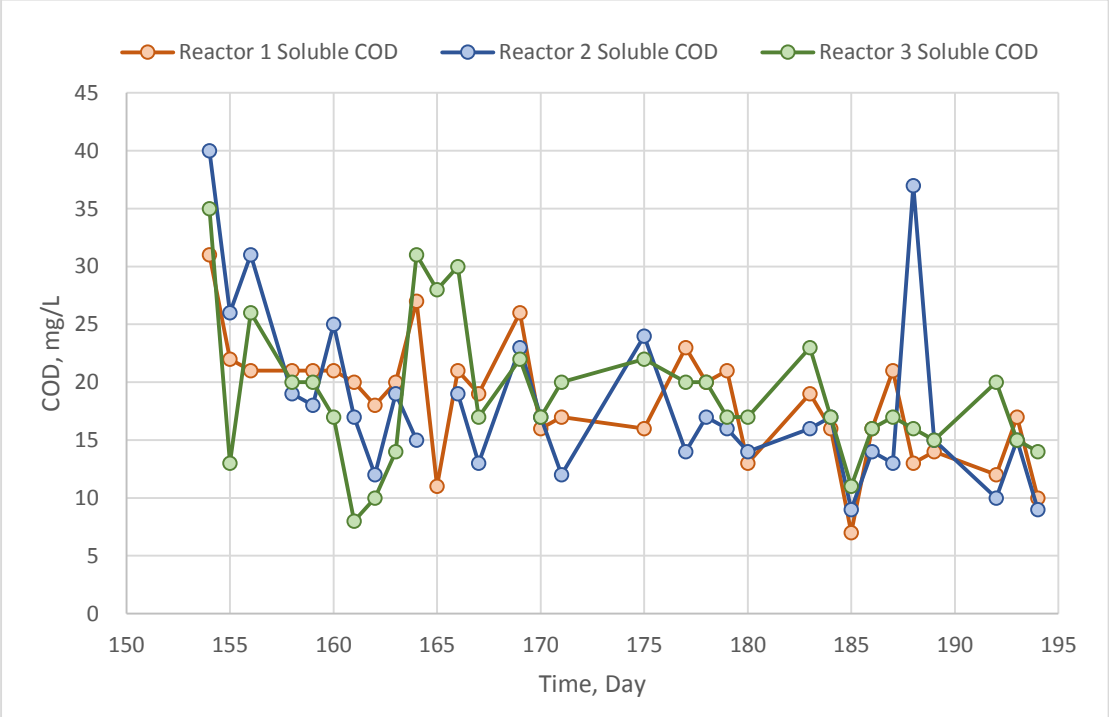
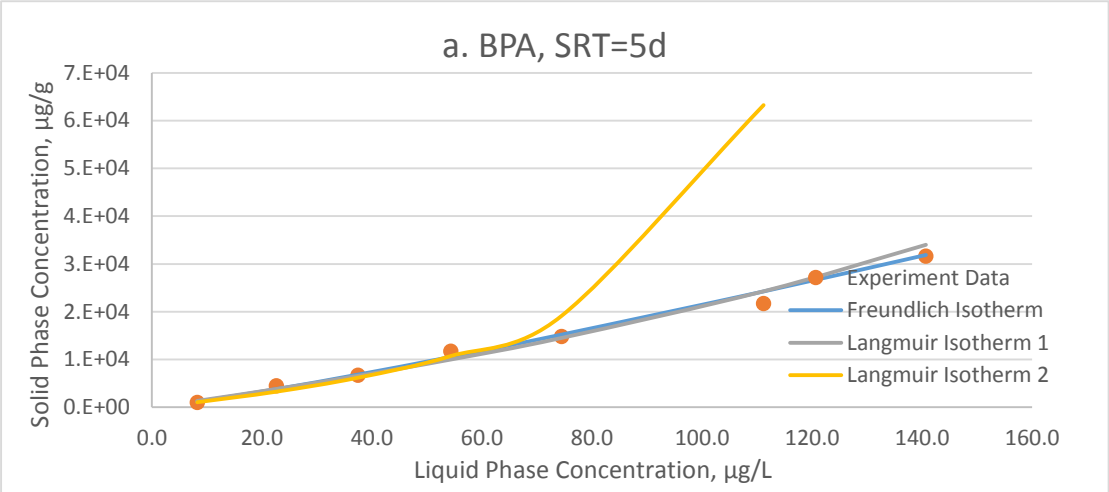
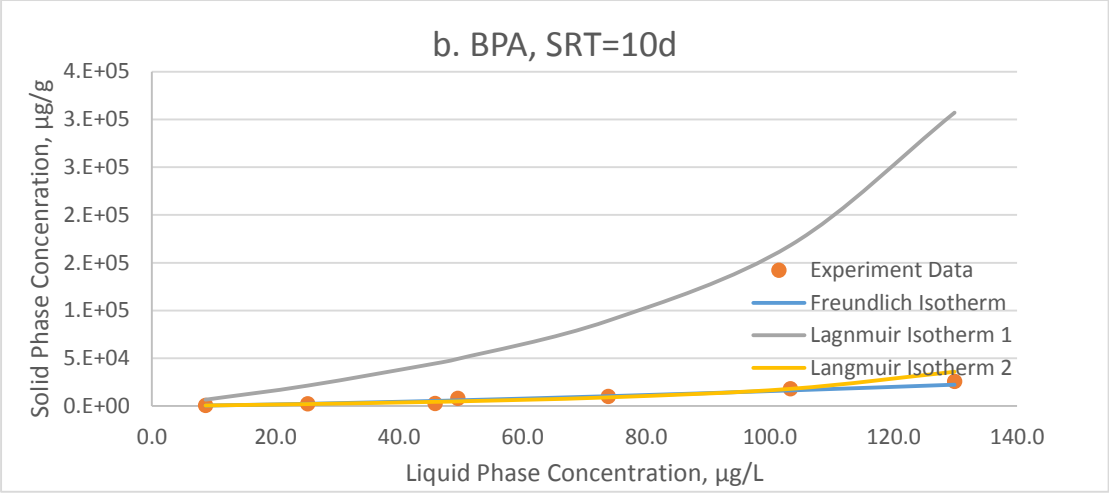


c. Effluent (Soluble) COD at Aluminum Dosage 3

Figure A. 4 Effluent COD of Three Bioreactors at Different Aluminum Dosages

Appendix B





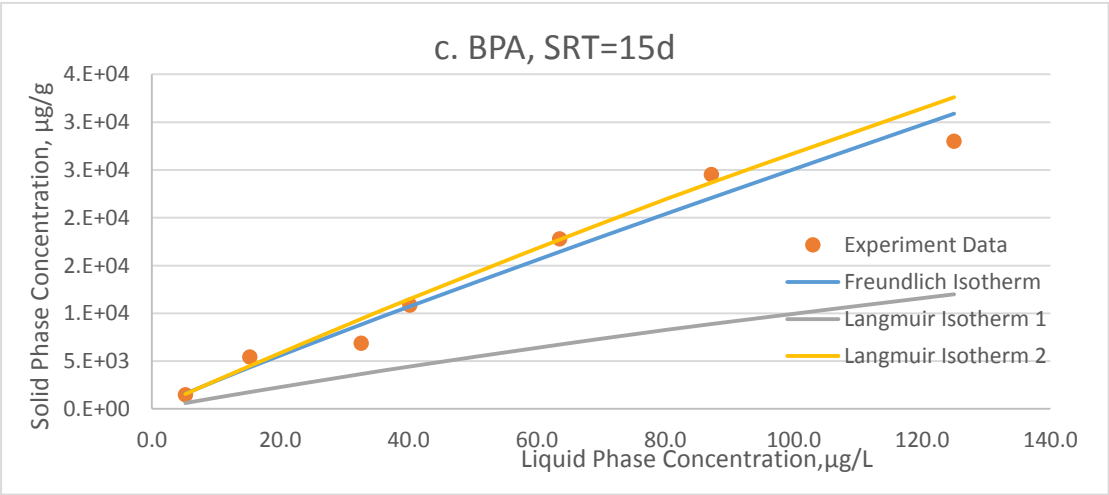
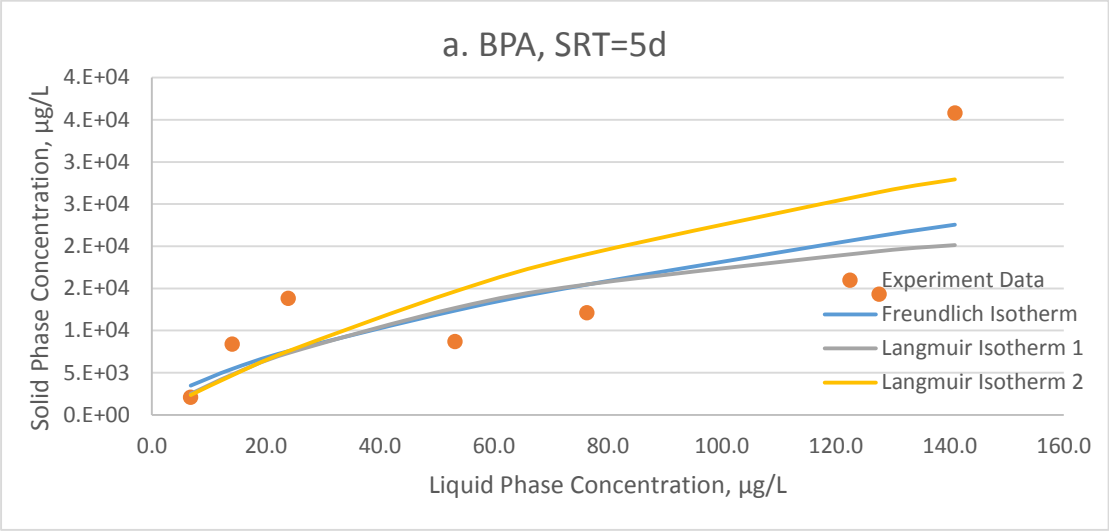
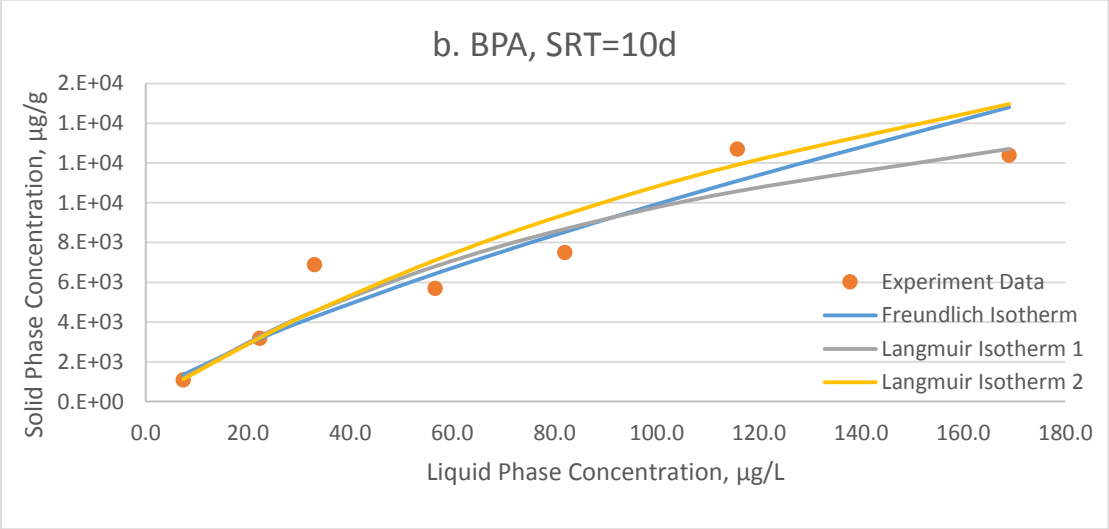


Figure B. 1 Sorption Isotherms Obtained by Linear Regression Compared with Experimental Data, BPA at Aluminum Dosage 1





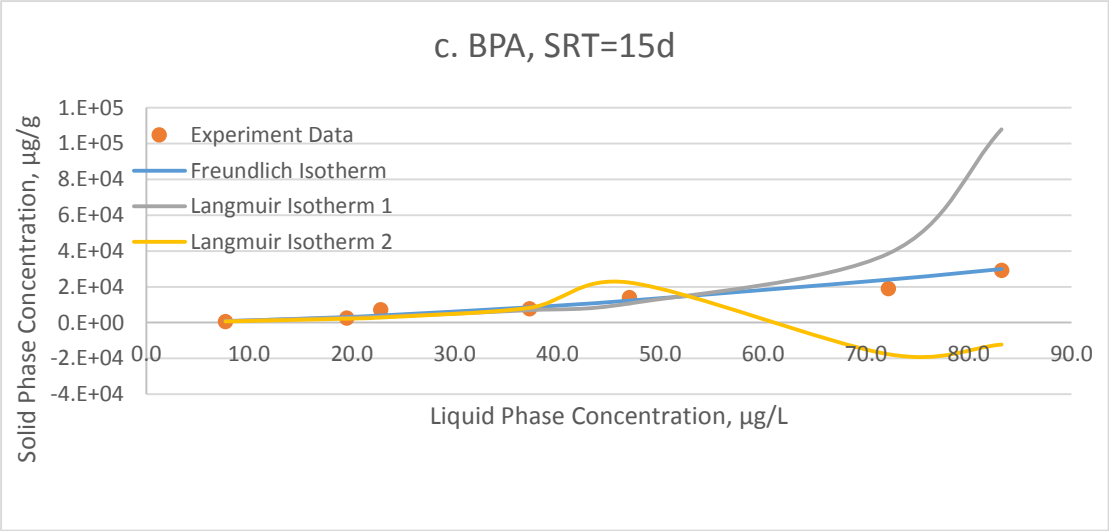
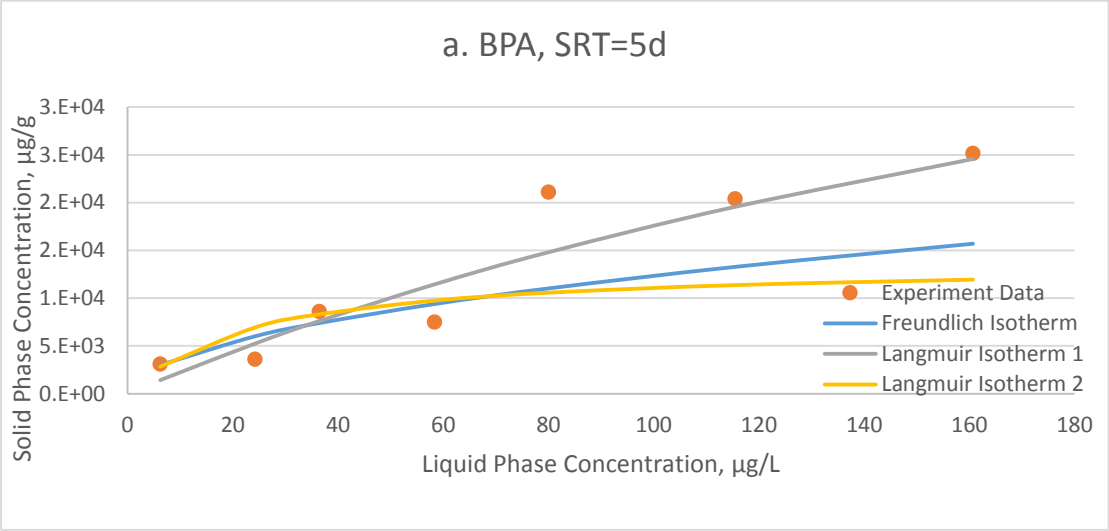
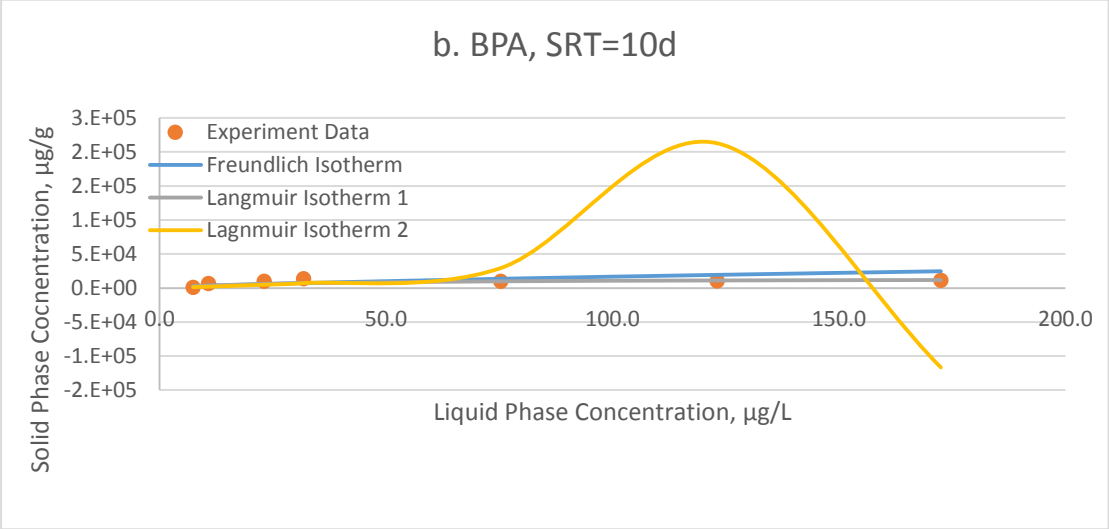


Figure B. 2 Sorption Isotherms Obtained by Linear Regression Compared with Experimental Data, BPA at Aluminum Dosage 2





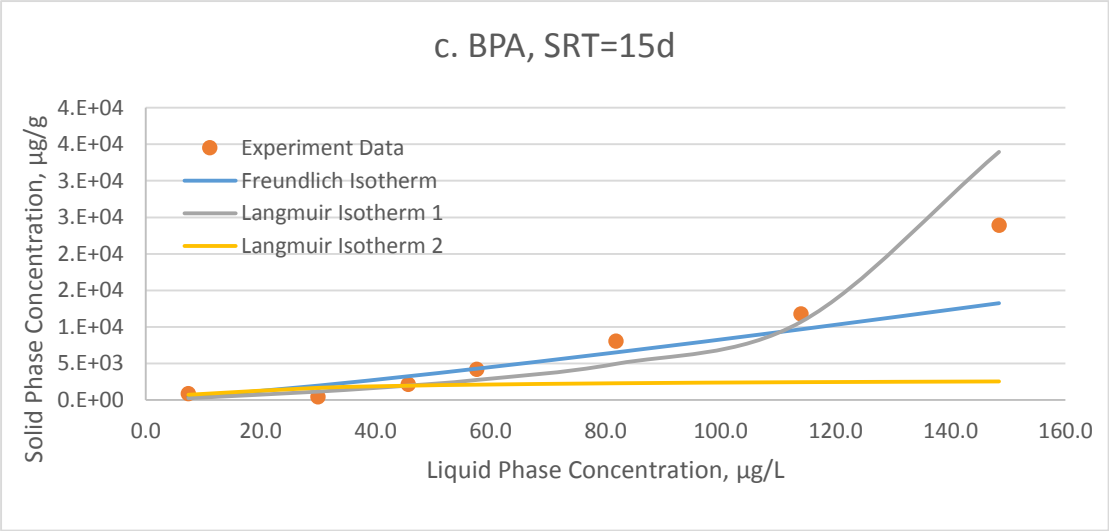
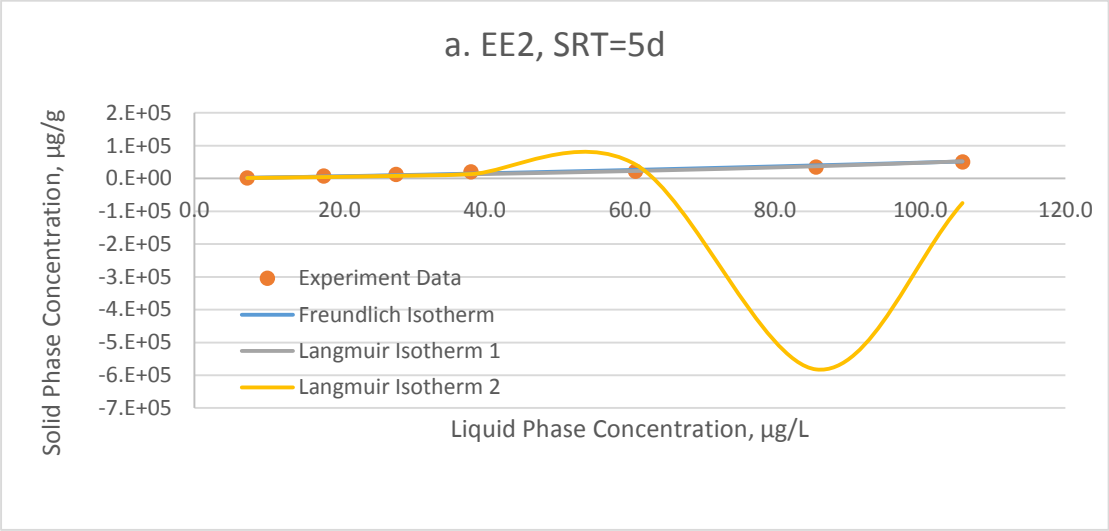
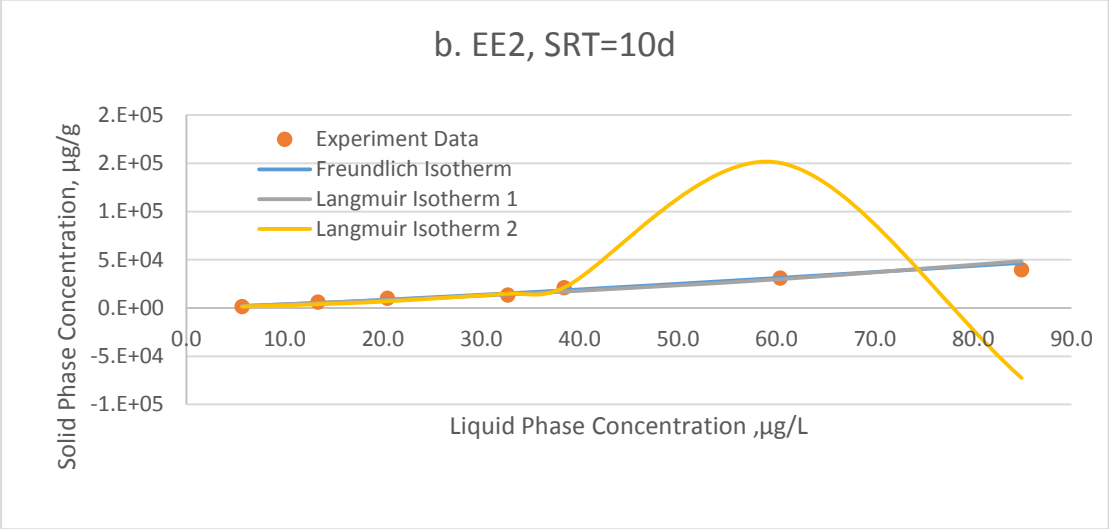


Figure B. 3 Sorption Isotherms Obtained by Linear Regression Compared with Experimental Data, BPA at Aluminum Dosage 3





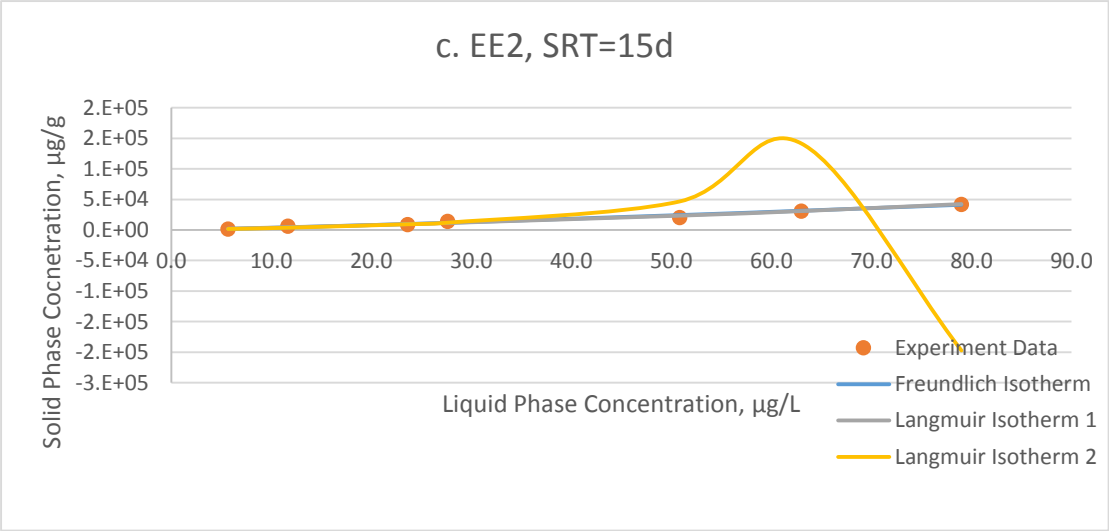
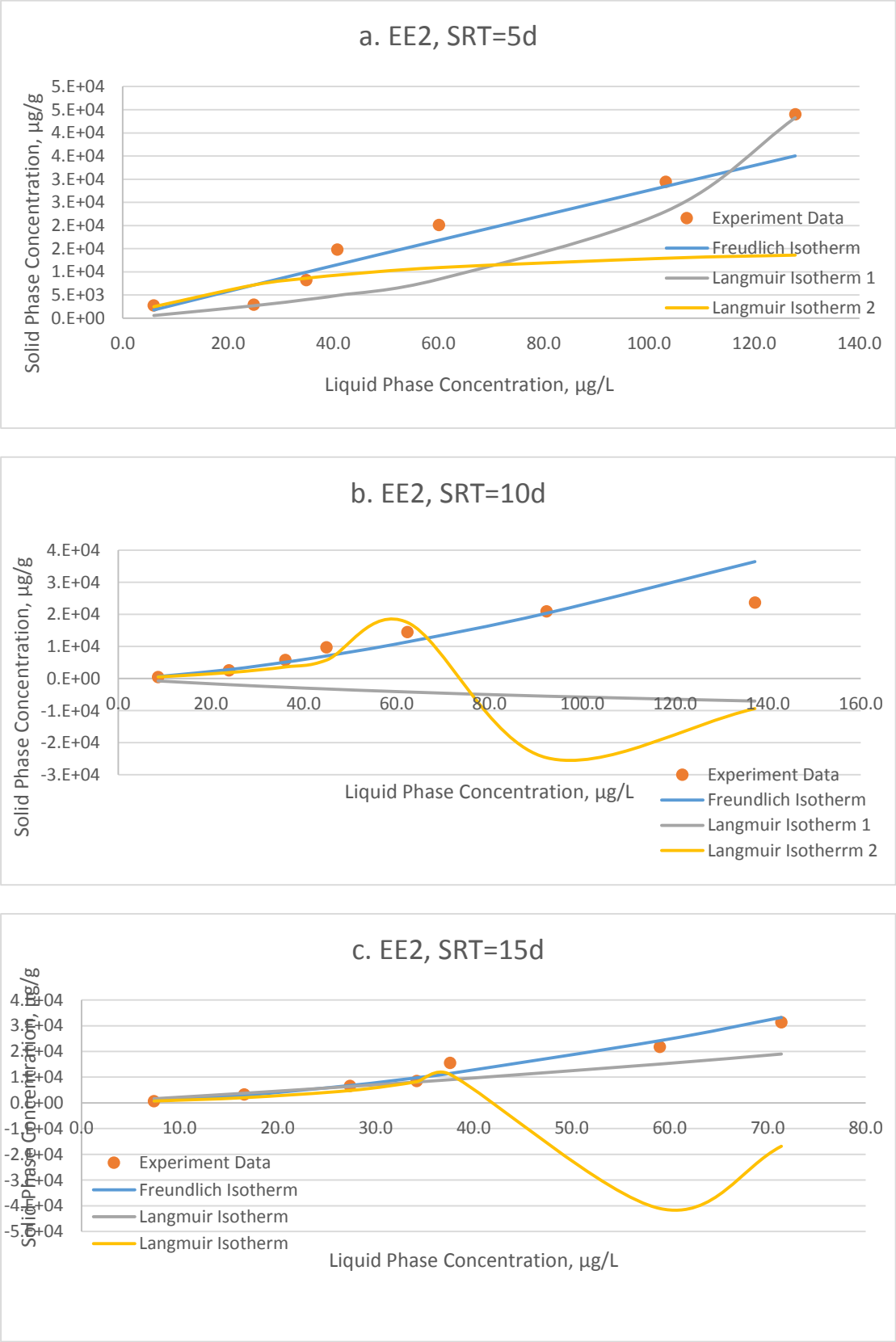


Figure B. 4 Sorption Isotherms Obtained by Linear Regression Compared with Experimental Data, EE2 at Aluminum Dosage 1



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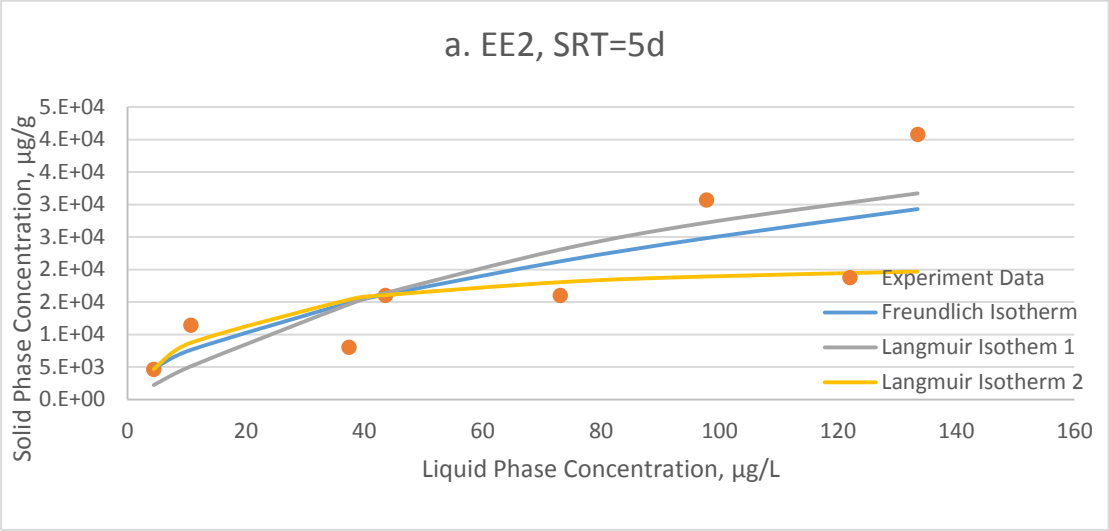
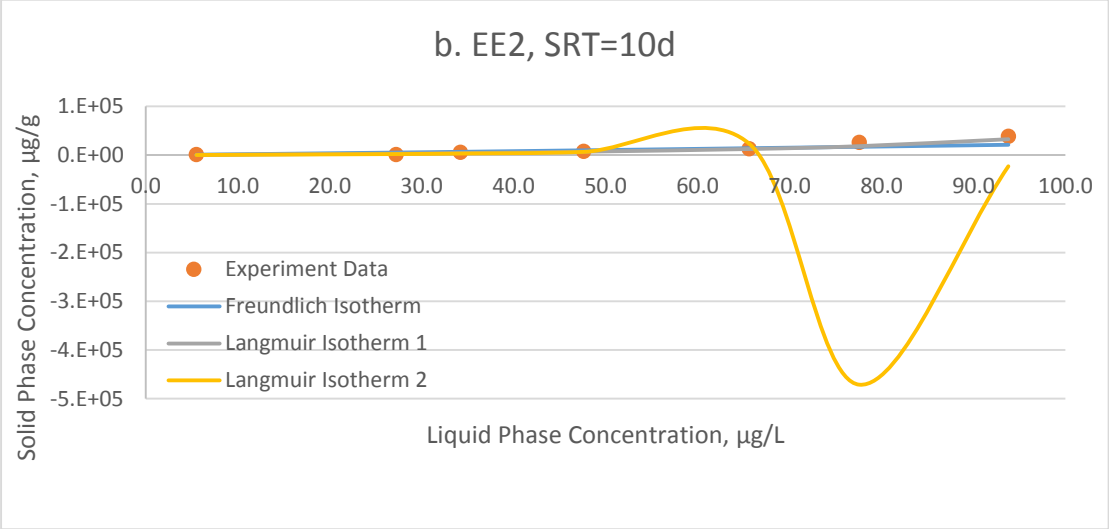




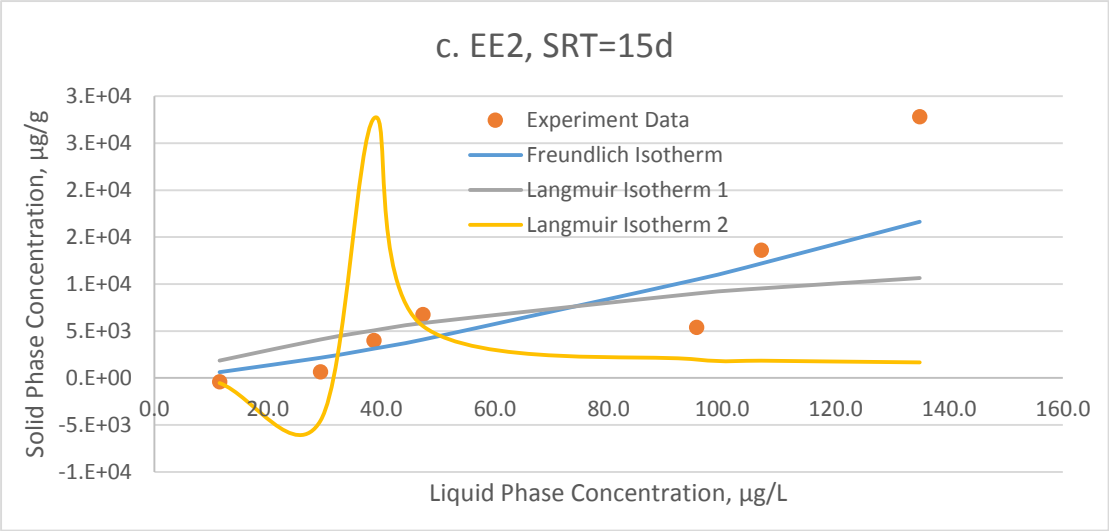
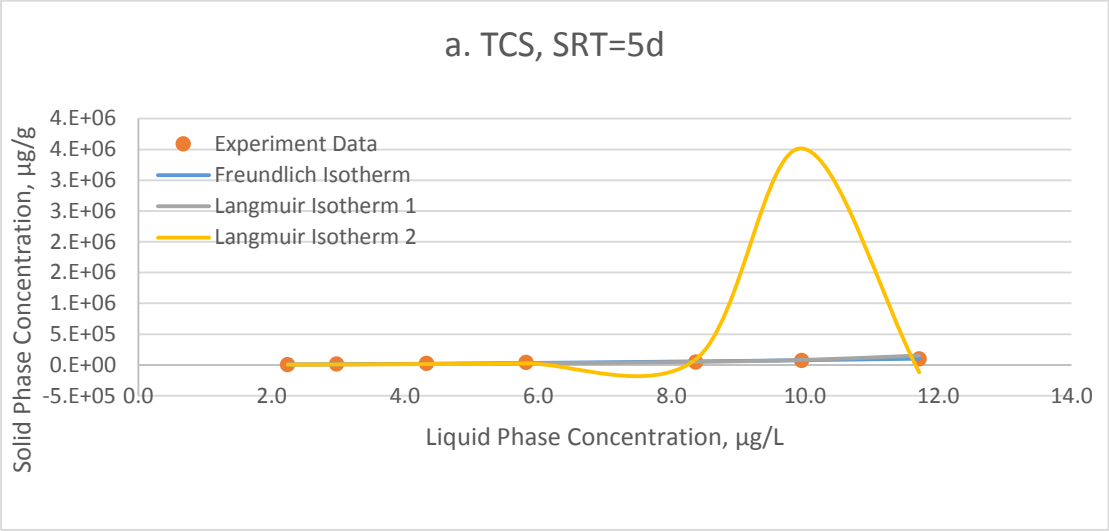
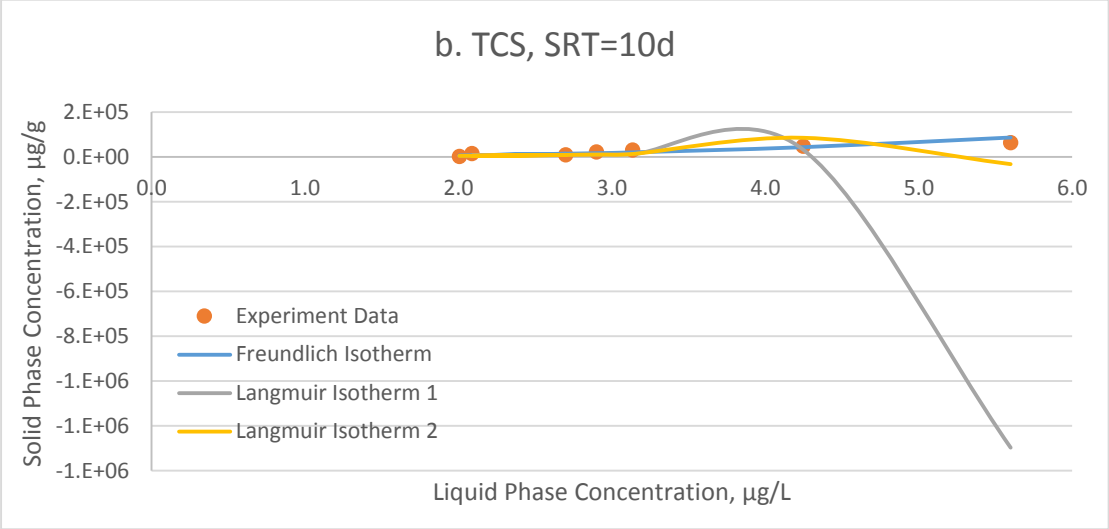


Figure B. 6 Sorption Isotherms Obtained by Linear Regression Compared with Experimental Data, EE2 at Aluminum Dosage 3





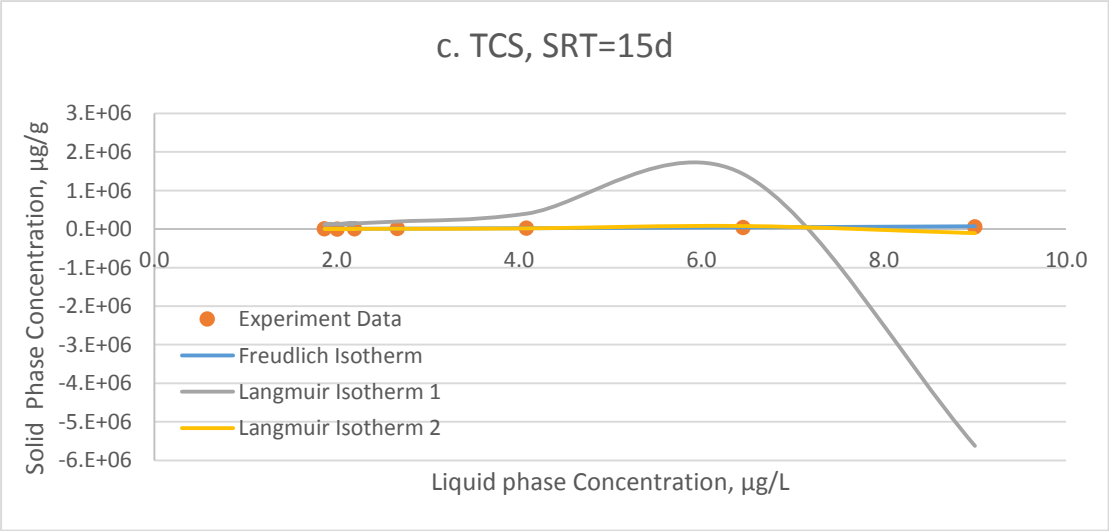
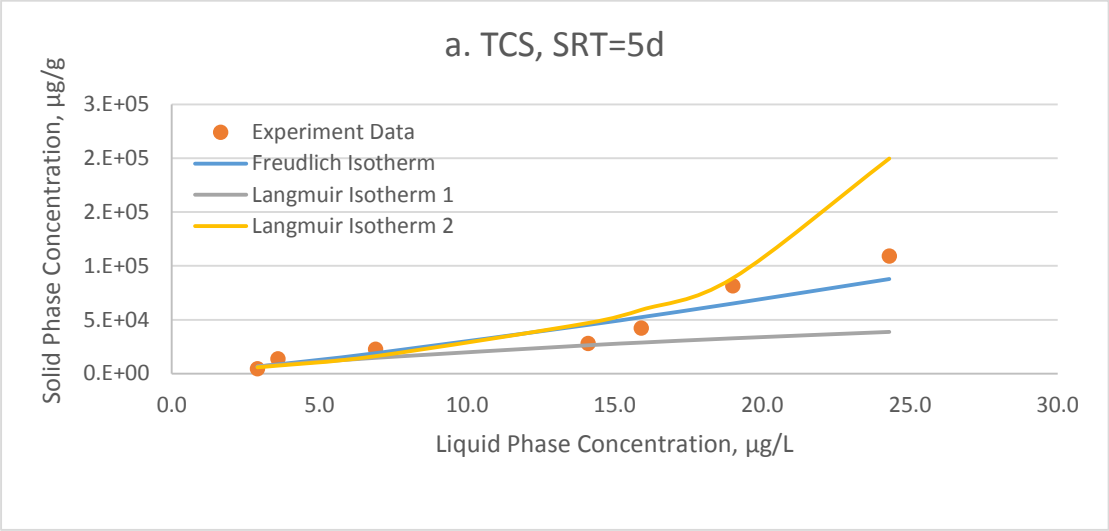
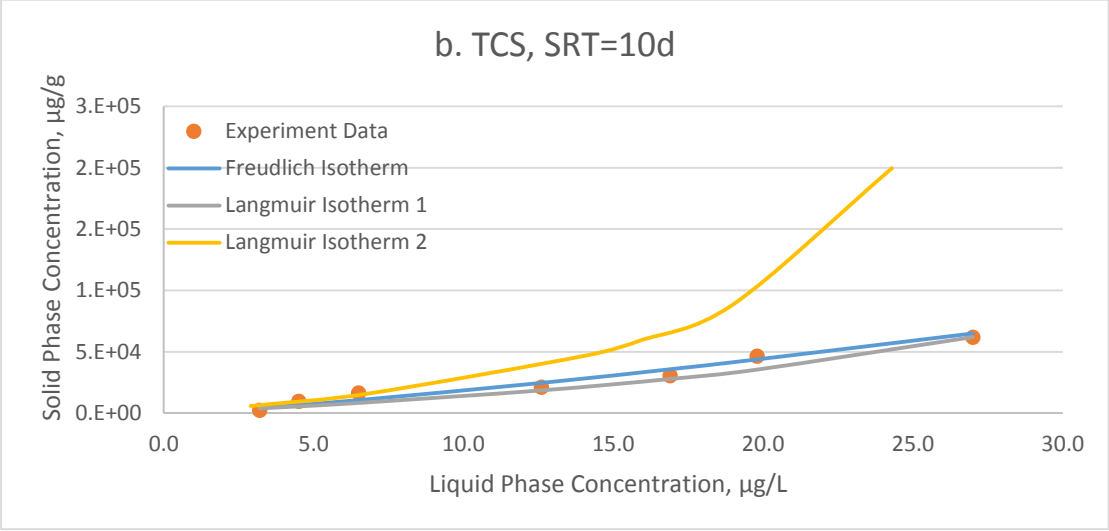


Figure B. 7 Sorption Isotherms Obtained by Linear Regression Compared with Experimental Data, TCS at Aluminum Dosage 1





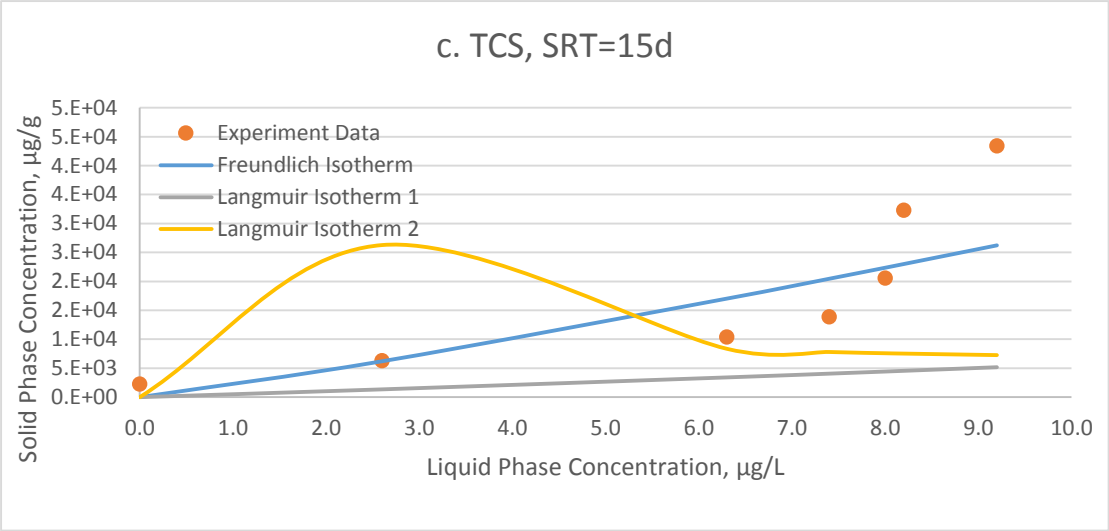
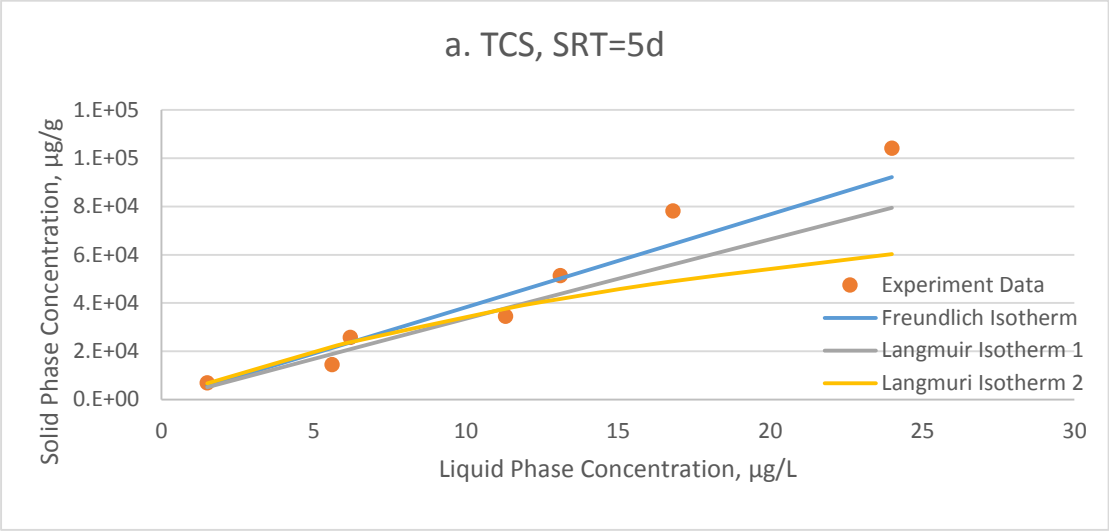
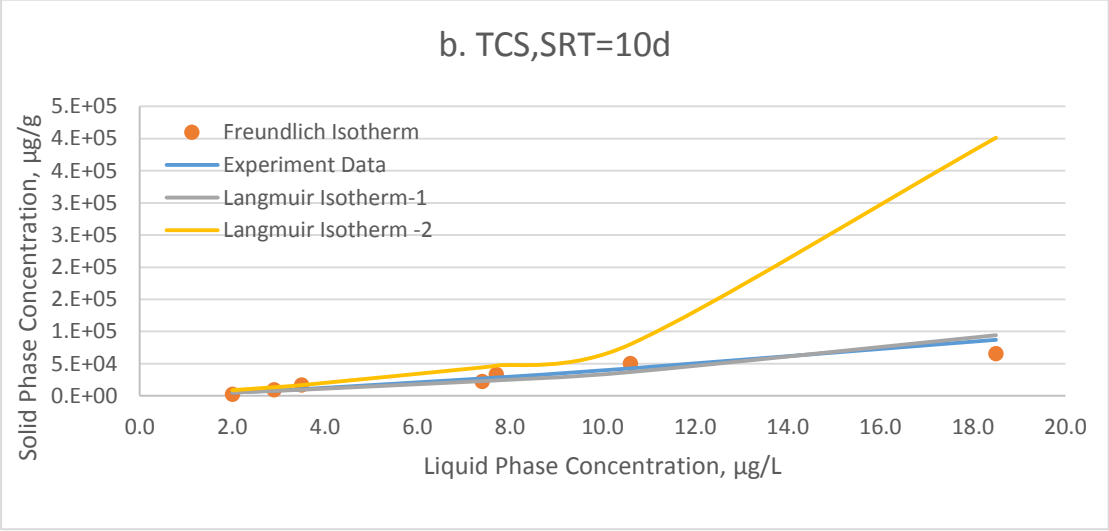


Figure B. 8 Sorption Isotherms Obtained by Linear Regression Compared with Experimental Data, TCS at Aluminum Dosage 2





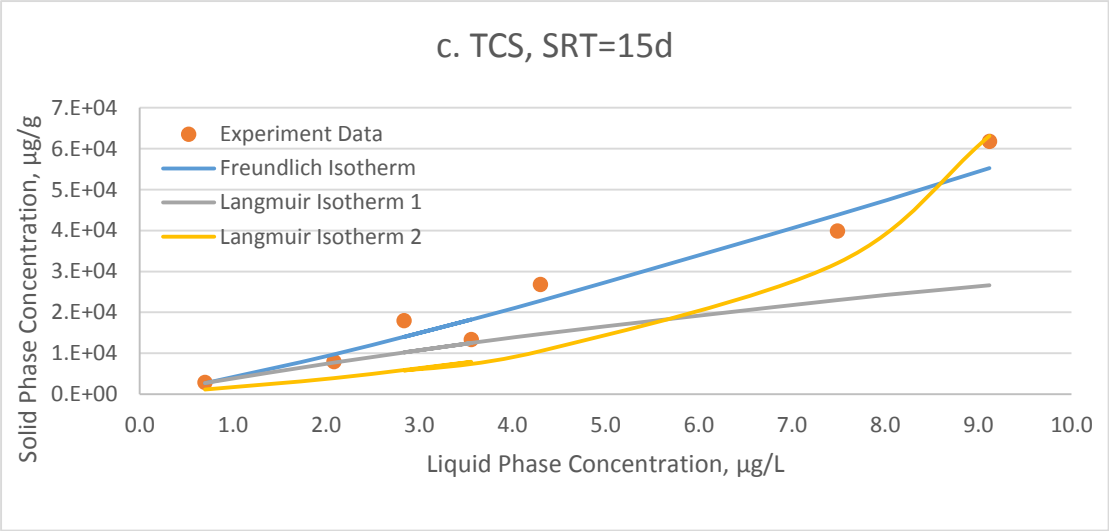
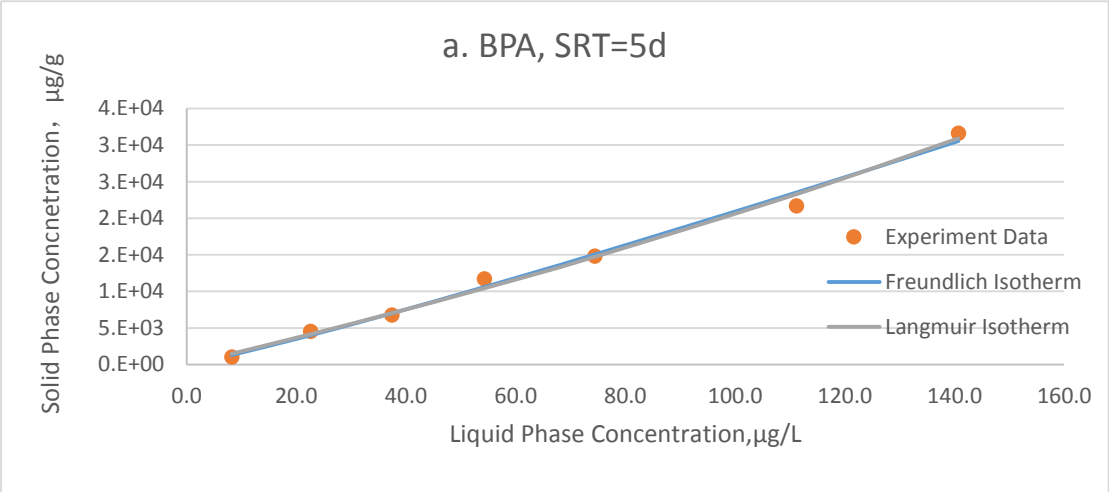
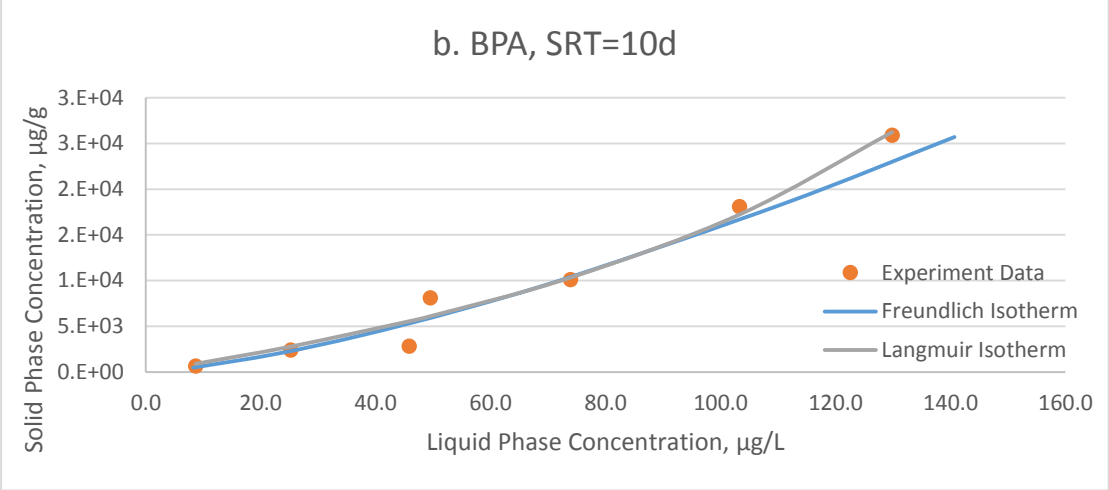


Figure B. 9 Sorption Isotherms Obtained by Linear Regression Compared with Experimental Data, TCS at Aluminum Dosage 3

Appendix C





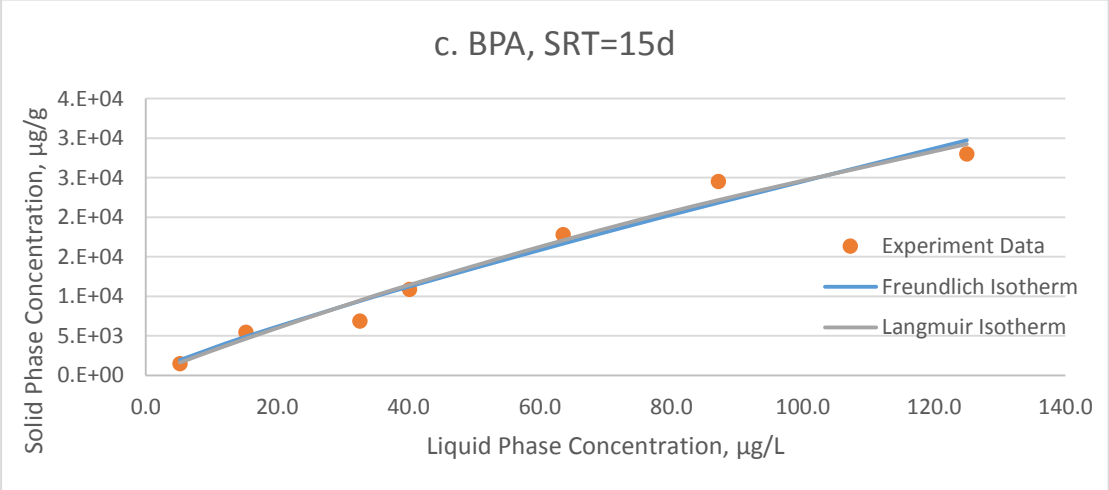


Figure C 1 Sorption Isotherms Obtained by Non-Linear Regression Compared with Experimental Data, BPA at Aluminum Dosage 1

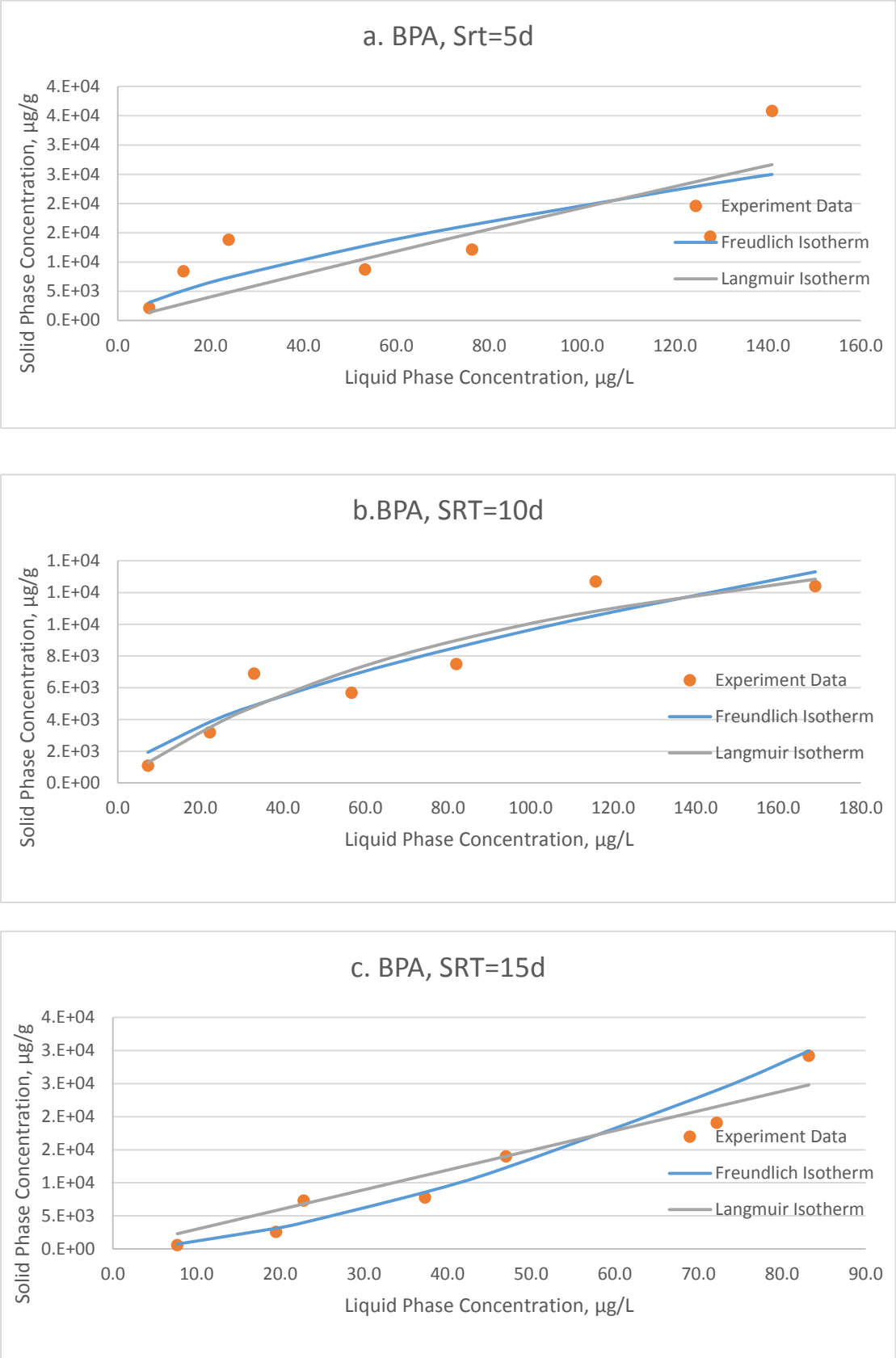
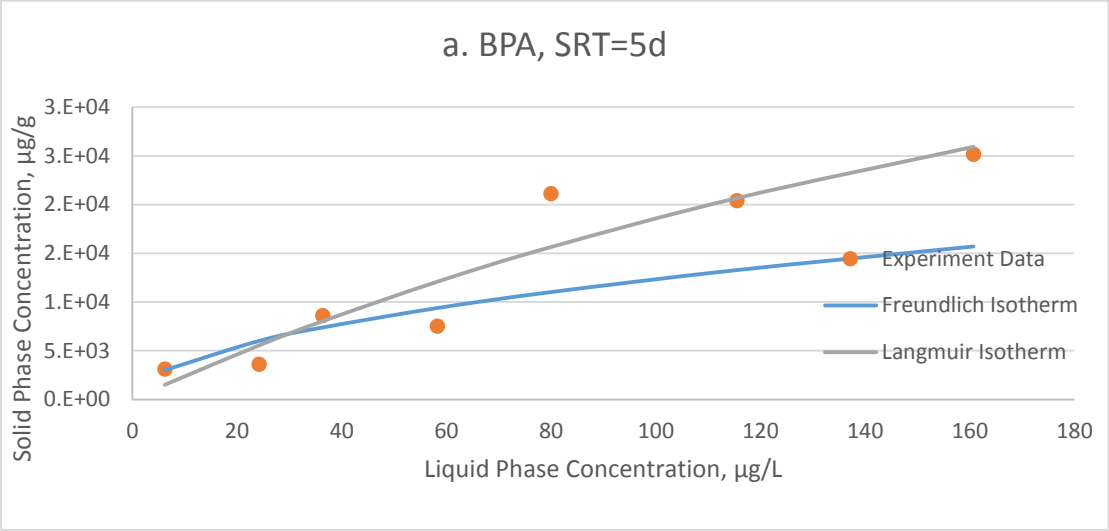
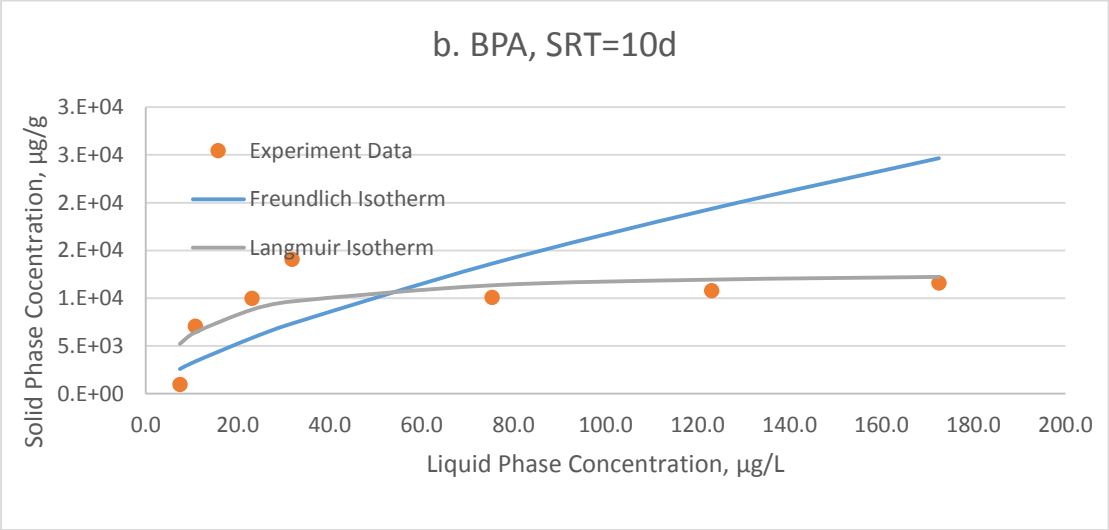


Figure C 2 Sorption Isotherms Obtained by Non-Linear Regression Compared with Experimental Data, BPA at Aluminum Dosage 2





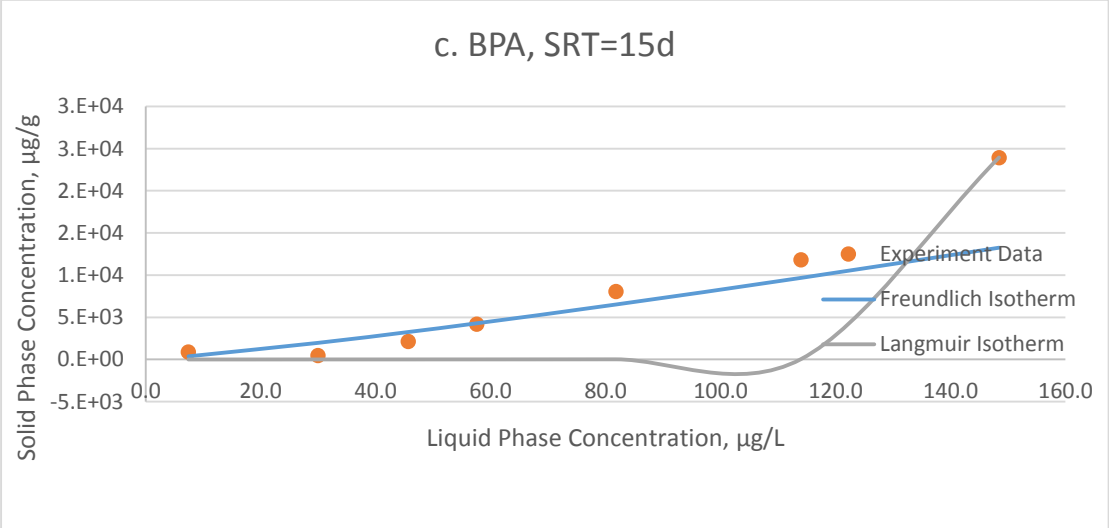
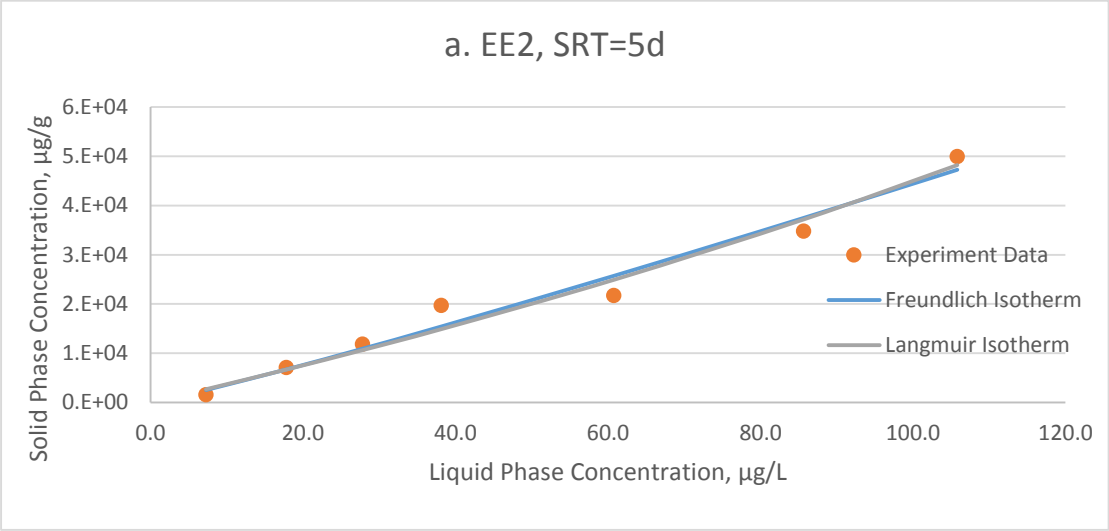
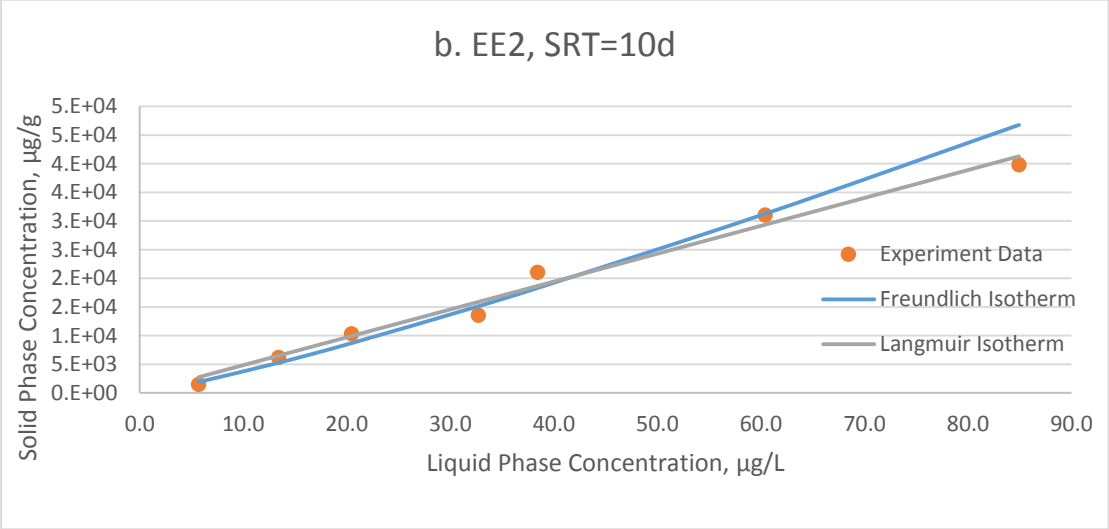


Figure C 3 Sorption Isotherms Obtained by Non-Linear Regression Compared with Experimental Data, BPA at Aluminum Dosage 3





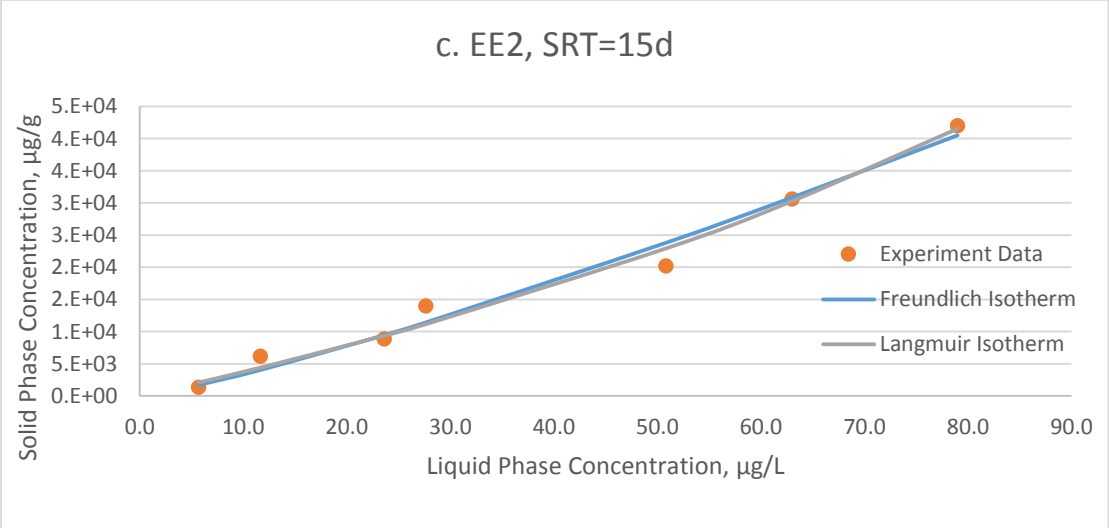
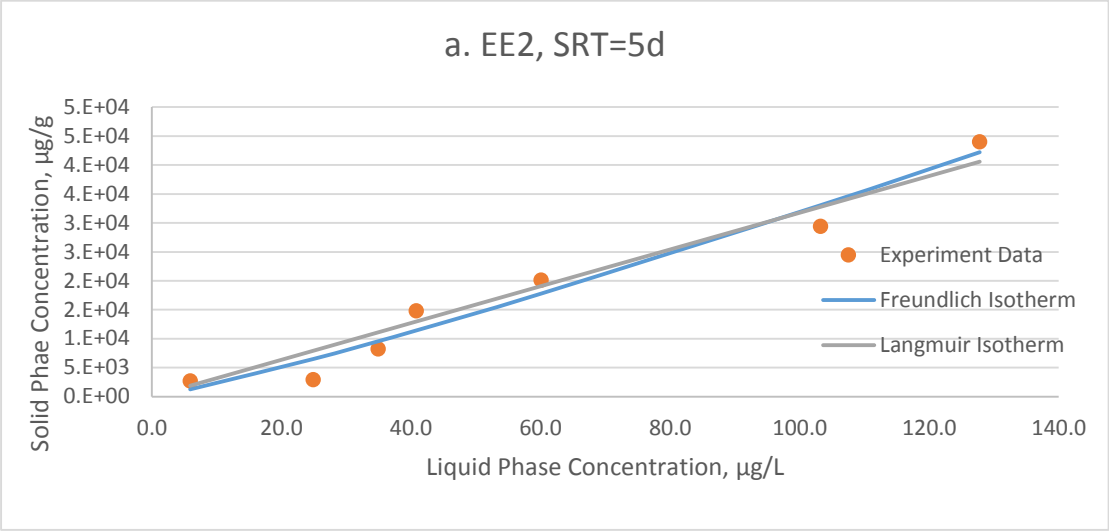
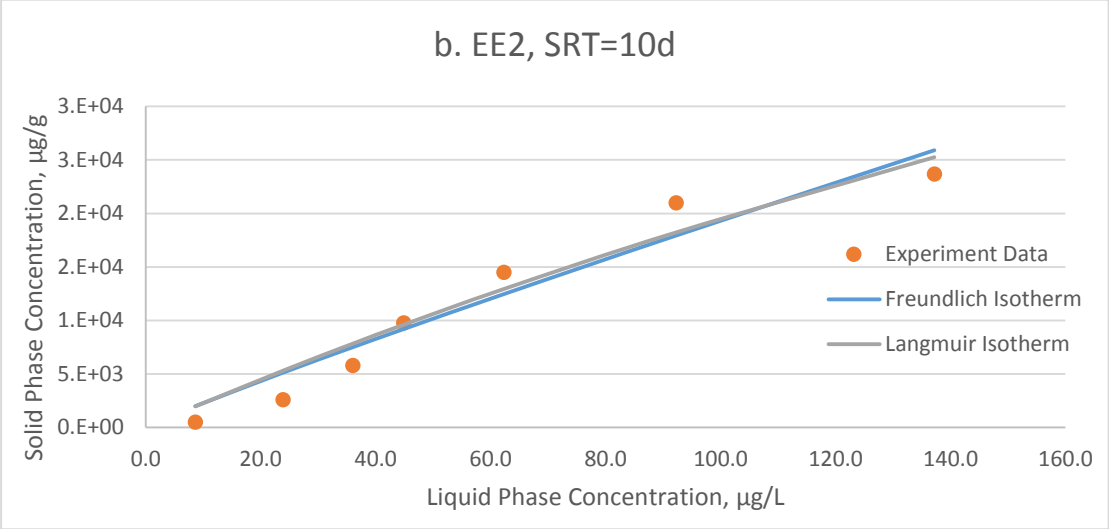


Figure C 4 Sorption Isotherms Obtained by Non-Linear Regression Compared with Experimental Data, EE2 at Aluminum Dosage 1





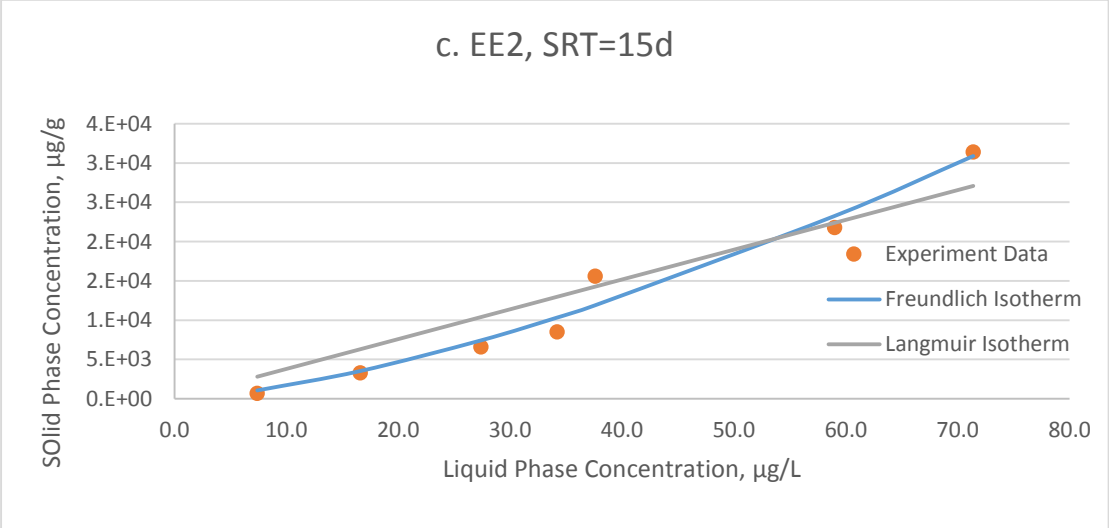
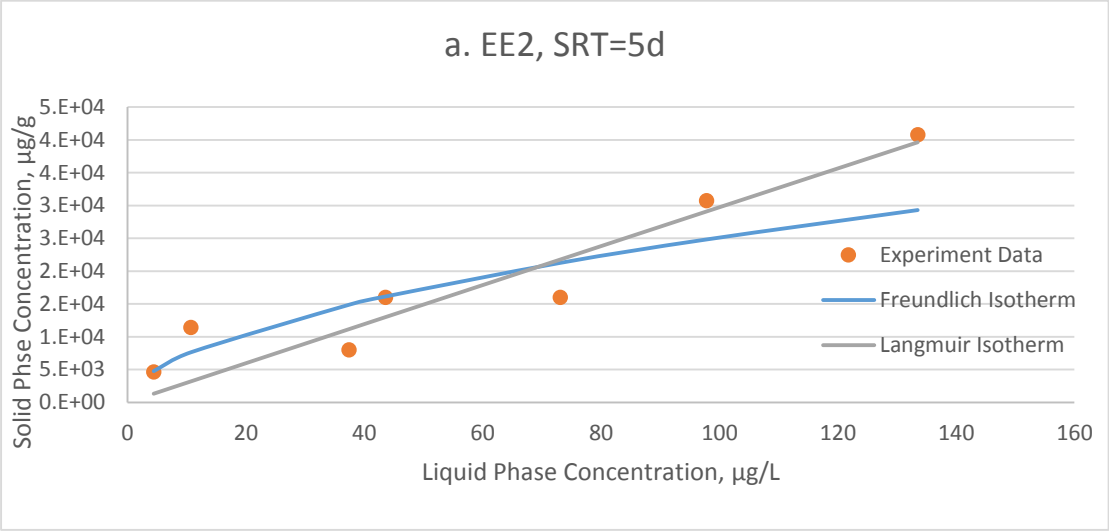
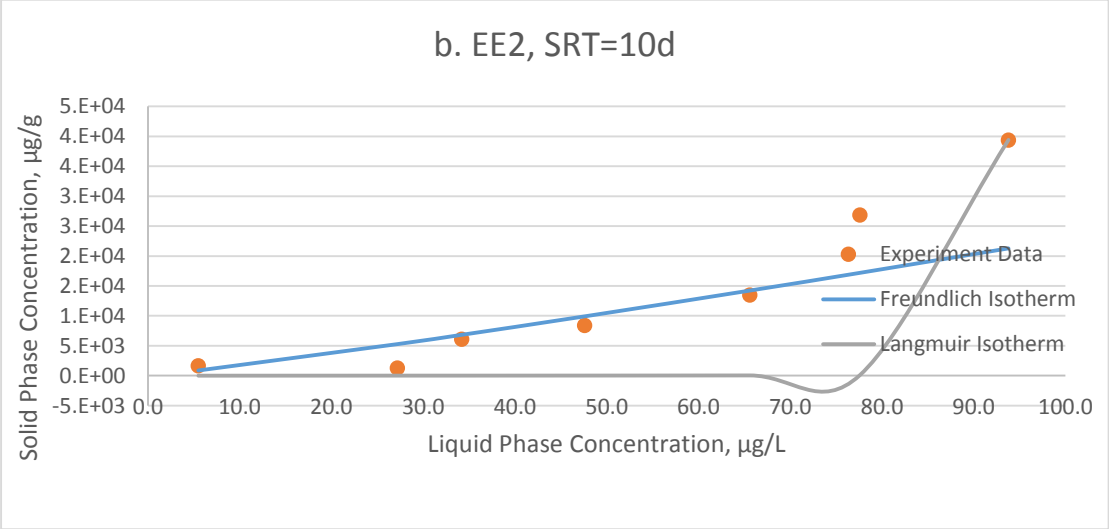


Figure C 5 Sorption Isotherms Obtained by Non-Linear Regression Compared with Experimental Data, EE2 at Aluminum Dosage 2





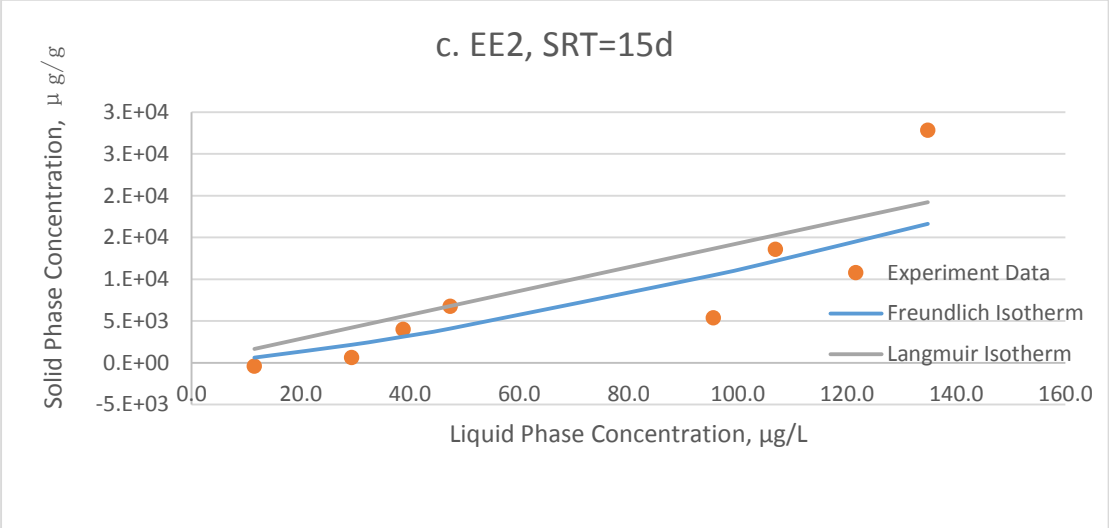
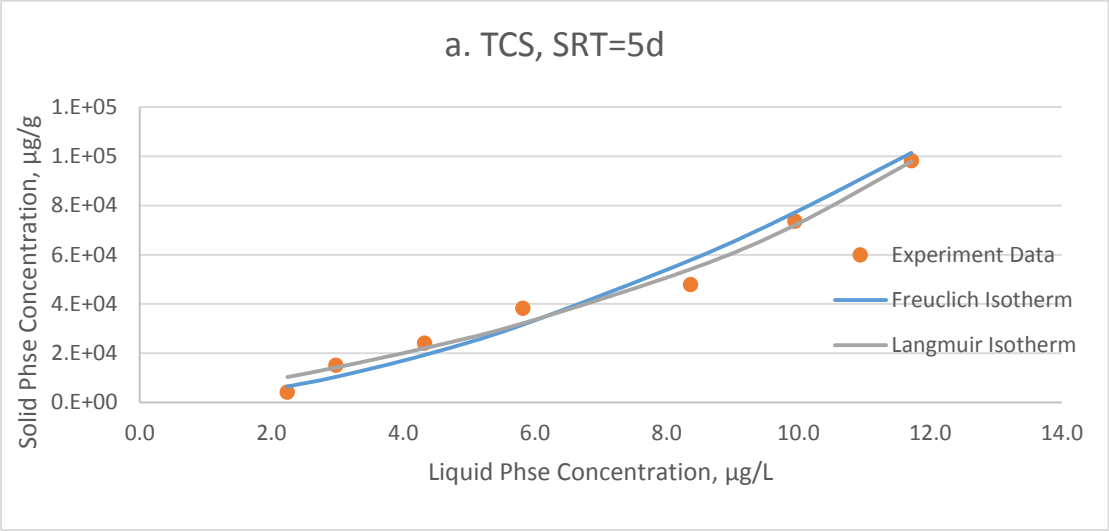
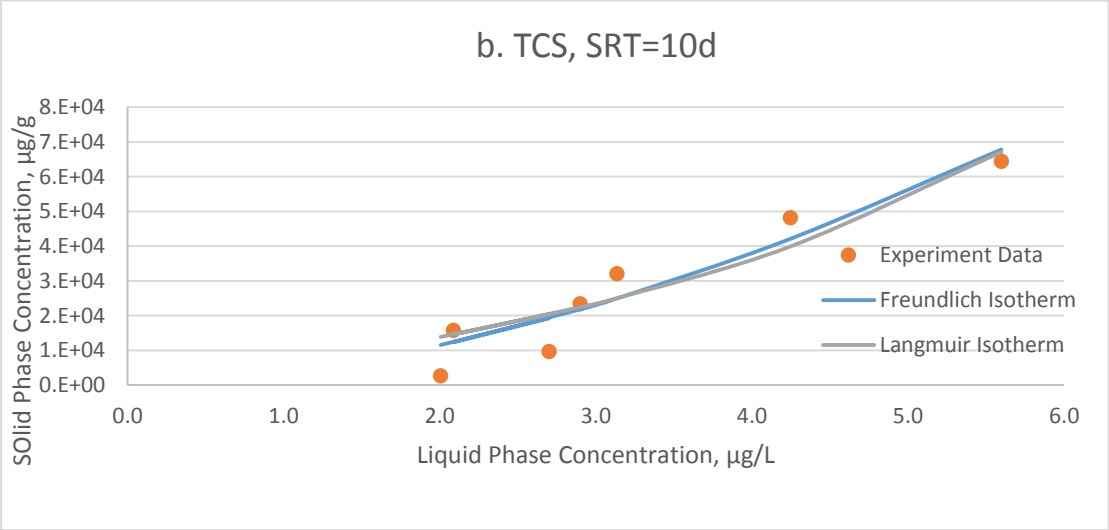


Figure C 6 Sorption Isotherms Obtained by Non-Linear Regression Compared with Experimental Data, EE2 at Aluminum Dosage 3





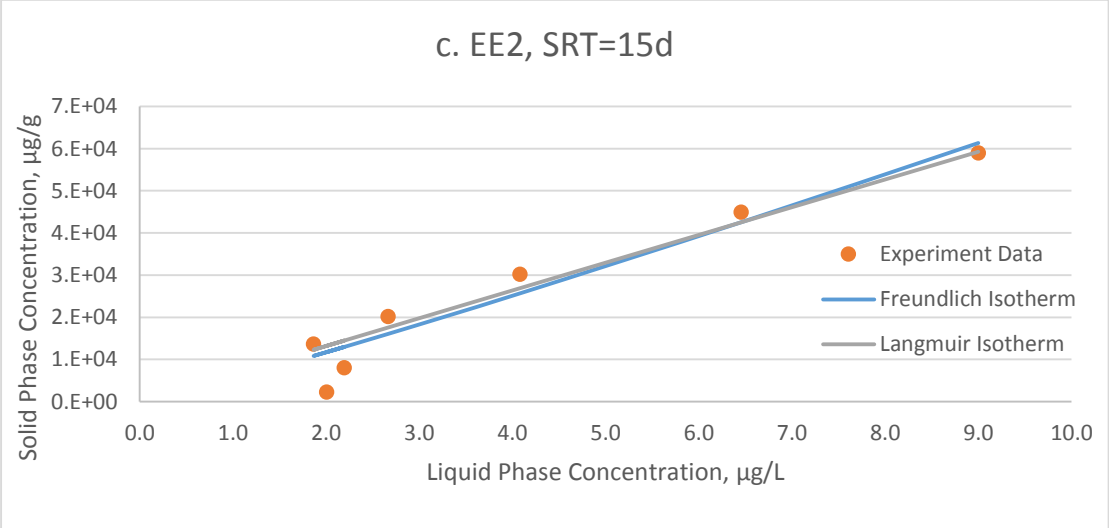
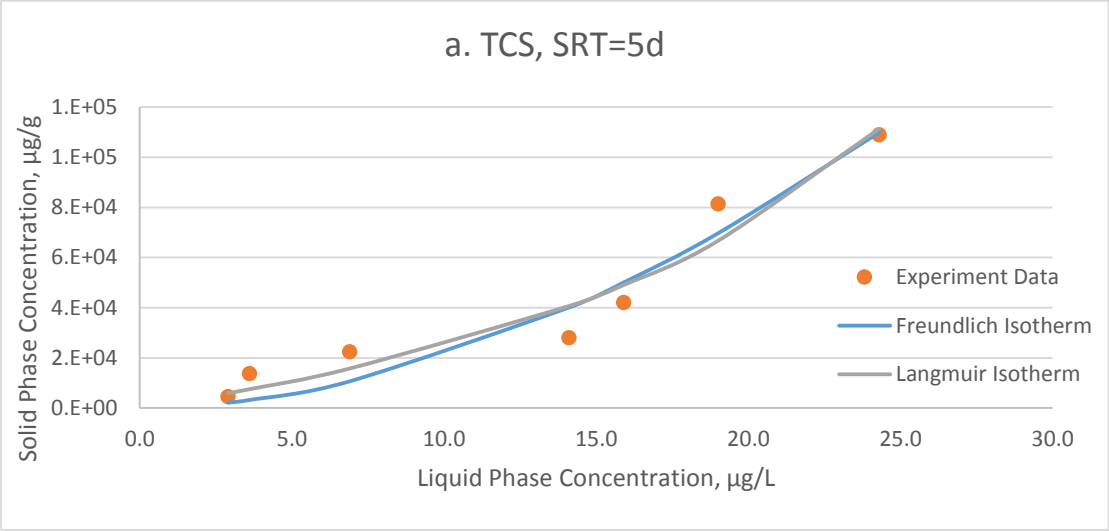
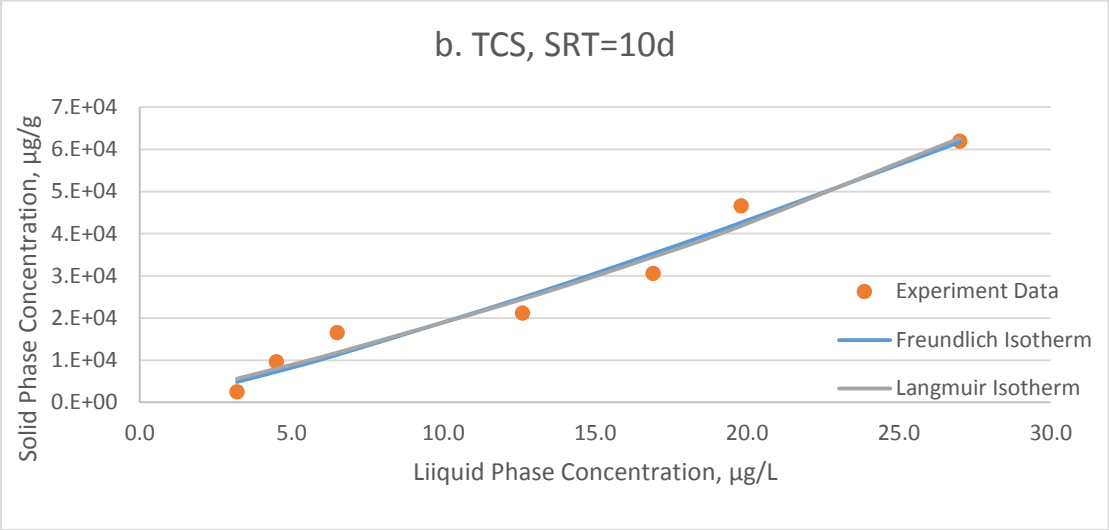


Figure C 7 Sorption Isotherms Obtained by Non-Linear Regression Compared with Experimental Data, TCS at Aluminum Dosage 1





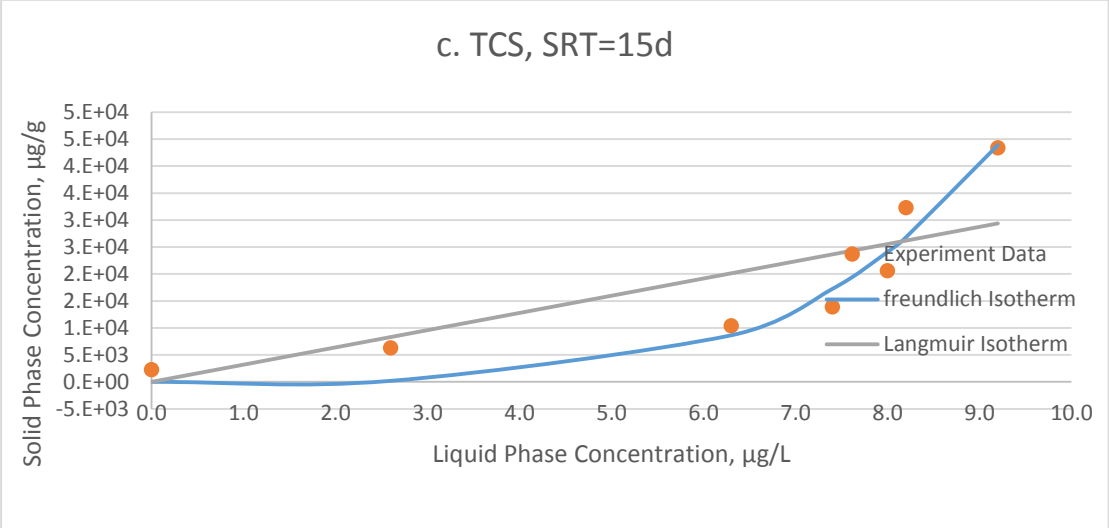
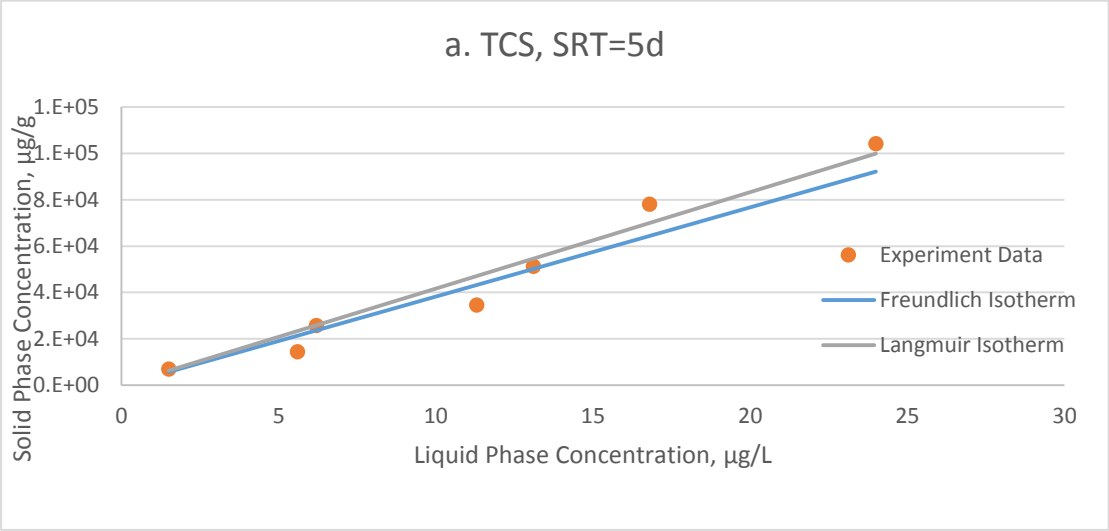
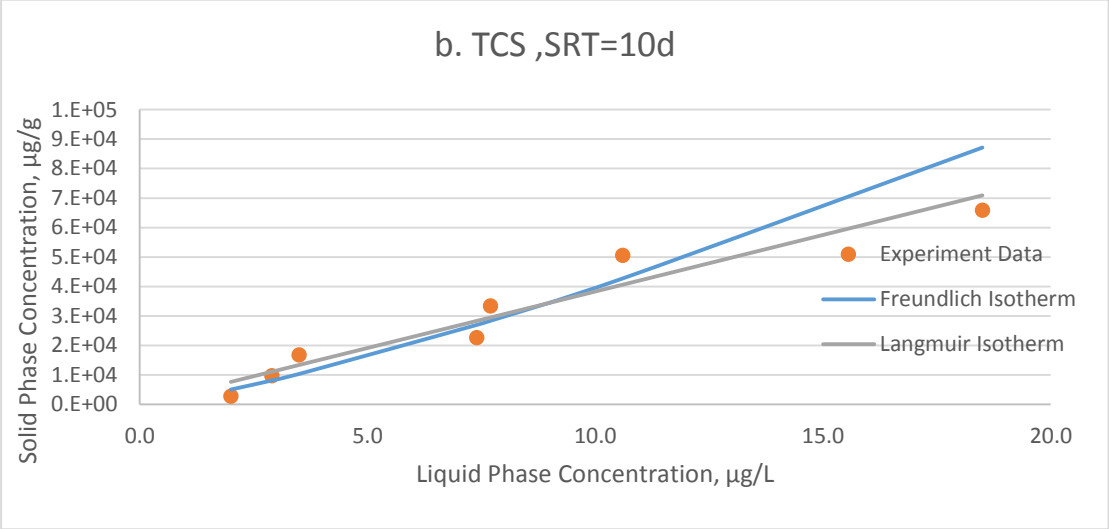


Figure C 8 Sorption Isotherms Obtained by Non-Linear Regression Compared with Experimental Data, TCS at Aluminum Dosage 2





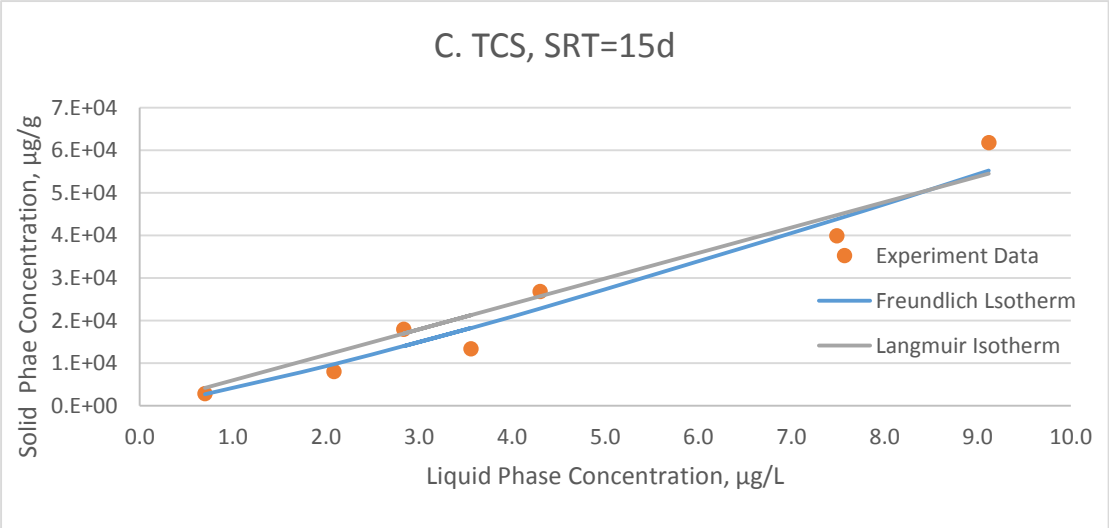


Figure C 9 Sorption Isotherms Obtained by Non-Linear Regression Compared with Experimental Data, TCS at Aluminum Dosage

Appendix D

In order to verify the reliability of the experimental method applied for sorption kinetics and isotherms experiments, a mass balance was carried out by testing both the solid and liquid phase concentrations. Solid phase concentrations were tested by applying microwave-assisted extraction method to the samples. Details of microwave-assisted extraction method can be seen in the study of Banihashemi (2012).

Three 100 mL sample (MLSS collected from reactor 2 at alum dosage 2) were deactivated for 24 h by adding sodium azide at concentration of 0.2% (W:V). Then MCs were spiked to the samples at 70 μg/L and mixed for another 24 h, then centrifuge was applied to the sample to separate solid and liquid. Both solid and liquid parts were collected for further analysis. The liquid part was analyzed by the method described in Section 3.3. The microwave-assisted extraction procedure was applied to the solid part (mainly contains biomass). First, 10 g anhydrous sodium sulphate was added to the solid parts and well mixed with the solids. The purpose of adding sodium sulphate is to absorb the extra moisture in the solid matrix and to grind the biomass cake into small particles to increase the surface area of the biomass. Then 20 mL extraction solvent, a mixture of hexane and acetone, was added to biomass samples. The extraction procedure can be repeated for many times as needed by adding new solvent to the biomass. As for this experiment, a total of 50 mL extraction solvent was used for each sample by adding 20 mL at the first two times and 10 mL the last time. The ratios of hexane over acetone were different for the three samples. Details are in Table D. 1. Extracted solvent and biomass were then moved to the vessel of the Mars 5® (MW Accelerated Reaction System; CEM Corporation) MW oven. After the mixture was heated to over 100^{o}C, it was removed from the microwave vessel and the extracted solvent was collected. The 50 mL extract solvent was dried with nitrogen gas. Then the dried sample, which contains MCs, was dissolved in 100 mL water. The 100 mL sample

was then analyzed by applying the liquid phase experimental method described in Section 3.3.

The experimental method is summarized in the following table:

Table D.1 Summarization of Experimental Procedure for Microwave-assisted Extraction Method

	Sample 1	Sample 2	Sample 3
Solid (Biomass) Weight (g)	2.27	2.30	2.21
Sodium Sulphate Added (g)		10	
Extraction Solvent Volume	20 mL for the first two extraction, 10 mL for the last extraction. A total of 50 mL.		
Extraction Solvent Composition (Acetone : Hexane, V:V)	1:1	3:1	1:3
Solvent Exchange	Extraction solvent dried by nitrogen gas, then dissolved by 100 mL water.		

The mass balance equation is shown in equation D.1,

$$M_{RC} = W_{solid} \times C_{solid} + V_{liquid} \times C_{liquid} \quad \text{Eq. D.1}$$

where M_{RC} is the total mass recovered, μg,

W_{solid} is weight of biomass listed in Table D.1, g,

C_{solid} is the tested concentrations of MCs in solid phase, μg/g,

V_{liquid} is the volume of the liquid part, which is 0.1L,

C_{liquid} is the tested concentrations of MCs in the liquid phase, μg/L.

Total recovery rate is calculated by equation D.2,

$$Total\ Recovery\ Rate = \frac{M_{RC}}{M_{Dosed}} \times 100\% \quad \text{Eq. D.2}$$

where M_{Dosed} is the mass of MCs dosed into the samples, which was 7 μg,

Since the liquid phase recovery rate was 91.8, 96.3 and 77.3% for BPA, EE2 and TCS, respectively, the solid phase recovery rate can be calculated by equation D.3:

$$Solid\ Phase\ Recovery\ Rate = \frac{W_{solid} \times C_{solid}}{M_{Dosed} - \left(\frac{V_{liquid} \times C_{liquid}}{Liquid\ Phase\ Recovery\ Rate}\right)} \times 100\%$$

Eq. D.3

Both liquid phase and solid phase concentrations are listed in the following table. Total recovery rates and solid phase recovery rates are calculated according to equations D.2 and D.3.

Table D.2 Total Recovery Rate of MCs (n=2)

		Sample 1	Sample 2	Sample 3
C_{solid} (μg/g)	BPA	0.62	0.22	0.45
	EE2	0.88	1.30	1.37
	TCS	0.52	1.19	1.16
C_{liquid} (μg/L)	BPA	43.0	47.6	45.0
	EE2	33.4	38.6	36.7
	TCS	9.4	11.8	10.2
M_{RC} (μg)	BPA	5.7	5.3	5.5
	EE2	5.3	6.8	6.7
	TCS	2.1	3.9	3.6
Total Recovery Rate (%)	BPA	82	75	79
	EE2	76	98	96
	TCS	30	56	51
Solid Phase Recovery	BPA	61	28	47
Rate (%)	EE2	57	100	95
	TCS	21	50	45

Based on the results in Table D.2, the total recovery rates for BPA and EE2 are all over 70%, however, almost 50% of TCS was lost. When examining the solid phase recovery rate, different samples shows significantly difference. Samples 2 and 3, where the extraction solvent composition is acetone : hexane (V:V) of 3:1 and 1:3, respectively, have high recovery rates for EE2, but not for BPA and TCS. However, sample 1, where the extraction solvent composition is acetone : hexane (V:V) of 1:1, the BPA recovery rate of the solid phase is the highest among the three compounds. The total experiment is based on the assumption that sodium azide is 100% effective to deactivate the biomass so that no biodegradation would take place.