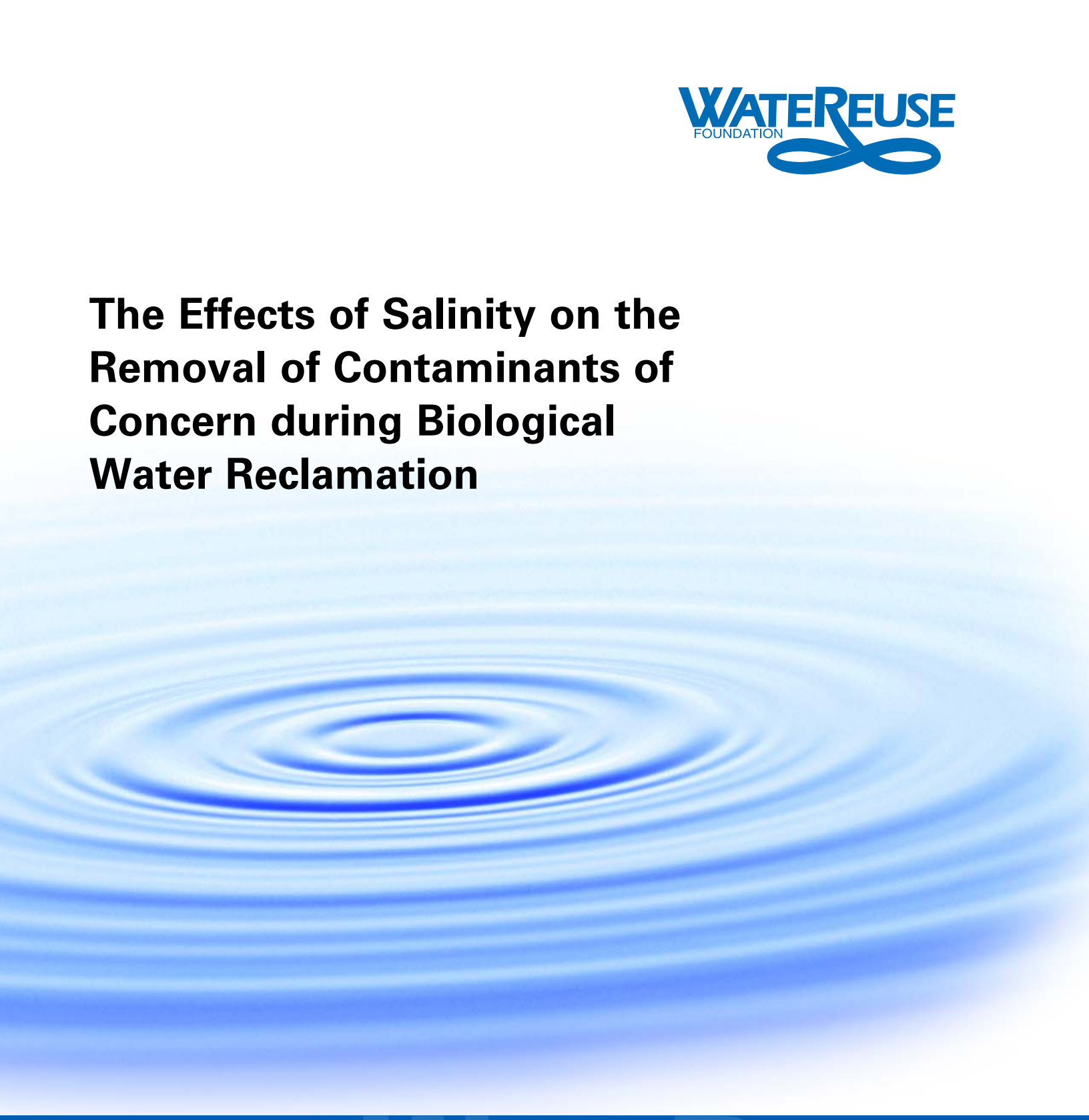
The Effects of Salinity on the Removal of Contaminants of Concern during Biological Water Reclamation



WateReuse Foundation

The Effects of Salinity on the Removal of Contaminants of Concern during Biological Water Reclamation

About the WateReuse Foundation

The mission of the WateReuse Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the Southwest Florida Water Management District, the California Energy Commission, and the California Department of Water Resources. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations. The Foundation also conducts research in cooperation with the Global Water Research Coalition.

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Peter Fox, Ph.D.
Arizona State University

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For more information, contact:
WateReuse Foundation
1199 North Fairfax Street, Suite 410
Alexandria, VA 22314
703-548-0880
703-548-5085 (fax)
www.WateReuse.org/Foundation

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ACRONYMS AND ABBREVIATIONS

AA	Atomic absorption
CAFOs	Concentrated animal feed operations
COD	Chemical oxygen demand
DCBT	Divalent cation bridging theory
DLVO	Derjaguin, Landau, Verwey, and Overbeek
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EPS	Exocellular polymeric substances
E1	Estrone
E2	17β-estradiol
EE2	17α-ethynylestradiol
HPLC	High-performance liquid chromatography
K_A	Capacity parameter
KWRF	Kyrene Water Reclamation Facility
M/D	Monovalent to divalent
MLSS	Mixed liquor suspended solids
MNWWRP	Mesa Northwest Water Reclamation Plant
PE	Polyethylene
q_A	Equilibrium sorbent-phase concentration
RAS	Return activated sludge
SMPs	Soluble microbial products
SRF	Specific resistance to filtration
SRT	Solid retention time
SS	Suspended solids
SVI	Sludge volume index
TSS	Total suspended solids
UV	Ultraviolet

FOREWORD

The WateReuse Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high-quality water, protect public health, and improve the environment.

A Research Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities including water professionals, academics, and Foundation Subscribers. The Foundation's research focuses on a broad range of water reuse research topics including:

- Definition and addressing of emerging contaminants;
- Public perceptions of the benefits and risks of water reuse;
- Management practices related to indirect potable reuse;
- Groundwater recharge and aquifer storage and recovery;
- Evaluation and methods for managing salinity and desalination; and
- Economics and marketing of water reuse.

The Research Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project and provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The Foundation's primary funding partners include the Bureau of Reclamation, California State Water Resources Control Board, the Southwest Florida Water Management District, the California Energy Commission, Foundation Subscribers, water and wastewater agencies, and other interested organizations. The Foundation leverages its financial and intellectual capital through these partnerships and funding relationships.

This publication presents the results of a Foundation-sponsored research study. The study focused on the effect of the M/D ratio and cationic strength on the sorption of hydrophobic compounds. Increases to the M/D ratio have become a growing concern in water reclamation plants as the use of domestic ion exchange water softeners has increased in new and affluent communities.

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David L. Moore
President
WateReuse Foundation

G. Wade Miller
Executive Director
WateReuse Foundation

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Principal Investigator
Peter Fox, *Arizona State University*

Participating Agencies
Sanitation Districts of Los Angeles County
Southern Nevada Water Authority

Project Advisory Committee
Saied Delagah, *Bureau of Reclamation*
Phil Friess, *Sanitation Districts of Los Angeles County*
David Jenkins, *University of California–Berkeley*
Jim Kelly, *Central Contra Costa County Sanitary District*
Rich Mills, *California State Water Resources Control Board*
Margaret Nellor, *Nellor Environmental Associates, Inc.*

EXECUTIVE SUMMARY

Conventional wastewater treatment operations are dependent on the settleability of biosolids. Past research has shown that biosolid flocculation is dependent on the monovalent-to-divalent-cation ratio (M/D ratio). In other words, bioflocculation (aggregation of biological solids) is enhanced by the presence or absence of divalent cations such as calcium and/or magnesium ions and deteriorates with high concentrations of monovalent cations such as sodium, potassium, and ammonium ions. Some hydrophobic contaminants of concern are primarily removed during wastewater treatment by sorption into biosolids. Most estrogenic compounds are hydrophobic, and they were used as model compounds for this study. The primary hypothesis evaluated during this study was that sorption of hydrophobic compounds will be influenced by bioflocculation and that, consequently, increasing the M/D ratio will decrease sorptive capacity. Increases to the M/D ratio have become a growing concern in water reclamation plants as the use of domestic ion exchange water softeners has increased in new and affluent communities. Regeneration of the ion exchange water softeners adds salt to reclaimed water. Increases in total-dissolved-solid concentrations of greater than 400 mg/L have been observed and have been attributed to sodium chloride used for regeneration. This can increase the monovalent cation concentration in reclaimed water by 7 meq/L as compared to reclaimed water not impacted by water softeners. Consequently, increases in monovalent cation concentrations have the potential to increase estrogenic compound concentrations in reclaimed waters and thereby increase the risk of aquatic and human exposure.

This study focused on the effect of the M/D ratio and cationic strength on the sorption of hydrophobic compounds. The three compounds used in this study included bisphenol A, 17α-ethynylestradiol, and estriol, which are known to have estrogenic activity. Three different types of experiments were completed during this study. Sequencing batch reactors were used to evaluate sorption of hydrophobic compounds under simulated activated sludge-type conditions. Sorption isotherms were used to evaluate the sorption of hydrophobic compounds under various conditions with two different biosolids. Kinetic experiments were used to determine the time necessary for equilibrium and to observe concentration changes as a function of time.

Attempts to conduct the study in sequencing batch reactors were unsuccessful since the biomass became saturated at an influent concentration of 100 µg/L and since analytical limitations prevented the use of lower concentrations. Sorption and desorption breakthrough curves were developed for bisphenol A and 17α-ethynylestradiol in three reactor systems. The results were analyzed using a mass balance, and a Freundlich isotherm relationship was developed using the breakthrough curves. Since saturation occurred, no useful steady-state data could be obtained to compare operation at different M/D ratios and cationic strengths.

The majority of the study was completed using sorption isotherms with bisphenol A, 17α-ethynylestradiol, and estriol as the sorbate and with biosolids as the sorbent. The biosolids and effluent were collected from a nitrifying/denitrifying water reclamation plant (Mesa Northwest Water Reclamation Plant [MNWWRP]) and a membrane bioreactor reclamation plant (Kyrene Water Reclamation Facility [KWRF]). Sorption was studied by contacting the biosolids with various concentrations of sorbate at a constant temperature (isotherm). The isotherms used a constant concentration of biosolids with various concentrations of sorbate

from 100 to 1000 µg/L. The target M/D ratios were 1, 2, and 4, and the target cationic strengths were 12, 8, and 4 meq/L. Several sorption isotherms were performed using sodium azide to inhibit microbial activity in a synthetic water matrix. One set of isotherms was also completed with a target M/D ratio of 6 and a cation concentration of 20 meq/L, which represent some of the worst-case scenarios at water reclamation plants. Isotherms were analyzed using the Freundlich isotherm model. For the target M/D ratios of 1 to 4, a clear trend of decreasing sorption capacity with increasing M/D ratio was observed for the azide isotherms. The azide isotherms were biologically inhibited, and the results should represent abiotic removal mechanisms associated with bioflocculation. The abiotic results clearly supported the hypothesis of this study. However, isotherms performed with biologically active biosolids did not show a statistically significant trend regarding the M/D ratio effect on sorption capacity. This was true for isotherms completed in a reclaimed water matrix and for isotherms in a synthetic salt matrix. Therefore, the difference between abiotic and biotic conditions could not be attributed to the water matrix and must be attributed to the biosolids. In general, increasing the M/D ratio did decrease the sorption intensity parameter at the high cationic strengths. These cationic strengths would correspond to wastewaters in communities with a high percentage of homes with water softeners. The discrepancy between abiotic and biotic results could have to do with the biological uptake of compounds.

The isotherms with an M/D ratio of 6 and a cation concentration of 20 meq/L had statistically significantly lower sorption capacity than did all other biotic isotherms. The M/D ratio of 6 and the increased cation concentration might represent a threshold where sorption capacity is significantly affected independent of biological activity. This result was consistent with the hypothesis of this study. These high salt concentrations occur only in areas with high background salt concentrations or industrial influence.

The KWRF biosolids had consistently lower sorption capacity than did MNWWRP biosolids. The MNWWRP biosolids had a sludge volume index (SVI) that was approximately 50% that of the KWRF biosolids. A high SVI correlates with poor bioflocculation and sludge settling. Therefore, the poor bioflocculation behavior of the KWRF biosolids may limit sorption capacity. Since the SVI is not solely a measure of the flocculation, differences in the microbial population could also affect sorption.

The kinetic studies revealed that sorbate concentrations decreased rapidly to near detection limits 1 h after experiment initiation. Subsequently, sorbate concentrations increased until equilibrium was reached in fewer than 20 h. This was not expected and may be attributed to biological activity such as biological uptake. This activity may be responsible for the differences in the abiotic and biotic isotherms.

The results indicate that increasing the M/D ratio has the potential to reduce the sorption of hydrophobic compounds during water reclamation. Under abiotic conditions, increasing the M/D ratio clearly reduced sorption of hydrophobic compounds to biosolids. The original hypothesis was based on an abiotic mechanism, and the hypothesis was clearly supported. Under biotic conditions, the trends were not as clear as they were under abiotic conditions. However, when the biotic data are analyzed for both increasing M/D ratios and increasing cation concentrations, the sorption capacity of the biosolids decreased. The M/D ratio increased from 1 to 6, while the cation concentration increased from 4 to 20 in these data sets. However, the largest decrease in sorption occurred as the cation concentration increased from 8 to 20 meq/L and as the M/D ratio increased from 2 to 6. Water softeners increase both the cation concentration and the M/D ratio, and increases in these ranges have been observed at water reclamation facilities. The results of this study demonstrate that there could be reason

for concern when water softeners increase the M/D ratio above 2 while increasing the cation concentration above 8 meq/L. However, verification with continuous-flow systems at environmentally relevant concentrations must be done to determine real-world effects. Consequently, further research into the impacts of large increases in M/D ratios and cation concentrations at full-scale facilities should be conducted to determine if control measures should be implemented.

CHAPTER 1

BACKGROUND FOR HYPOTHESIS

1.1 FATE OF ESTROGENS IN THE ENVIRONMENT AND ENGINEERED SYSTEMS

Conjugated estrogens are biologically inactive and are able to dissolve more readily into water than are free estrogens (Khanal et al., 2006) because of the polar nature of their glucuronide and sulfate conjugate groups. Conjugated estrogens are excreted by humans into wastewater collection systems and are then hydrolyzed in the presence of bacteria into free estrogens. No detectable levels of conjugated estrogens have been found in the influents of water reclamation plants (Belfroid et al., 1999; D'Ascenso et al., 2003). Free estrogens are considered to be biologically active. Some estrogens are naturally occurring, such as estrone (E1), 17β-estradiol (E2), and estriol. Others are synthetically produced for oral contraceptives, such as 17α-ethynylestradiol (EE2), and some are organic compounds, such as bisphenol A, an antioxidant used in the production of plastics, or originate from surfactants such as nonylphenol and octylphenol.

Johnson and Williams (2005) studied excretion rates of E1, E2, and EE2 using data collected from the influents of sewage treatment plants and population data. They reported that E1 and E2 had excretion rates per capita of 10.5 and 6.6 µg/day, respectively, with a 3.3-µg/day transformation of E1 to E2. EE2 was reported to have an excretion rate of 1 µg/day per capita. Bisphenol A was found in sewage influent at a concentration between 0.09 and 0.15 µg/L (Rudel et al., 1998).

Estrogenic compounds have been reported in various surface waters around the United States. Koplin et al. (2002) surveyed 139 streams from 30 states for 95 organic waste compounds that are considered contaminants. Bisphenol A, estriol, EE2, E2, and E1 were found in 35, 15, 11, 9, and 5 samples, respectively. The maximum concentrations of these compounds were 1200, 51, 831, 200, and 112 ng/L, respectively, and the median concentrations were 140, 19, 73, 116, and 27 ng/L, respectively. These compounds enter the surface waters either from the effluent of wastewater treatment plants or overland runoff from concentrated animal feed operations (CAFOs). The persistence of these compounds in surface water has adversely affected the reproductive systems in both freshwater and marine aquatic species (Jobling et al., 1998; Panter et al., 1998; Tabata et al., 2001; Irwin et al., 2001).

Removal of estrogenic compounds from wastewater may be primarily by sorption of these compounds to activated sludge (AS) flocs during wastewater treatment. Removal of natural estrogens from wastewater varies depending on the type of treatment processes. Ternes et al. (1999) studied the removal of natural estrogens in both AS and trickling filter treatment systems. The study found that AS removed over 99.9% of free estrogens and that the trickling filter removed only 92%. Braga et al. (2005) studied the fate of steroid hormones from enhanced primary and advanced treatment facilities in Australia. In this study, E1 and E2 were removed by 85 and 96%, respectively, in the sequencing batch reactors. The enhanced primary treatment facilities removed 7% of E1 and 0% of E2. This shows that secondary treatment processes are responsible for the majority of removal.

Khanal et al. (2006) performed a critical review of the removal of estrogens in natural systems. They found that estrogens are removed from wastewater mainly by adsorption into the solid phase, either sludge flocs or soil. After sorption, bacteria will further remove the natural estrogens by biodegradation into harmless substances (Irwin et al., 2001). Sorption of estrogens is affected by three parameters, the solid retention time (SRT), the concentration of mixed liquor suspended solids (MLSS), and the primary substrate biodegradation rate of microorganisms. Ternes et al. (1999) reported that the removal efficiency of E1 and E2 increased from 75 to 96% when the SRT was increased from 6 to 11 days. Strenn et al. (2003) reported that removal of specific hormones was negligible for an SRT below 1 day and that higher SRTs resulted in higher biomass concentrations and greater removal of hormones. Kikuta and Urase (2003) reported E1 and E2 concentrations fell from 7.9 and 26.3 ng/L to 2.2 and 10.3 ng/L, respectively, as the MLSS increased from 1000 to 10,000 mg/L. Vader et al. (2000) reported that nitrifying bacteria had a higher removal rate than did conventional AS, attributing the removal to biotransformation. Treatment processes with nitrification would yield a higher removal rate of natural estrogens based on both a longer SRT for the nitrifying process and the higher rate of biodegradation of natural estrogens by nitrifying bacteria. Nasu et al. (2001) conducted a study of 27 wastewater treatment plants for 30 estrogenic compounds. Both influent and effluent concentrations were sampled in three seasons: summer, autumn, and winter. They found that the influent median concentrations of bisphenol A and E2 were 1.0 µg/L and 42 ng/L and that the median effluent concentrations were 0.04 µg/L and 14 ng/L, respectively. This corresponded to 96% removal of bisphenol A and 67% removal of E2. Removal of estrogenic compounds by sorption has been correlated with the octanol-water partitioning coefficient. Birkett and Lester (2003) stated that compounds with a log K_{ow} over 4 will be removed by sorption and that compounds with a log K_{ow} between 1.5 and 4 have a moderate affinity for solids. Khanal et al. (2006) found that compounds with a log K_{ow} between 2.6 and 4.0 are readily sorbed onto solids.

1.2 FLOCCULATION OF BIOSOLIDS: THE DCBT

Bioflocculation is the aggregation of bacteria into flocculates. It is an important mechanism that occurs in AS systems for both effluent quality and solid handling. Bacteria have polymers that exist on their surface. These polymers are known as exocellular polymeric substances (EPS). They are typically negatively charged and consist of proteins, polysaccharides, nucleic acids, and lipids (Sutherland, 1972; Tenney and Verhoff, 1973; Brown and Lester, 1980; Barber and Veenstra, 1986; Eriksson and Alm, 1991; Urbain et al., 1993; Frolund et al., 1996). These polymers form a complex structure around the bacterial cell and aid in the flocculation process. For flocculation to occur, the bacteria need to come in close contact; however, the negatively charged surfaces of the bacteria would prevent this close contact because of electrostatic forces. These electrostatic forces can be reduced by the sorption of either monovalent or divalent cations. The divalent cation bridging theory (DCBT) states that if divalent cations bind to negatively charged EPS, they form an electrical/chemical bridge between the bacteria. This bridging (Figure 1.1) forms strong flocs; however, if monovalent cations are sorbed, no bridging occurs between the bacteria, which leads to poor floc characteristics.

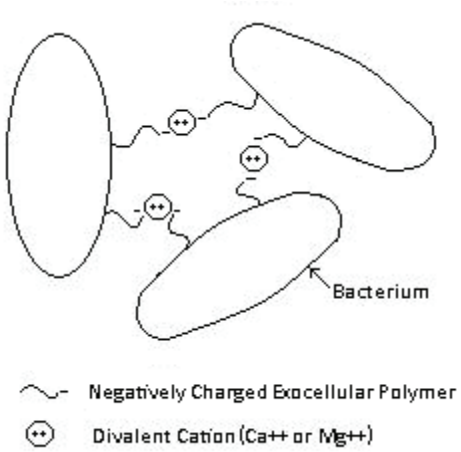


Figure 1.1. Depiction of DCBT.

1.3 FORMATION OF THE DCBT

McCalla (1940) showed that cations in solution were adsorbed to bacterial surfaces. Bacteria are negatively charged and will attract cations toward their surface, allowing the electrostatic forces to decrease. McKinney (1952) proposed a theory of floc formation and suggested that flocculation occurred by reducing the electrostatic forces by the addition of inorganic salts, thus reducing the electrostatic potential between bacteria and allowing for flocculation. The flocs that were formed had good floc strength and could not be broken. This prompted the thought that covalent bonds such as esters were suggested to play a role in flocculation as well as the addition of inorganic salts. However, Tezuka (1969) was able to separate flocs by suspending them in deionized water, which showed that permanent covalent bonds by ester linkages did not occur in flocculates as was suggested by McKinney. Furthermore, Tezuka (1969) observed that flocculation was influenced by magnesium and calcium ions. After separation of a monoculture of *Flavobacterium* biological flocculates by suspension of them in deionized water, calcium and/or magnesium ions were added. When both magnesium and calcium ions were added to suspension, good flocculation occurred and flocculation was not dependent on cellular viability. These results suggest that magnesium and calcium ions are important in the flocculation process. Other studies of monocultures showed results conflicting with those of Tezuka (1969). Angelbeck and Kirsch (1969) grew a monoculture of *Zoogloea ramigera* and found that bioflocculation occurred despite the absence or presence of calcium and magnesium ions. Others showed dependence on either calcium or magnesium alone, depending on the monoculture of organisms (Endo et al., 1976; Shimizu and Odawara, 1985).

The previously discussed studies were performed on monocultures of bacteria, but AS is a mixed culture of bacteria. Higgins and Novak (1997) studied how flocculation occurred in a mixed culture by using AS. They judged the flocculation strength on parameters such as the sludge volume index (SVI), which is an indicator of floc settling characteristics and specific resistance to filtration and cake solids, which are indicators of the dewatering characteristics of biosolids. This study showed the cation composition of wastewater has a major impact on the settling and dewatering of AS flocculates. Both the concentration of magnesium and calcium ions and the monovalent-to-divalent-cation ratio (M/D ratio) in laboratory-scale

reactors impacted the settling and dewatering of AS. They observed that after magnesium or calcium was added to the feed, the SVI and specific resistance to filtration (SRF) decreased. Calcium and magnesium ion addition increased the shear resistance of flocs; calcium was needed for the control of filamentous growing bacteria. Higgins and Novak (1997) concluded that magnesium and calcium needed to have a minimum concentration of 0.7 to 2.0 meq of each ion/L for acceptable settling and dewatering. If sodium was added to exceed an M/D ratio of 2, decreased settling and dewatering of AS flocs occurred, showing an increase in SVI and SRF. This decreased settling happened because the monovalent cations would replace the divalent cations by an ion exchange process. This cation exchange occurs at high monovalent cation concentrations. Thus, the electrochemical bridging between the bacteria is weakened, and the floc disassociates, causing poorer settling and dewatering. The ion exchange process was also observed by Bruus et al. (1992), who were able to displace calcium ions from AS with sodium, potassium, magnesium, and protons and show that the displacement of calcium increased the SRF.

Novak et al. (1998) studied the potential dewatering benefit of adding calcium and magnesium to industrial waste and showed that, when the M/D ratio of either potassium or sodium was greater than 2, the dewatering properties of the flocs became poorer and addition of polymer was needed. They also showed that, if the concentration of sodium and potassium ions increased above 10 meq/L, the physical characteristics of the flocs deteriorated and that the addition of magnesium ion improved the dewatering and setting characteristics of the floc. Higgins et al. (1994) studied the effects of calcium and magnesium on the floc properties of AS in industrial waste. They operated a pilot plant that was fed industrial waste from a pharmaceutical plant and measured various parameters such as influent and effluent chemical oxygen demand (COD), total SS (TSS), SVI, and filamentous bacterial growth. They changed the M/D ratio by adding either magnesium or calcium to observe the impacts of these cations on the aforementioned parameters. They found that the addition of both calcium and magnesium decreased the SVI, effluent COD, and effluent TSS and that the M/D ratio was a good indicator of the settling and dewatering properties of the flocs.

These studies show that biofloculation is enhanced by the presence or absence of divalent cations such as calcium and/or magnesium ions and deteriorates with high concentrations of monovalent cations such as sodium, potassium, and ammonium ions.

1.4 CLASSICAL THEORY ON BIOFLOCCULATION: DLVO THEORY

Particles in water are usually negative in nature. This negative charge produces a double-layer effect around the particles' surface. The first layer is the Stern layer, in which there is a layer of positively charged counter-ions that interact with the surface followed by a diffuse layer that has both positive and negative ions. The closer the ions are to the surface of the particle, the higher the concentration of positive ions and the farther away from the surface the concentration of positive ions is diminished. The diffuse layer is followed by electrically neutral water, in which there are equal numbers of positive and negative ions. This ion imbalance provides an electrical cloud around the particle that will repel other particles that have the same cloud. This double-layer thickness can be reduced by the increasing ionic strength of a solution; the reduction of the diffuse layer will allow particles to come close enough together to flocculate.

Zita and Hermansson (1994) studied the effects of ionic strength on floc stability. They collected AS and changed the ionic strengths by the addition of either potassium or calcium ions and found that, as the ionic strength increased to 10^{-1}, the stability of the flocs increased

for both potassium and calcium by improvements in both SVI and SRF. Their findings suggested that Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory best represented floc stability. Cousin and Ganczarczyk (1998) showed that, after the addition of various concentrations of NaCl, as the concentration of sodium increased, the percentage of smaller flocs decreased and the percentage of larger flocs increased. The finding also suggests that ionic effect alone best describes floc stability.

Sobeck and Higgins (2002) examined the differences in the DLVO theory and the DCBT by comparing the additions of calcium, magnesium, and sodium to three separate continuous-flow reactors. The floc stability was compared by various parameters that included floc strength, SVI, SRF, MLSS, and others. The addition of sodium ions to the feed caused a deterioration of all the above parameters; the addition of calcium and magnesium improved all of the parameters. This was in direct disagreement with Zita and Hermansson (1994) but in agreement with others (Endo et al., 1976; Novak et al., 1998).

1.5 RESEARCH HYPOTHESIS

Estrogenic/hydrophobic compounds have been shown to be removed from wastewater by sorption into biosolids. The more advanced biological treatment processes increase the relative removal of these compounds. It was also shown that flocculation and settling of solids are dependent on the cations present in the wastewater. The M/D ratio was inversely proportional to the flocculation strength and settling of biosolids. The proposed hypothesis is that removal of hydrophobic compounds from wastewater may depend on the composition of cations that affect the bioflocculation and stability of biosolids. Thus, an increase in M/D ratio should have a negative impact on the sorption of estrogenic compounds into biosolids from advance treatment processes.

This hypothesis was studied by performing developing adsorption isotherms for several estrogenic compounds (bisphenol A, EE2, and estriol) with biosolids collected from two different treatment facilities. The Mesa Northwest Water Reclamation Plant (MNWWRP) has a nitrifying/denitrifying AS treatment process (Figure 1.2). The average rate of flow to this plant is 9.5 million gallons per day (MGD). The MLSS changes are 3800 mg/L in the summer and 4200 mg/L in the winter, with a sludge age of 16 days. The hydraulic retention time (HDR) varies depending on the influent flow rate and averages around 12 h. The Kyrene Water Reclamation Facility (KWRF) uses a nitrifying/denitrifying AS treatment process with membrane filtration for separation of biosolids (Fig.3). The average rate of flow through the plant is 5 MGD. The concentration of MLSS was designed to be between 8000 and 10,000 mg/L. This plant has a sludge age of 10 days and an average HDR of 3.5 h.

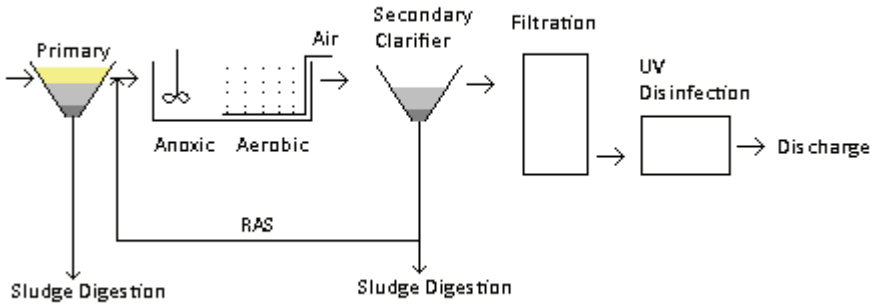


Figure 1.2. MNWWRP treatment process schematic.

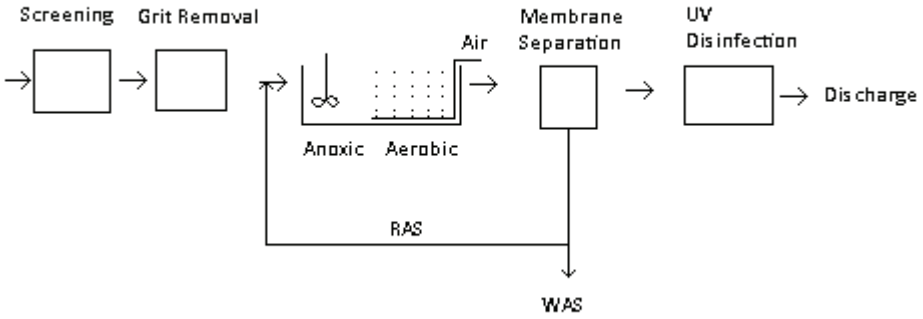


Figure 1.3. KWRF treatment process schematic.

CHAPTER 2

ANALYTICAL METHODS

2.1 DOC

Dissolved organic carbon (DOC) was measured as nonpurgeable organic carbon with a Shimadzu 5050A TOC analyzer containing a Shimadzu ASI-5000A autosampler. Standards were prepared with potassium hydrogen phthalate at concentrations of 1, 3, 5, and 10 ppm. Samples were diluted, placed in autosampler vials, acidified with 2 N HCl to a pH of 2 or less, and purged for 4 min with ultrazero air at a flow rate of 30 mL/min. Samples and standards were analyzed with an injection volume of 58 µL and with a flow rate of 150 mL of ultrazero air/min. The pH was tested by putting a drop of sample onto pH paper. Prior to DOC analysis, autosampler vials were washed in either a 10% HCl or 10% HNO_3 bath for 24 h, rinsed with deionized water for a minimum of 1 h, wrapped in aluminum foil, and dried in a muffle furnace at 550 ^{o}C.

2.2 HPLC

Bisphenol A, EE2, and estriol were analyzed by high-performance liquid chromatography (HPLC) with fluorescence detection, a Waters 2695 Separations Module, and a Waters 2475 Fluorescence Detector, respectively. A 4.6- by 100-mm Waters LiChrosorb® 10-µm-pore-size RP18 analytical column was used for separation. The method used a 10-µL injection volume. The mobile phase consisted of 45% 10 mM phosphoric acid and 55% methanol solution and was run at a flow rate of 1 mL/min. Fluorescence detection was performed at an excitation wavelength of 280 nm and emission wavelength of 310 nm for all target compounds.

Standards were prepared by diluting 22.8 mg of bisphenol A, 29.6 mg of EE2, and 28.8 mg of estriol with 100 mL of methanol at room temperature in individual 100-mL glass volumetric flasks to make a 10^{-3} M standard of each compound. Standards were diluted at 10^{-1} M intervals with methanol to 10^{-5} M. Then additional dilutions were performed with water at 10^{-1} M intervals to obtain a 10^{-6} M and 10^{-7} M standard.

The method consisted of purging the injector syringe with 45% 10 mM phosphoric acid and 55% methanol solution for 6.5 min and conditioning the column for 10 min prior to injections. This was followed with the injection of samples and standards followed by a column conditioning for 10 min after the last sample. The column was stored at room temperature.

2.3 AA SPECTROSCOPY

Sodium, potassium, calcium, and magnesium ions were analyzed with a Perkin-Elmer Atomic Absorption (AA) Spectrometer 3110. Standards (1000 µg/mL) were purchased from J. T. Baker. Standards were diluted, and 0.5-, 1-, 5-, 10-, 15-, and 20-mg/L standards were prepared for sodium; 0.5-, 1-, 5-, 10-, and 20-mg/L standards were prepared for calcium and potassium; and 0.05-, 0.1-, 1-, and 3-mg/L standards were prepared for magnesium. Potassium, calcium and magnesium ions were measured at wavelengths of 766.5, 422.7, and 285 nm, respectively, with a slit width of 0.70 nm and a slit height setting of “High.” Sodium

was measured at a wavelength of 589.0 nm with a slit width of 0.20 nm and slit height setting of "High." An air acetylene flame was used for atomization.

Samples were diluted with water to either 10^{-1} or 10^{-2} dilution prior to analysis.

2.4 NITROGEN AMMONIUM (N-NH_4)

Ammonium ion was analyzed using a Hach 51927-00 Ammonia Gas Sensing Combination Electrode with a Corning 340 pH meter in accordance with Clesceri et al. (1998) for ammonia detection.

2.5 UV ABSORBANCE

A Hewlett-Packard 8452 UV Spectrometer was used for UV_{254} absorbance. A 1-cm-path-length quartz cell was used. A blank was run using deionized water followed by analyzing samples. Prior to and after each sample, the quartz cell was rinsed twice with deionized water. Each sample was analyzed with three absorbance readings.

2.6 pH

The pH of each sample was analyzed with a combination pH electrode with a Corning 340 pH meter in accordance with *Standard Methods* (Clesceri et al., 1998).

2.7 SS

Glass fiber filters (Whatman GF-A or GF-C) were prepared by rinsing each filter with nanopure water followed by placing them in an aluminum weighting dish and drying at 103 ^{o}C until constant weight was attained. The glass fiber filter and aluminum weighting dish were weighed prior to filtering the biosolids. Biosolids were suspended by using a beaker with a magnetic stirring bar. Samples were filtered with prepared glass fiber filters that were rinsed with 20 mL of nanopure water three times. The filters were put back on the aluminum weighting dish and dried at 103 ^{o}C until constant weight was attained. The SS was calculated as follows:

$$\frac{Mass\ of\ dried\ SS+filter\ (g)-Mass\ of\ filter\ (g)}{Volume\ filtered\ (L)} \times \frac{1000mg}{g} \qquad (2.1)$$

2.8 SVI

One liter of TSS was placed in a 1-L graduated cylinder, and biosolids were settled for 30 min. The volume of the settled biosolids was recorded in milliliters per liter, and the SVI was calculated as follows:

$$\frac{Volume\ of\ Settled\ Solids\ (\frac{mL}{L})}{Suspended\ Solids\ (\frac{mg}{L})} \times \frac{1000mg}{g} \qquad (2.2)$$

2.9 DO

Dissolved oxygen (DO) was measured with an Orion Model 97-08 Oxygen Electrode and a Beckman 255 pH/Temp/mV Meter. The air pressure was set to 733 torr to match the correct atmospheric pressure of Tempe, AZ. Samples were done in accordance with *Standard Methods* (Clesceri et al., 1998) for DO with a membrane electrode.

CHAPTER 3

EXPERIMENTAL DESIGN FOR SORPTION ISOTHERMS

3.1 ISOTHERM DESIGN

Isotherms were developed with various M/D ratios and cationic strengths. Target M/D ratios were 1, 2, 4, and 6 and target cationic strengths were 4, 8, 12, and 20 meq/L, as shown in Table 3.1. Isotherms were prepared by targeting a constant mass of SS and varying the concentration of the target compound. Ten nominal compound concentrations were used that varied from 100 to 1000 µg/L by 100-µg/L increments.

Isotherms were prepared in 25-mL serum bottles. The 25-mL serum bottles were prepared by washing them in 10% HCl solution for a minimum of 24 h followed by rinsing with deionized water, wrapping in aluminum foil, and drying in a muffle furnace at 550 ^{o}C.

Isotherms were initially prepared by adding appropriate volumes of clarifier effluent from MNWWRP and membrane permeate from KWRF, stock salt solutions, stock target compound solution, and deionized water. Biosolids were added, and serum bottles were rotated between 170 and 200 rpm in a dark room to keep biosolids suspended in the bottles and to prevent photolysis. The contact time for the isotherms was 24 ± 2 h with the exception of one isotherm, MNWWRP bisphenol A. It had a cationic strength of 12 meq/L and a contact time of 48 h.

Table 3.1. Experimental Design of Cations in Isotherms

Target Compound	M/D Ratio	Cationic Strength (meq/L)			
		20	12	8	4
Bisphenol A	1		x	x	x
	2		x	x	x
	4		x		
	6	x		x	x
EE2	1		x	x	x
	2		x	x	x
	4		x		
	6	x		x	x
Estriol	1		x		
	2		x		
	4		x		
	6	x			

Additional isotherms were prepared to determine the potential role of biological activity and water matrix composition. For a biological activity control, a laboratory solution of sodium azide, calcium chloride, and magnesium sulfate was used for target compounds bisphenol A and EE2. For water matrix control, a laboratory solution of sodium chloride, calcium chloride, and magnesium sulfate was used for the target compound bisphenol A. Both the azide and the salt isotherms were prepared with a cationic strength of 12 meq/L and M/D ratios of 1, 2, and 4.

3.2 SAMPLE COLLECTION OF PERMEATE AND CLARIFIER EFFLUENT

Clarifier effluent was collected from MNWWRP in a 20-L polyethylene (PE) container, and permeate was collected from KWRF in the same manner. Both permeate and clarifier effluents were filtered with a 0.45-µm-pore-size filter after collection and stored at 4 °C. After filtration, permeate and clarifier effluents were analyzed for cationic composition prior to use in the isotherm. This was done to determine the cationic strength, measured in milliequivalents per liter, and the M/D ratio of the source water. Sodium, potassium, calcium and magnesium ions were analyzed by AA, and N-NH_4 was analyzed for ammonium ion concentrations, which can be found in Table 3.2.

Table 3.2. Cationic Composition of Effluent from the Water Reclamation Plants

	Attributes of:					
	MNWWRP Clarifier (05/14/2007)		MNWWRP Clarifier (09/14/2007)		KWRF Permeate (09/21/2007)	
Ion or variable	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Mg^{2+}	21	1.72	21	1.73	32	2.6
Ca^{2+}	55	2.77	57	2.85	76	3.81
K^{+}	18	0.46	21	0.54	21	0.54
Na^{+}	211	9.19	245	10.65	291	12.66
N-NH_4^{+}	2.0	0.14	0.7	0.05	3.1	0.22
M/D [(meq/L)/(meq/L)]		2.15		2.44		2.06
Cationic Strength		14.13		15.77		19.62

The M/D ratio was determined as follows:

$$\frac{\sum monovalent\ cation\ [\frac{meq}{L}]}{\sum divalent\ cation\ [\frac{meq}{L}]} \quad (3.1)$$

The monovalent cations are sodium and potassium ions, and the divalent cations are calcium and magnesium. The cationic strength was determined by the summation of each ion as in the following equation.

$$\sum monovalent\ cations\ [\frac{meq}{L}] + \sum divalent\ cations\ [\frac{meq}{L}] \quad (3.2)$$

3.3 SAMPLE COLLECTION OF RAS AND AS

Preliminary experiments suggested that a concentration between 300 and 600 mg of SS/L should be used for the isotherm experiments to determine sorption of the target compounds in the appropriate analytical range for HPLC. It was predicted that the concentration of return AS (RAS) and AS would be between 5000 and 10,000 mg/L. Because the isotherms were performed in a 25-mL volume, 1.5 mL of RAS or AS would be added to each bottle to achieve nominal solid concentration of 300 to 600 mg/L. RAS was collected from the recycle pump station at MNWWRP in a 1-L PE sample bottle. AS was collected from the aeration basin of KWRF in a 1-L PE sample bottle. Samples were promptly taken to the lab, and 1.5 mL was spiked into each isotherm bottle. Then the mass of the SS was determined by suspending 1.5 mL of SS in 10 mL of nanopure water in a filter flask funnel. This was followed by filtering and drying as mentioned in *Standard Methods* (Clesceri et al., 1998). Three samples were analyzed for the mass of SS in the RAS or AS. The average of the three was multiplied by the dilution factor 1.5/25 to determine the average mass of SS in each of the isotherm bottles. The averages for each sample and the isotherms associated with the sample can be seen in Tables 3.3 through 3.5.

The SVI was measured after the completion of the isotherms for the biosolids from MNWWRP and KWRF. It was done by collecting RAS or AS and diluting it by adding 60 mL of RAS to 940 mL of clarifier effluent or permeate, respectively. The SVIs were 90 mL/g and 125 mL/g for MNWWRP and KWRF, respectively, as shown in Table 3.6. The MNWWRP biosolids were also diluted with clarifier effluent that was changed to meet the target M/D ratio and cationic strength and were placed on a rotary table for 24 h to see if the SVI changed over time. The SVI was rather constant and varied from 84 to 90 mL/g during the study as shown in Figure 3.1. The KWRF operational period as a membrane bioreactor was under 1 year. The plant has had a history of operational problems.

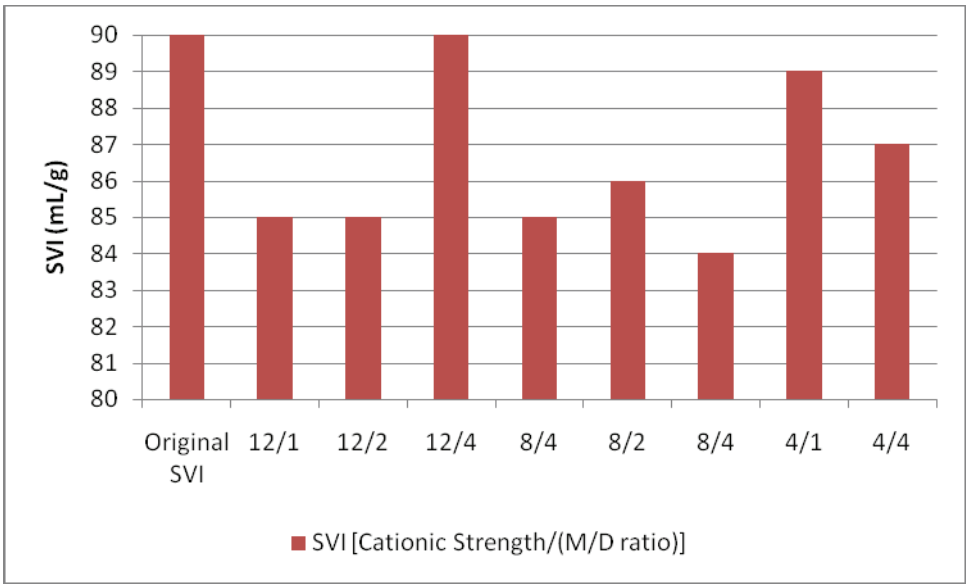


Figure 3.1. SVI of MNWWRP biosolids after a 24-h period in contact with target cationic strengths and M/D ratios.

Table 3.3. Mass of SS in Bisphenol A Isotherms

Isotherm Source	Target M/D Ratio	Target Cationic Strength (meq/L)	SS (mg/L)
MNWWRP	1–4	12	260
MNWWRP	1–4	8	329
MNWWRP	1–4	4	329
Azide	1–4	12	254
Salt	1–4	12	333
KWRF	1–4	12	535
MNWWRP	6	20	953

Table 3.4. Mass of SS in EE2 Isotherms

Isotherm Source	Target M/D Ratio	Target Cationic Strength (meq/L)	SS (mg/L)
MNWWRP	1–4	12	526
MNWWRP	1–4	8	333
MNWWRP	1–4	4	333
Azide	1–4	12	254
KWRF	1–4	12	535
KWRF	1–4	12	530
MNWWRP	6	20	953

Table 3.5. Mass of SS in Estriol Isotherms

Isotherm Source	Target M/D Ratio	Target Cationic Strength (meq/L)	SS (mg/L)
MNWWRP	1–4	12	328
KWRF	1–4	12	484
MNWWRP	6	20	953

Table 3.6. Original SVI for MNWWRP and KWRF

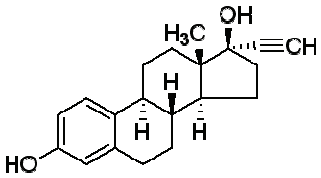
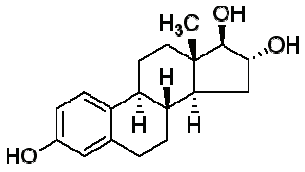
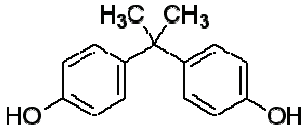
Biosolid Source	SVI (mL/g)	SS (mg/L)
MNWWRP	90	830
KWRF	125	450

3.4 PREPARATION AND STORAGE OF STOCK SOLUTIONS

One-liter stock salt solutions of sodium chloride, magnesium sulfate, and calcium chloride were prepared in concentrations of 125, 15, and 20 meq/L, respectively. The salts used to make the stock solutions were sodium chloride, calcium chloride hexahydrate, and anhydrous magnesium sulfate. Concentrations were verified by AA, and measured concentrations were determined to be 130, 15, and 19 meq/L for sodium, magnesium, and calcium stock solutions, respectively. The target concentration was used to determine the volume of stock solution to be added to the isotherms. Stock solutions were stored at room temperature on the shelf. Magnesium and calcium ion stock solutions were stored in 1-L amber glass bottles, and sodium stock solution was stored in a clear 1-L glass bottle.

Stock solutions of bisphenol A, EE2, E1, and estriol were prepared by first making 10^{-3} M solutions with methanol as the solvent. These solutions were diluted with a 25% methanol and 75% water solution to get the desired 10^{-4} M stock solution. Stock solutions were stored in amber 250-mL glass bottles at room temperature. The chemical properties of the target compounds can be found in Table 3.7.

Table 3.7. Chemical Properties of Target Compounds

Target Compound	Chemical Formula	Molecular Structure[a]	Log K_{ow}	Solubility (mg/L)
EE2	$C_{20}H_{24}O_2$		3.67	6.96
Estriol	$C_{18}H_{24}O_3$		2.45	82.1
Bisphenol A	$C_{15}H_{16}O_2$		3.32	39.2

[a]Molecular structures were made by the Sigma-Aldrich Co.

3.5 FILTERING AND STORAGE OF SAMPLES

After the SS were in contact with the target compound for 24 h, isotherm bottles were placed on the lab bench to allow SS to settle. Each sample was filtered with a 0.45-µm-pore-size cellulose membrane filter. Initially, samples were stored in the refrigerator at 4 ^{o}C until analysis of target compounds by HPLC and cations by AA. This occurred for the MNWWRP bisphenol A and EE2 isotherms with samples that had a target cationic strength of 12 meq/L and M/D ratios of 1, 2, and 4, as well as the azide isotherms. All other samples were acidified by adding two drops of 6 N HCl to each sample from a 100-µL pipette. A drop from one sample from each isotherm was placed on pH paper, which showed the pH had been reduced to 2 or less. A 1-mL volume of each sample was transferred to HPLC autosampler vials and frozen at -20 ^{o}C until analysis by HPLC. The remaining samples were stored in the refrigerator at 4 ^{o}C for analysis of cations by AA. Analysis by HPLC and AA was performed within 2 weeks of the filtration.

3.6 MASS BALANCE OF TARGET COMPOUNDS

To account for the mass sorbed onto the solids during the isotherm, a mass balance was performed. Because each isotherm had many samples, an initial concentration of each sample was not done. To find the initial concentration, a 1-mL sample of each nominal target compound concentration was taken for two isotherm trains. The average of the two initial concentrations was taken and assumed to be the initial concentration for that target nominal

concentration in every train. The final concentration was determined for each sample in each isotherm. The mass sorbed is the difference between these two.

3.7 CALCULATION FOR VOLUME ADDITION OF SALTS, TARGET COMPOUNDS, AND WATER

The following equations were used to determine the concentration of each ion required for experimental design of isotherm.

$$M + D = Target\ Cationic\ Strength \tag{3.3}$$

$$M/D = Target\ M/D\ Ratio \tag{3.4}$$

$$D = \frac{Target\ Cationic\ Strength}{Target\ M/D\ Ratio+1} \tag{3.5}$$

$$M = Target\ Ionic\ Strength - D \tag{3.6}$$

M is the sum of the monovalent cations (milliequivalents per liter); D is the sum of the divalent cations (milliequivalents per liter). Because the clarifier effluent and permeate both had M/D ratios higher than 2.00 (Table 3.1), all of the required monovalent cations calculated in equation 4 were supplied by the clarifier effluent and permeate for the design M/D ratios of 1 and 2. Stock magnesium sulfate and calcium chloride solutions provided the remaining required divalent cations as seen in the following equations. In the following equations, "Effluent" will refer to either permeate or clarifier effluent.

$$M \times Experimental\ Design\ Volume = (Na + K) \times Volume\ of\ Effluent \tag{3.7}$$

$$\frac{M \times 0.025\,(L) \times \frac{1000mL}{L}}{(Na+K) \times \frac{1000mL}{L}} = Volume\ of\ Effluent \tag{3.8}$$

M is the monovalent cation concentration (milliequivalents per liter) from equation 3.6; Na and K are the sodium ion and potassium ion concentrations in the permeate or clarifier effluent (milliequivalents per liter). The required volume of the magnesium stock solution was calculated by the following equations.

0.4D x *Experimental Design Volume – Mg* x *Volume of Effluent =*

Concentration of Stock Mg solution x *Volume of Stock Magnesium Solution* (3.9)

$$\frac{0.4D \times 0.025\,(L) \times \frac{1000mL}{L} - Mg \times Volume\ of\ Effluent}{10\left(\frac{meq}{L}\right) \times \frac{1000mL}{L}} = Volume\ of\ Stock\ Mg\ Solution\ (mL) \tag{3.10}$$

D is the required divalent cation ratio in milliequivalents per liter found in equation 3.5, Mg is the magnesium ion concentration in the permeate or clarifier effluent, and volume of

effluent was the volume calculated in equation 3.8. The required volume of calcium stock solution was calculated by the following equations.

$$0.6D \times Experimental\ Design\ Volume - Ca \times Volume\ of\ Effluent = Concentration\ of\ Stock\ Ca\ Solution \times Volume\ of\ Stock\ Calcium\ Solution \quad (3.11)$$

$$\frac{0.6D \times 0.025(L) \times \frac{1000mL}{L} Ca \times Volume\ of\ Effluent}{20\left(\frac{meq}{L}\right) \times \frac{1000mL}{L}} = Volume\ of\ Ca\ Stock\ Solution\ (mL) \quad (3.12)$$

D is the required divalent cation concentration (milliequivalents per liter) from equation 3.5; Ca is the concentration of calcium ions in the permeate or clarifier effluent (milliequivalents per liter) shown in Table 3.1; and volume of effluent was the volume calculated in equation 3.8. Because the clarifier effluent and permeate had a divalent cation composition of roughly 40% magnesium and 60% calcium, the required divalent cation composition, D, was multiplied by 0.4 for magnesium and 0.6 for calcium as seen in equation 3.10 and equation 3.12, respectively, to maintain the same ratio as the source water.

Conversely, all of the required divalent cations were supplied by the clarifier effluent or permeate for the design M/D ratio of 4, and the stock salt solution of sodium chloride supplied the remaining monovalent cations. It was calculated by the following equations.

$$D \times Experimental\ Design\ Volume = (Ca + Mg) \times Volume\ of\ Effluent \quad (3.13)$$

$$\frac{D \times 0.025(L) \times \frac{1000mL}{L}}{(Ca+Mg) \times \frac{1000mL}{L}} = Volume\ of\ required\ Effluent \quad (3.14)$$

D is the required divalent cation concentration (milliequivalents per liter) from equation 3.5, and Ca and Mg are the concentrations of calcium and magnesium ion in the permeate or clarifier effluent (milliequivalents per liter) in the wastewater effluent. The remaining sodium ion was supplied by the stock sodium solution and was calculated as seen in the following equations.

$$M \times Experimental\ Design\ Volume - (Na + K) \times Volume\ of\ Effluent = Concentration\ of\ Stock\ Na\ solution \times Volume\ of\ Stock\ Sodium\ Solution \quad (3.15)$$

$$\frac{M \times 0.025(L) \times \frac{1000mL}{L} (Na+K) \times Volume\ of\ Effluent}{126\left(\frac{meq}{L}\right) \times \frac{1000mL}{L}} = Volume\ of\ Stock\ Na\ Solution\ (mL) \quad (3.16)$$

M is the required monovalent cations as seen in equation 3.6, Na and K are the concentrations of sodium and potassium in the clarifier effluent or permeate (milliequivalents per liter), and volume of effluent is the required clarifier effluent or permeate volume as calculated in equation 3.8. The actual volume of clarifier effluent was subtracted by the volume of RAS or AS addition. It was assumed that the collected RAS has the same ionic composition as the

clarifier effluent or permeate even though the collection dates were not the same. Actual concentrations of all ions were verified by AA after the isotherm was complete.

The required volume of stock target compound solution was calculated as follows:

$$\frac{Target\ Concentration\ \left(\frac{ug}{L}\right) \times Experimental\ Design\ Volume\ (L)}{Concentration\ of\ Target\ Compound\ \left(\frac{ug}{L}\right)} \times \frac{1000mL}{L} =$$

$$Volume\ of\ Target\ Compound\ (mL) \tag{3.17}$$

The volume of deionized water added to the isotherms was calculated as follows:

$$Experimental\ Design\ Volume - Volume\ RAS - Volume\ of\ Effluent -$$

$$Volume\ Target\ Compound - Volume\ of\ Mg, Ca, and\ Na\ Stock\ Salt\ solutions =$$

$$Volume\ of\ deionized\ water. \tag{3.18}$$

CHAPTER 4

ISOTHERM RESULTS

The Freundlich isotherm model (Crittenden et al., 2005) was used to compare the data from each isotherm. This model was chosen since it is empirical and can accurately fit a wide range of sorption data. The empirical formula for this model is shown in the following equation.

$$q_A = K_A C_e^{1/n} \tag{4.1}$$

In it, q_A is the equilibrium sorbent-phase concentration [mg-Target Compound/g-SS], C_A is the liquid-phase equilibrium concentration [mg/L], 1/n is the intensity parameter [dimensionless], and K_A is the capacity parameter [(mg-Target Compound/g-SS)(L/mg)$^{1/n}$]. The log of each side of equation 4.1 can be taken and the intensity and capacity parameters can be found by plotting the data and applying a linear regression line as shown in the following equation. The capacity parameter indicates the sorption capacity of the solid phase for the sorbent, while the intensity parameter indicates how much the sorption capacity increases as the equilibrium phase concentration increases.

$$\log(q_A) = \left(\frac{1}{n}\right)\log(C_A) + \log(K_A) \tag{4.2}$$

The paired *t* test may be used to determine if treatment processes are equivalent. McBean and Rovers (1998) stated that when two treatment methods are compared, the differences between the two pairs of measurements are of interest. These differences can then be used in a *t* test to establish statistically significant differences. The *t** value is found by

$$t^* = \frac{D}{\frac{S}{\sqrt{n}}} \tag{4.3}$$

where D is the mean of the differences of the pairs, S is the standard deviation, and n is the number of samples. This value is compared with the critical *t* (t_c) for statistically significant differences. If *t** is less than t_c, then the two treatment types are not statistically significantly different from each other. Each isotherm group was examined for comparison of different M/D ratios for statistically significant differences by the paired *t* test.

The isotherm results are presented in the following sections. Unless it is stated that azide was added to create abiotic conditions, the isotherm results are for biotic conditions.

4.1 BISPHENOL A ISOTHERM RESULTS

4.1.1 Target Cationic Strength = 12 Meq/L

Figures 4.1 to 4.3 contain the results of the isotherms performed with target M/D ratios of 1, 2, and 4 and cationic strength of 12 meq/L with MNWWRP biosolids. Figure 4.1 contains the results of the isotherm with a measured M/D ratio of 1.11 and cationic strength of 11.97 meq/L. The intensity parameter for this isotherm is 1.07, and the capacity parameter is 0.98. Figure 4.2 contains the results of the isotherm with a measured M/D ratio of 2.33 and cationic

strength of 13.00 meq/L. The intensity parameter is 0.84, and the capacity parameter is 0.83. Figure 4.3 contains the results for the isotherm with a measured M/D ratio of 3.82 and cationic strength of 11.89 meq/L. The intensity parameter is 0.51, and the capacity parameter is 0.76. The intensity and capacity parameters clearly decrease with increasing M/D ratio. The capacity and intensity parameters from the isotherms in this set were used to plot the adsorptive capacity as a function of concentration on a linear plot using equation 4.2 (Figure 4.4). As observed in Figure 4.4, there does not appear to be a significant difference between isotherms. The paired *t* test results for this set of isotherms are contained in Table 4.1. The paired *t* test results indicate that the findings are not significantly different.

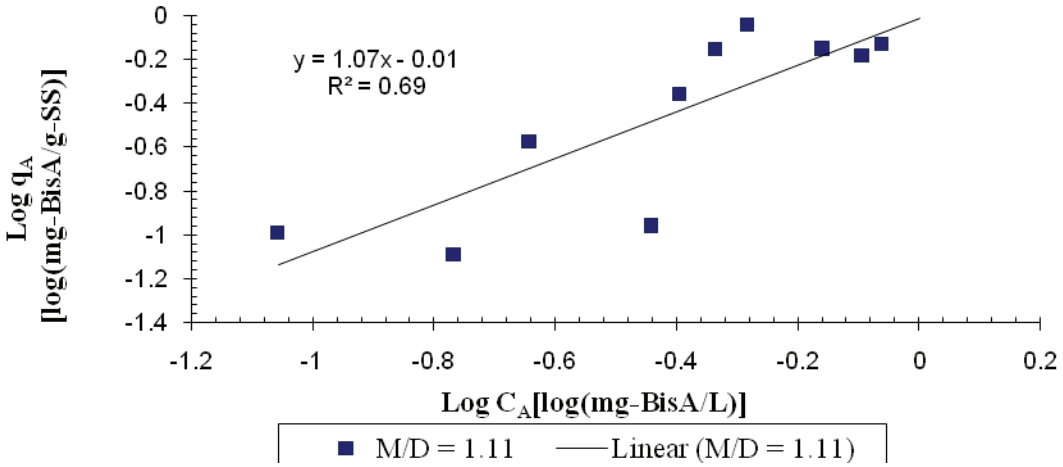


Figure 4.1. Freundlich isotherm with MNWWRP biosolids and M/D ratio and cationic strength of 1.11 and 11.97 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

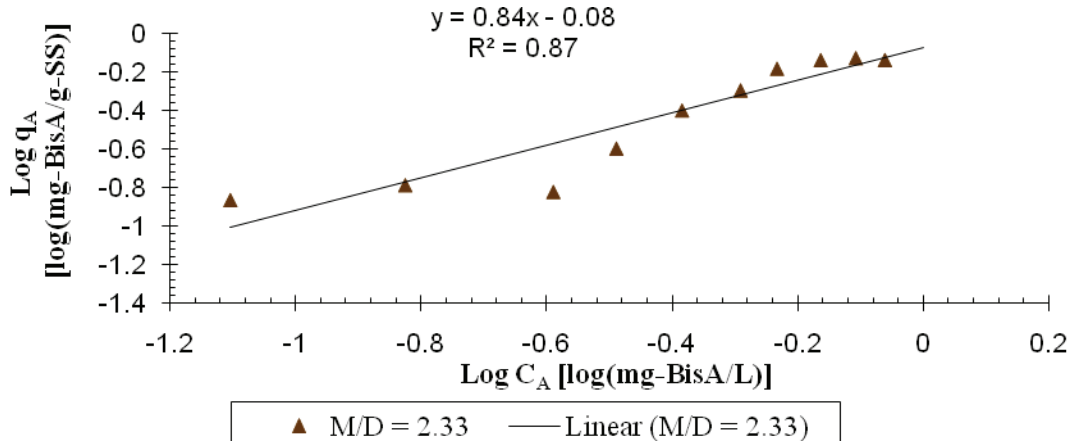


Figure 4.2. Freundlich isotherm with MNWWRP biosolids, M/D ratio of 2.33, and cationic strength of 13.00 meq/L. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

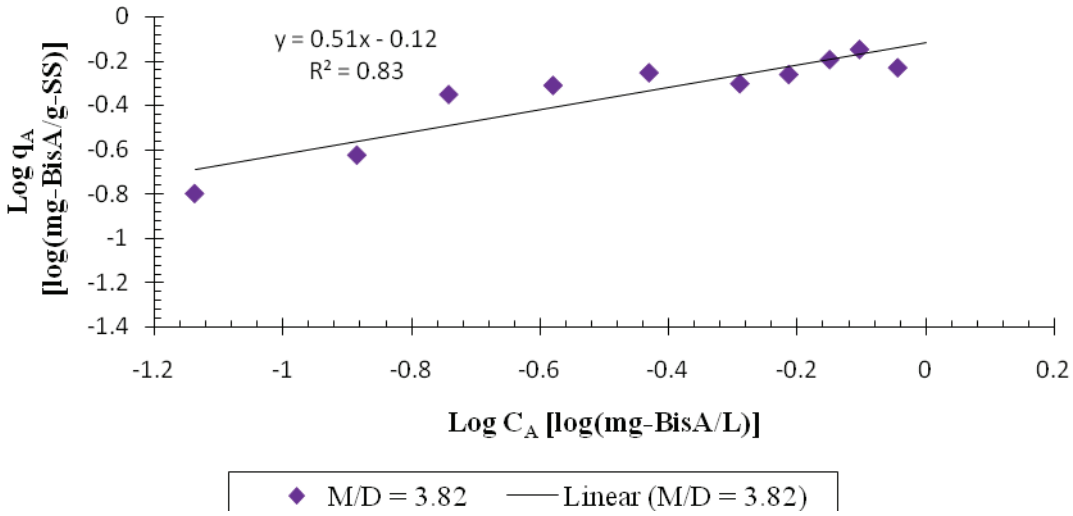


Figure 4.3. Freundlich isotherm with MNWWRP biosolids, M/D ratio of 3.82, and cationic strength of 11.89 meq/L. The target M/D ratio and cationic strength were 4 and 12 meq/L, respectively.

Table 4.1. Paired *t* Test Results of the Isotherms with Bisphenol A as the Target Compound, MNWWRP as the Biosolid Source, and Target Cationic Strength of 12 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* Test	*t**	t_c
Low	1.11	11.97	Low-Med	0.612	1.833
Med	2.33	13.00	Low-High	0.269	1.860
High	3.82	11.89	Med-High	0.9219	1.860

[a]Pairing each isotherm using q_A and M/D ratio.

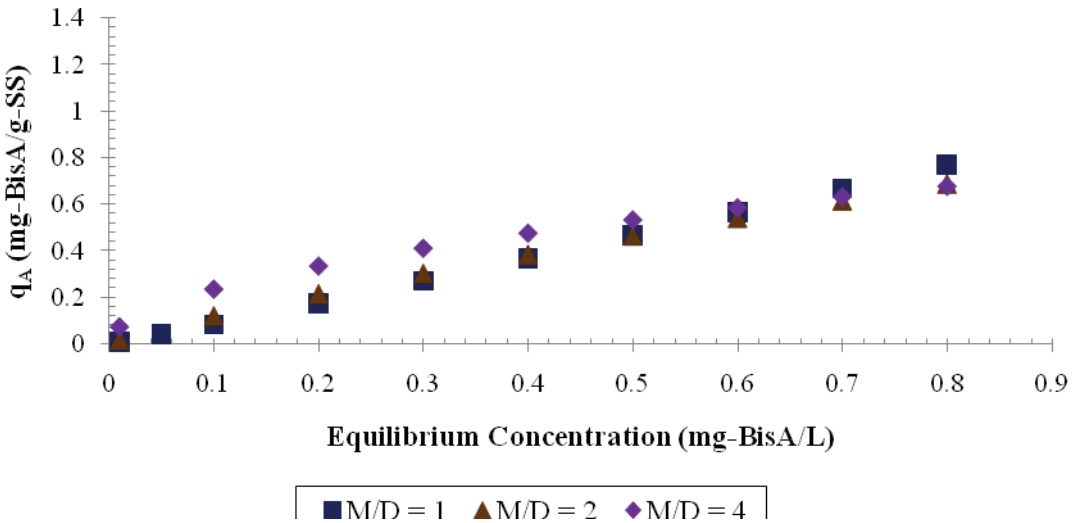


Figure 4.4. Combined Freundlich isotherm equations generated from the results of the isotherms with MNWWRP biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 12 meq/L.

4.1.2 Target Cationic Strength = 8 Meq/L

Figures 4.5 to 4.7 contain the results of the isotherms performed at target M/D ratios of 1, 2, and 4 with a target cationic strength of 8 meq/L and MNWWRP biosolids. Figure 4.5 contains the results for the isotherm with a measured M/D ratio of 0.92 and cationic strength of 7.47 meq/L. The intensity parameter for this isotherm is 1.18, and the capacity parameter is 1.10. Figure 4.6 contains the results of the isotherm with a measured M/D ratio of 1.92 and cationic strength of 7.42 meq/L. The intensity parameter is 0.99, and the capacity parameter is 0.82. Figure 4.7 contains the results for the isotherm with a measured M/D ratio of 4.72 and cationic strength of 9.14 meq/L. The intensity parameter is 0.90, and the capacity parameter is 0.63. Similar to the findings for a cation strength of 12 meq/L, the intensity and capacity parameters decrease as the M/D ratio increases. The capacity and intensity parameters from the isotherms were used to plot the adsorptive capacity as a function of concentration on a linear plot using equation 4.2 (Figure 4.8). The paired *t* test results for this set of isotherms are contained in Table 4.2. The predictions are consistent with expected results of decreasing sorptive capacity with increasing M/D ratio. The results show a statistically significant difference between only the M/D ratio of 1 and the M/D ratio of 4.

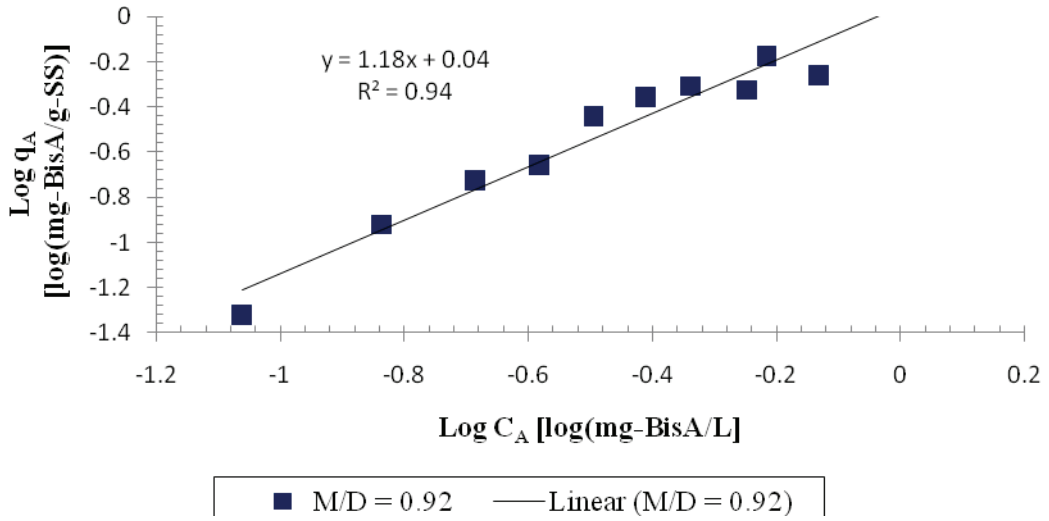


Figure 4.5. Freundlich isotherm with MNWWRP biosolids and M/D ratio and cationic strength of 0.92 and 7.47 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 8 meq/L, respectively.

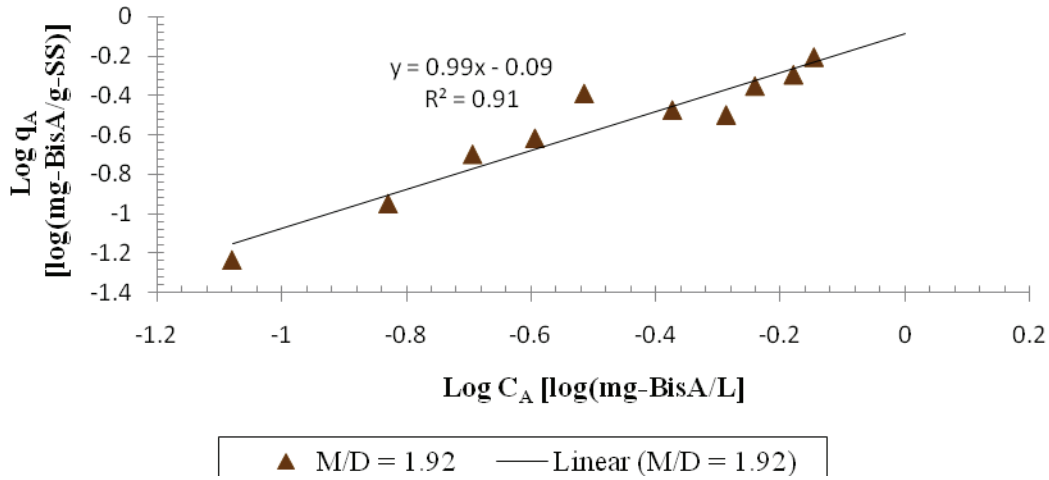


Figure 4.6. Freundlich isotherm with MNWWRP biosolids and M/D ratio and cationic strength of 1.92 and 7.42 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 8 meq/L, respectively.

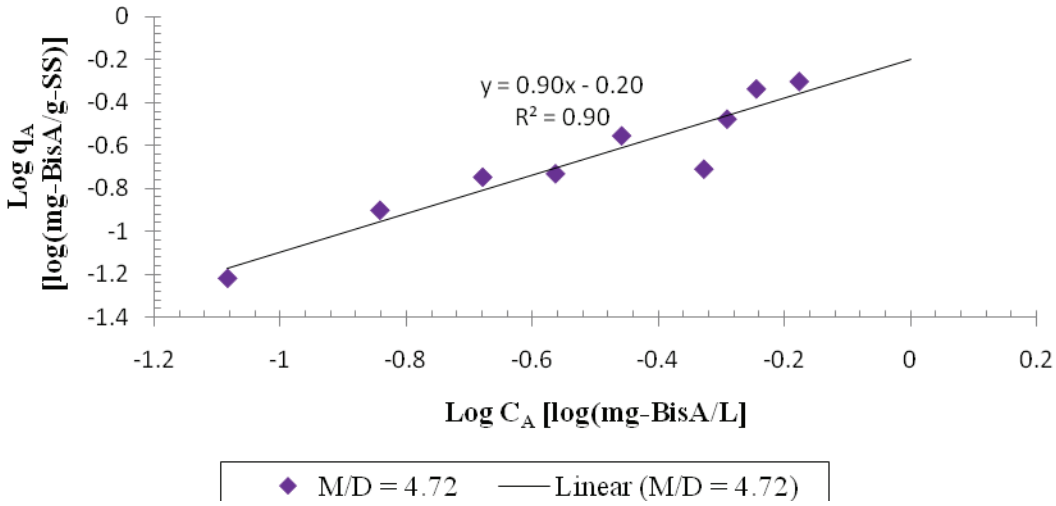


Figure 4.7. Freundlich isotherm with MNWWRP biosolids and M/D ratio and cationic strength of 4.72 and 9.18 meq/L, respectively. The target M/D ratio and cationic strength were 4 and 8 meq/L, respectively.

Table 4.2. Paired *t* Test Results of the Isotherms with Bisphenol A as the Target Compound, MNWWRP as the Biosolid Source, and Target Cationic Strength of 8 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* Test	*t**	t_c
Low	0.92	7.47	Low-Med	1.236	1.833
Med	1.92	7.42	Low-High	2.511	1.860
High	4.72	9.18	Med-High	1.607	1.860

[a]Pairing each isotherm using q_A and M/D ratio.

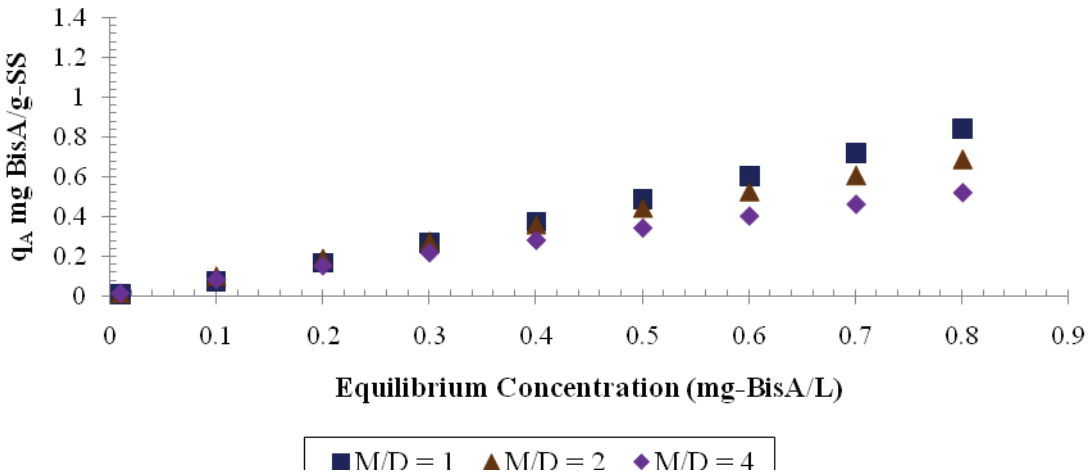


Figure 4.8. Combined Freundlich isotherm equations generated from the results of the isotherms with MNWWRP biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 8 meq/L.

4.1.3 Target Cationic Strength = 4 Meq/L

Figures 4.9 to 4.11 contain the results of the isotherms performed at target M/D ratios of 1, 2, and 4 with a target cationic strength of 4 meq/L and MNWWRP biosolids. Figure 4.9 contains the results for the isotherm with a measured M/D ratio of 0.95 and cationic strength of 3.97 meq/L. The intensity parameter for this isotherm is 0.66, and the capacity parameter is 0.46. Figure 4.10 contains the results of the isotherm with an actual M/D ratio of 1.84 and cationic strength of 3.99 meq/L. The intensity parameter is 0.86, and the capacity parameter is 0.56. Figure 4.11 contains the results for the isotherm with an actual M/D ratio of 3.33 and cationic strength of 4.14 meq/L. The intensity parameter is 0.94, and the capacity parameter is 0.85. The intensity and capacity parameters exhibit a trend that is opposite of what was observed at higher cation concentrations. Therefore, the sorptive capacity could be increasing as the M/D ratio increases. The capacity and intensity parameters from the isotherms were used to plot the adsorptive capacity as a function of concentration on a linear plot using equation 4.2 (Figure 4.12). As expected, the predicted sorptive capacity does increase as the M/D ratio increases. The paired *t* test for this set of isotherms is contained in Table 4.3. Two out of the three comparisons completed were statistically significant.

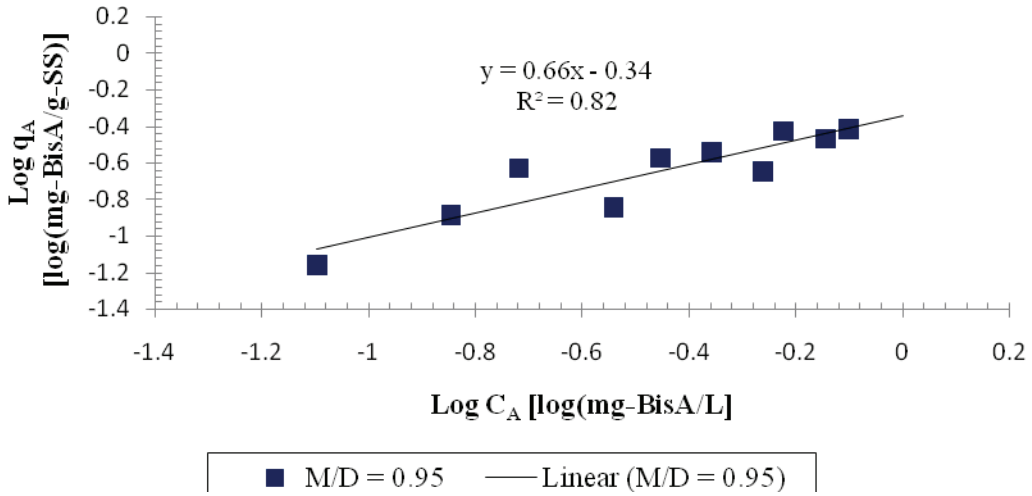


Figure 4.9. Freundlich isotherm with MNWWRP biosolids and M/D ratio and cationic strength of 0.95 and 3.97 meq/L, respectively. Target M/D ratio of 1 and cationic strength of 4 meq/L.

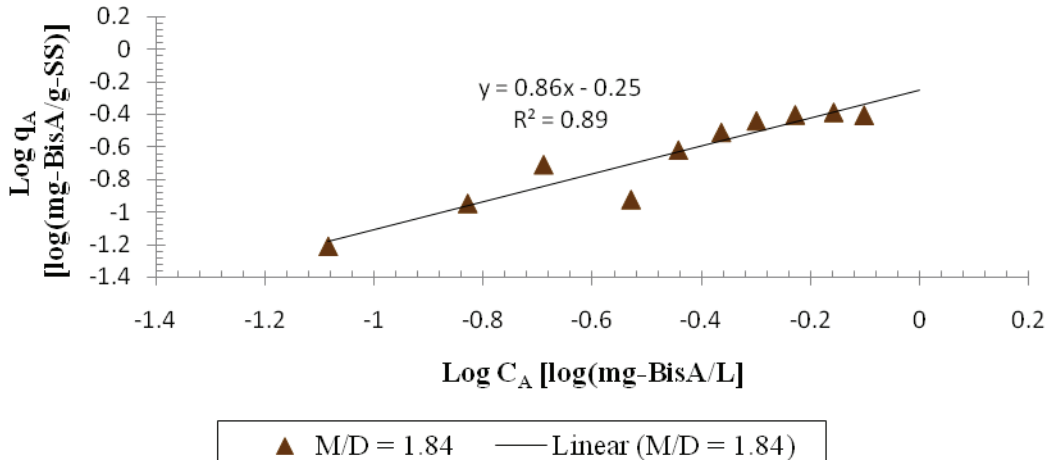


Figure 4.10. Freundlich isotherm with MNWWRP biosolids and M/D ratio and cationic strength of 1.84 and 3.99 meq/L, respectively. Target M/D ratio of 2 and cationic strength of 4 meq/L.

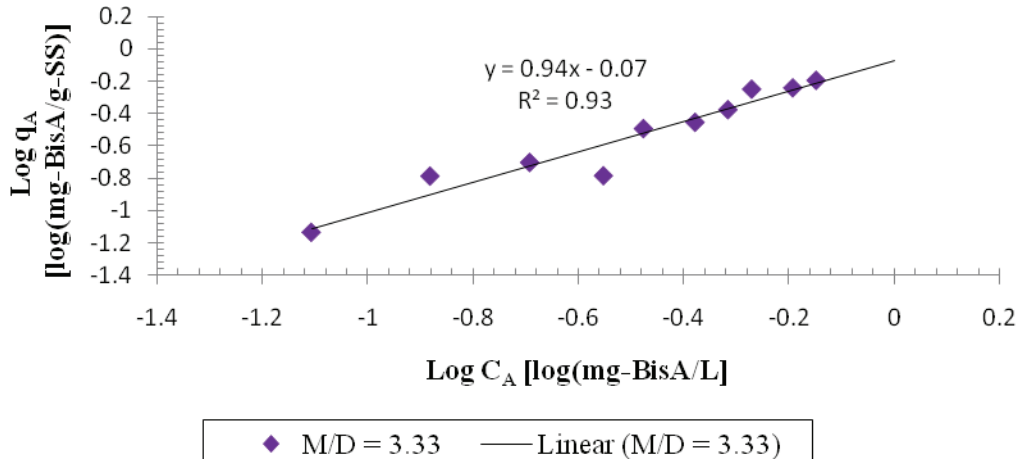


Figure 4.11. Freundlich isotherm with MNWWRP biosolids and M/D ratio and cationic strength of 3.33 and 4.14 meq/L, respectively. Target M/D ratio of 4 and cationic strength of 4 meq/L.

Table 4.3. Paired *t* Test Results of the Isotherms with Bisphenol A as the Target Compound, MNWWRP as the Biosolid Source, and Target Cationic Strength of 4 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* test	*t**	t_c
Low	0.95	3.97	Low-Med	0.789	1.833
Med	1.84	3.99	Low-High	3.038	1.833
High	3.33	4.14	Med-High	3.507	1.833

[a]Pairing each isotherm using q_A and M/D ratio.

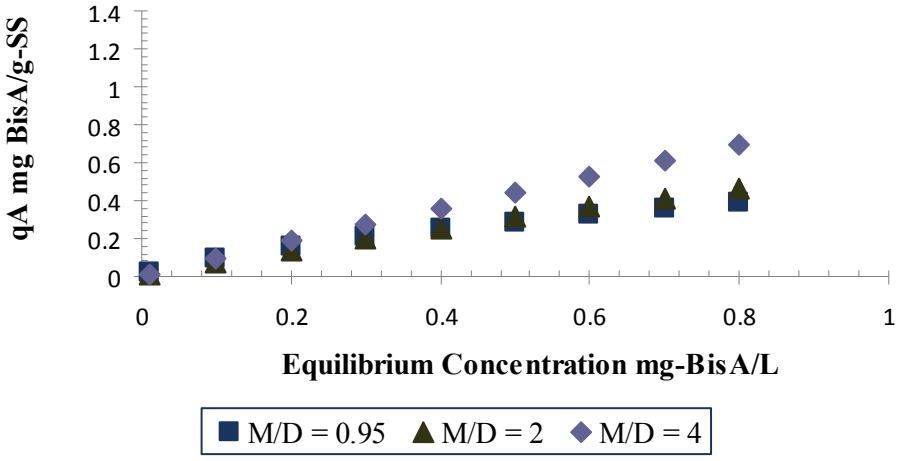


Figure 4.12. Combined Freundlich isotherm equations generated from the results of the isotherms with target M/D ratios of 1, 2, and 4 and target cationic strength of 4 meq/L.

4.1.4 Biological Control with Sodium Azide

Figures 4.13 to 4.15 contain the results of isotherms performed at target M/D ratios of 1, 2, and 4 with a target cationic strength of 12 meq/L with sodium azide to control biological activity, calcium chloride, magnesium sulfate, and MNWWRP biosolids. Figure 4.13 contains the results for the isotherm with a measured M/D ratio of 1.07 and cationic strength of 12.72 meq/L. The intensity parameter for this isotherm is 0.97, and the capacity parameter is 1.93. Figure 4.14 contains the results of the isotherm with a measured M/D ratio of 2.07 and cationic strength of 13.00 meq/L. The intensity parameter is 0.84, and the capacity parameter is 1.29. Figure 4.15 contains the results for the isotherm with a measured M/D ratio of 4.24 and cationic strength of 12.74 meq/L. The intensity parameter is 0.88, and the capacity parameter is 0.76. The capacity and intensity parameters from the isotherms were used to calculate the adsorptive capacity as a function of concentration for a linear correlation using equation 4.2 (Figure 4.16). The M/D ratio strongly affected the sorption of bisphenol A as compared with the isotherms performed on active biosolids at the same cationic strength. The sorption capacity parameter increased by 98, 55, and 0% for M/D ratios of 1, 2, and 4, respectively, when compared with the sorption capacity of the isotherm performed with clarifier effluent and with the same target cationic strength. This suggests that either the inactive biosolids or the water matrix leads to the increase of capacity. The difference in sorption capacity between inactive and active biosolids may be due to the formation of colloids in active biosolids (Novak et al., 1998). Colloids sorb hydrophobic compounds and are smaller than the pore size of the cellulose nitrate filters. Another possibility could be explained by the kinetic experiments. The kinetic experiment results show that the target compound quickly sorbs to the biosolids and is released over time. The active biosolids may play a role in the uptake and release of the target compound. The last variable that may impact the results is the water source was different, which may play a role in the increased capacity parameters. The paired *t* test for this set of isotherms is contained in Table 4.4.

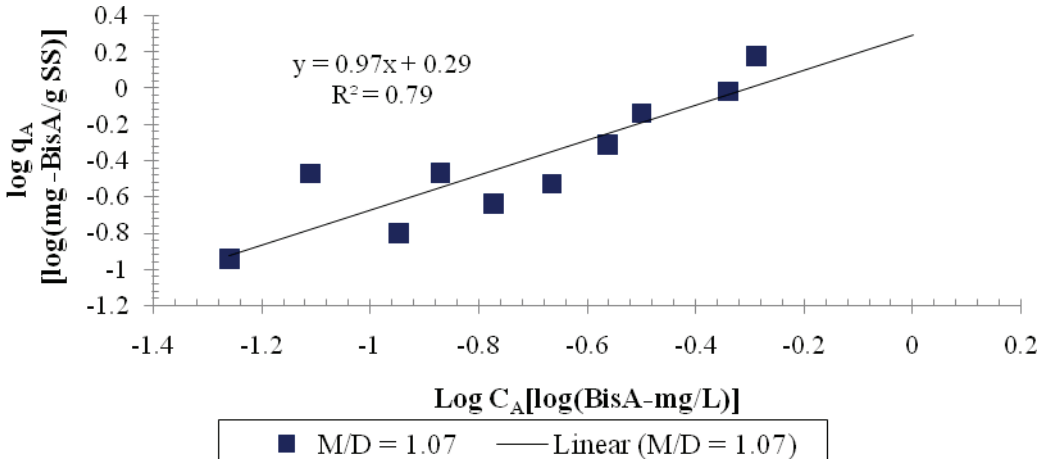


Figure 4.13. Freundlich isotherm to control biological activity by the presence of sodium azide. Isotherm performed with MNWWRP biosolids and an M/D ratio and cationic strength of 1.07 and 12.72 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

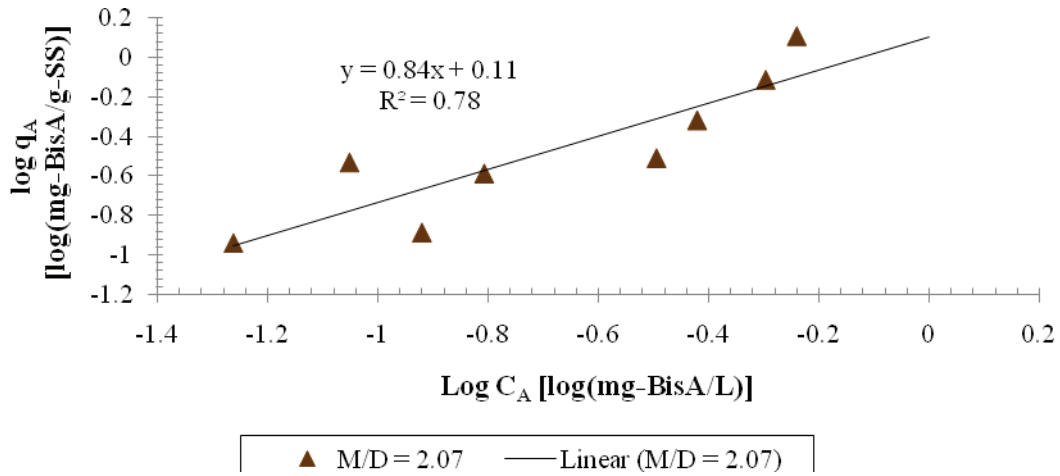


Figure 4.14. Freundlich isotherm to control biological activity by the presence of sodium azide. Isotherm performed with MNWWRP biosolids with an M/D ratio and cationic strength of 2.07 and 13.01 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

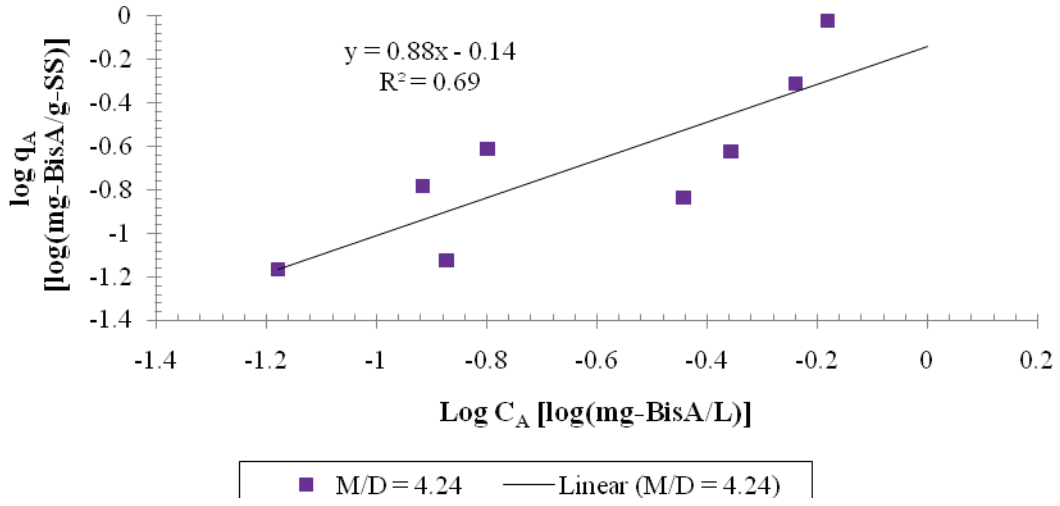


Figure 4.15. Freundlich isotherm to control biological activity by the presence of sodium azide. Isotherm performed with MNWWRP biosolids with an M/D ratio and cationic strength of 4.24 and 12.74 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

Table 4.4. Paired *t* Test Results of the Isotherms with Bisphenol A as the Target Compound, Sodium Azide to Control Biological Activity, MNWWRP as the Biosolid Source, and Target Cationic Strength of 12 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* test	*t**	t_c
Low	1.07	12.72	Low-Med	4.725	1.833
Med	2.07	13.01	Low-High	4.631	1.833
High	4.24	12.74	Med-High	3.641	1.833

[a]Pairing each isotherm using q_A and M/D ratio.

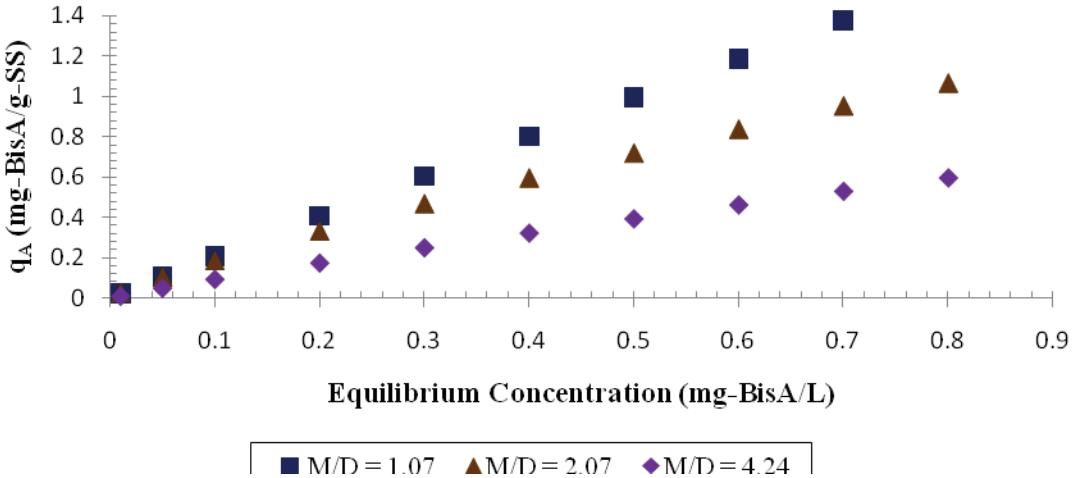


Figure 4.16. Combined Freundlich isotherm equations generated from the results of the isotherms with sodium azide to control biological growth; MNWWRP biosolids and target M/D ratios of 1, 2, and 4; and target cationic strength of 12 meq/L.

4.1.5 Water Matrix Control

Figures 4.17 to 4.19 contain the results of the isotherms performed at target M/D ratios of 1, 2, and 4 with a target cationic strength of 12 meq/L. Synthetic sources of cations used were sodium chloride, calcium chloride, and magnesium sulfate to create a control with the same matrix used in the sodium azide tests. Figure 4.17 contains the results for the isotherm with a measured M/D ratio of 1.01 and cationic strength of 11.10 meq/L. The intensity parameter for this isotherm is 0.67, and the capacity parameter is 1.62. Figure 4.18 contains the results of the isotherm with a measured M/D ratio of 1.91 and cationic strength of 12.08 meq/L. The intensity parameter for this isotherm is 0.69, and the capacity parameter is 1.38. Figure 4.19 contains the results for the isotherm with a measured M/D ratio of 3.40 and cationic strength of 11.57 meq/L. The intensity parameter is 0.72, and the capacity parameter is 1.74. The capacity and intensity parameters from the isotherms were used to calculate the adsorptive capacity as a function of concentration for a linear correlation using equation 4.2 (Figure 4.20). Since the capacity and intensity were similar, there does not appear to be an effect from the M/D ratio. In comparisons of the isotherm capacity parameters to that of the isotherm

performed with clarifier effluent, the capacity parameter increased 65, 66, and 128% for M/D ratios of 1, 2, and 4 respectively. This suggests that the water matrix affects the capacity strength but that sorption is not affected by the M/D ratio. The change in capacity may be due to competitive compounds that are present in clarifier effluent. The paired *t* test for this set of isotherms is contained in Table 4.5. There was not a statistically significant difference between the isotherms.

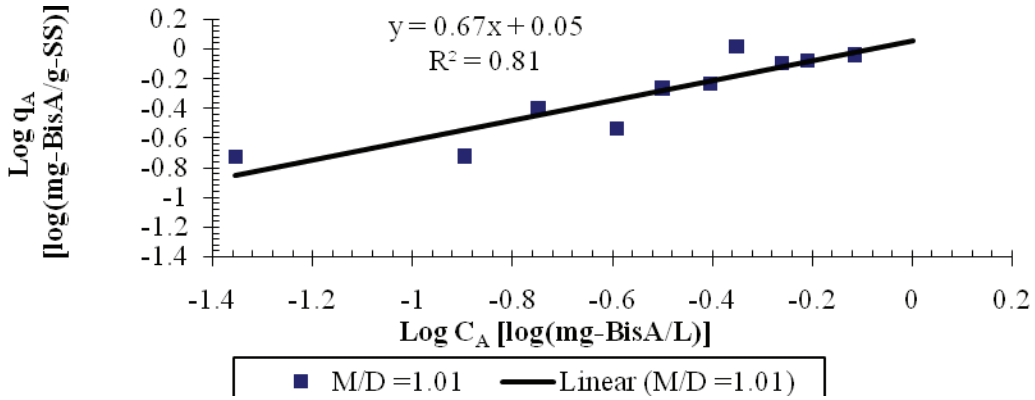


Figure 4.17. Freundlich isotherm to control the water matrix by using sodium chloride, calcium chloride, and magnesium salts as the water matrix. Isotherms were performed with MNWWRP biosolids with an M/D ratio and cationic strength of 1.01 and 11.10 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

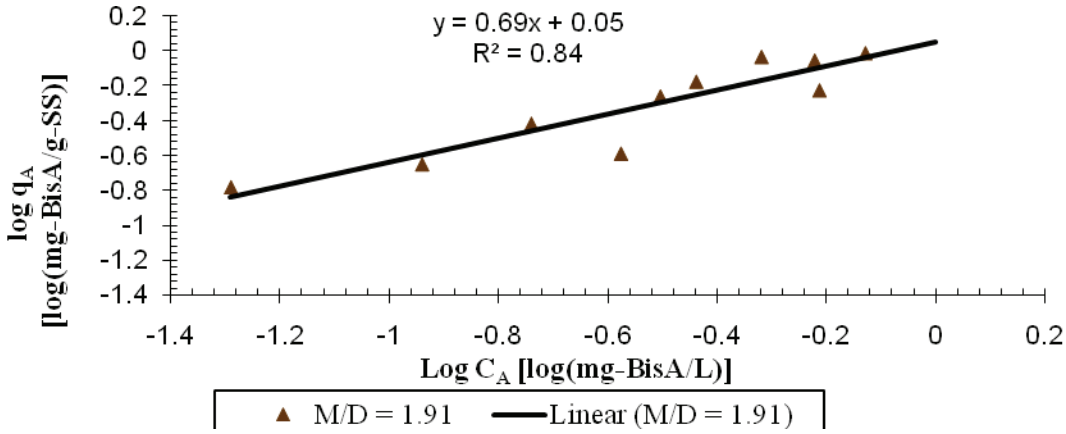


Figure 4.18. Freundlich isotherm to control the water matrix by using sodium chloride, calcium chloride, and magnesium sulfate as the salts in the water matrix. Isotherms were performed with MNWWRP biosolids with an M/D ratio and cationic strength of 1.91 and 12.08 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

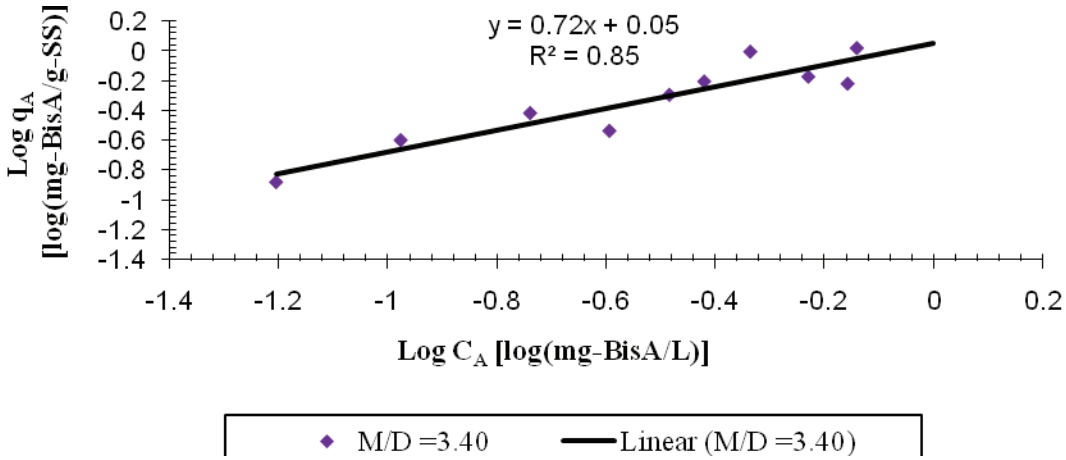


Figure 4.19. Freundlich isotherm to control the water matrix by using sodium chloride, calcium chloride, and magnesium salts as the water matrix. Isotherms were performed with MNWWRP biosolids with an M/D ratio and cationic strength of 1.01 and 11.10 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

Table 4.5. Paired *t* Test Results of the Isotherms with Bisphenol A as the Target Compound; Sodium Chloride, Calcium Chloride, and Magnesium Sulfate for Water Matrix Control; MNWWRP as the Biosolid Source; and Target Cationic Strength of 12 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* Test	*t**	t_c
Low	1.01	11.10	Low-Med	0.484	1.833
Med	1.91	12.08	Low-High	0.870	1.833
High	3.40	11.57	Med-High	0.447	1.833

[a]Pairing each isotherm using q_A and M/D ratio.

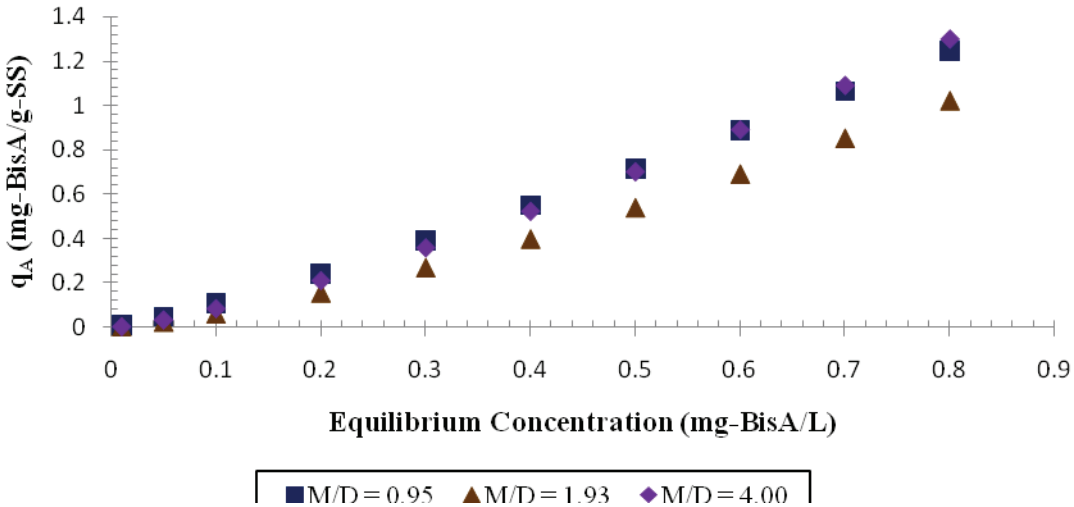


Figure 4.20. Combined Freundlich isotherm equations generated from the results of the isotherms with MNWWRP biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 4 meq/L.

4.1.6 KWRF Biosolids at Target Cationic Strength of 12 Meq/L

Figures 4.21 to 4.23 contain the results of the isotherms performed at target M/D ratios of 1, 2, and 4 with a target cationic strength of 12 meq/L and with KWRF biosolids and effluent. Figure 4.21 contains the results for the isotherm with a measured M/D ratio of 0.87 and cationic strength of 11.05 meq/L. The intensity parameter for this isotherm is 0.81, and the capacity parameter is 0.62. Figure 4.22 contains the results of the isotherm with a measured M/D ratio of 1.79 and cationic strength of 10.83 meq/L. The intensity parameter is 0.77, and the capacity parameter is 0.56. Figure 4.23 contains the results for the isotherm with a measured M/D ratio of 3.49 and cationic strength of 11.05 meq/L. The intensity parameter is 0.84, and the capacity parameter is 0.53. The capacity and intensity parameters from the isotherms in this set were plotted using equation 4.2 (Figure 4.24). As would be expected from the similarities between the capacity and intensity parameters, the predicted sorption is not a function of the M/D ratio. The paired *t* test for this set of isotherms is contained in Table 4.6, and the results confirm there is no statistically significant difference between M/D ratios. The lack of a correlation for KWRF sludge may be attributed to the poor settling characteristics of this sludge as compared to the MNWWRP sludge. KWRF will not have effective bioflocculation and would therefore be less affected by the M/D ratio. The sorption capacity of the KWRF biosolids was much lower than that of the MNWRRP biosolids.

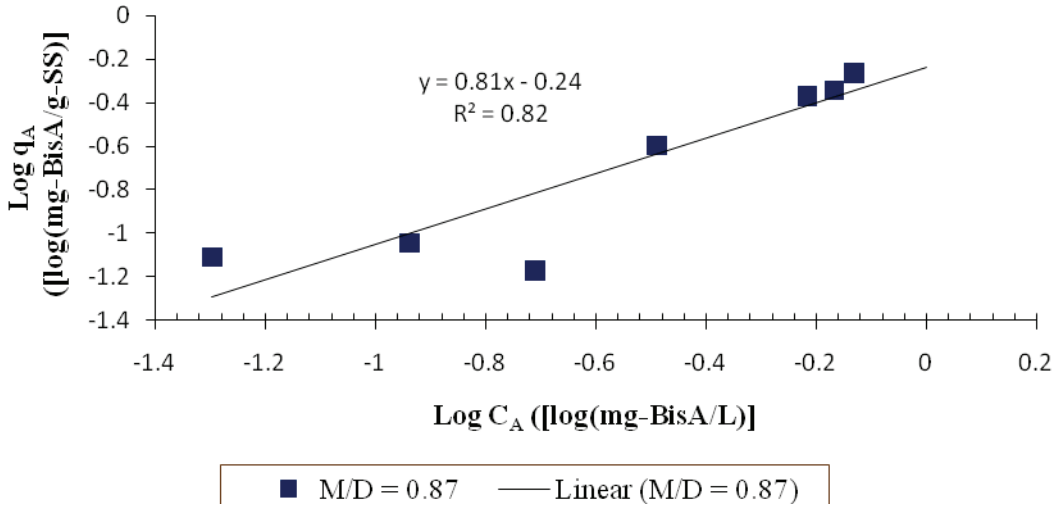


Figure 4.21. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 0.87 and 11.05 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

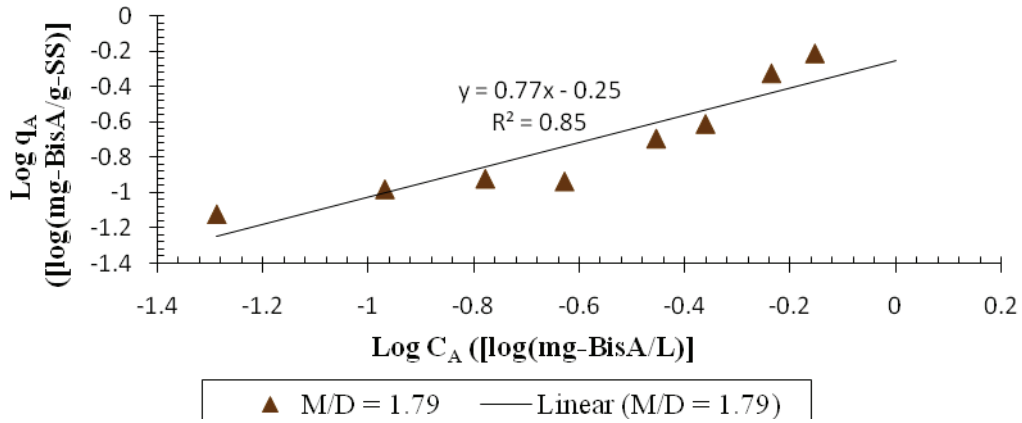


Figure 4.22. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 1.79 and 10.83 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

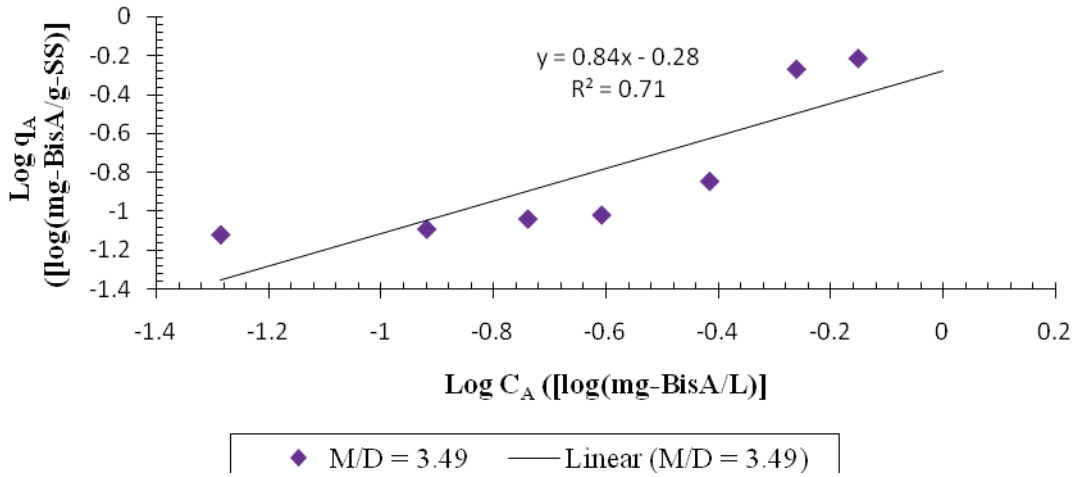


Figure 4.23. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 3.49 and 11.05 meq/L, respectively. The target M/D ratio and cationic strength were 4 and 12 meq/L, respectively.

Table 4.6. Paired *t* Test Results of the Isotherms with Bisphenol A as the Target Compound, KWRF as the Biosolid Source, and Target Cationic Strength of 12 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* test	*t**	t_c
Low	0.87	11.05	Low-Med	2.165	1.895
Med	1.79	10.83	Low-High	0.503	1.895
High	3.49	11.20	Med-High	1.342	1.895

[a]Pairing each isotherm using q_A and M/D ratio.

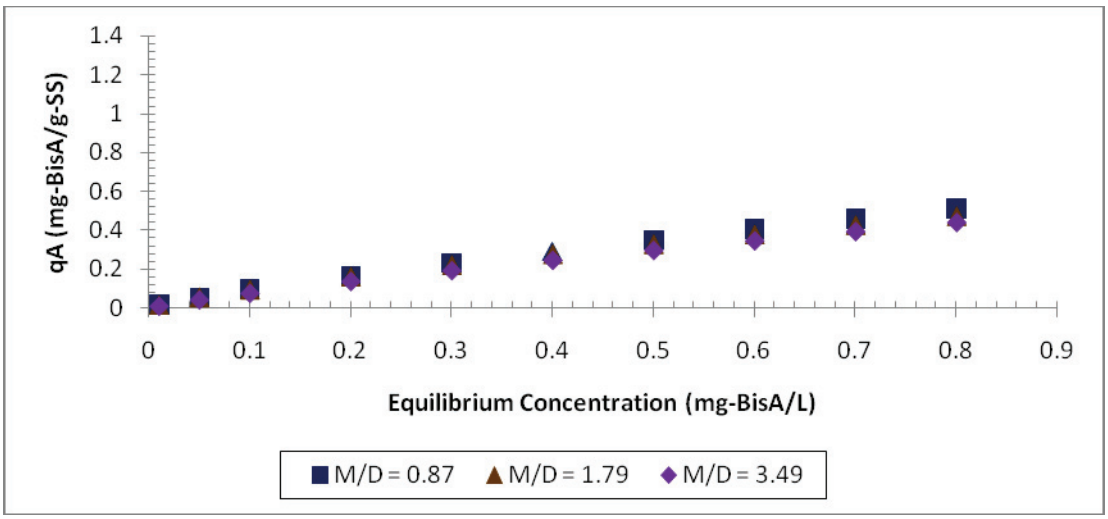


Figure 4.24. Combined Freundlich isotherm equations generated from the results of the isotherms with KWRF biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 12 meq/L.

4.1.7 Target Cationic Strength = 20 Meq/L (MNWWRP)

Figure 4.25 contains the result for the isotherm that was performed with a target M/D ratio of 6 and target cationic strength of 20 meq/L with MNWWRP biosolids. The M/D ratio measured by AA was 7.07, and the cationic strength was 18.99 meq/L. The intensity and capacity parameters were 0.83 and 0.54, respectively.

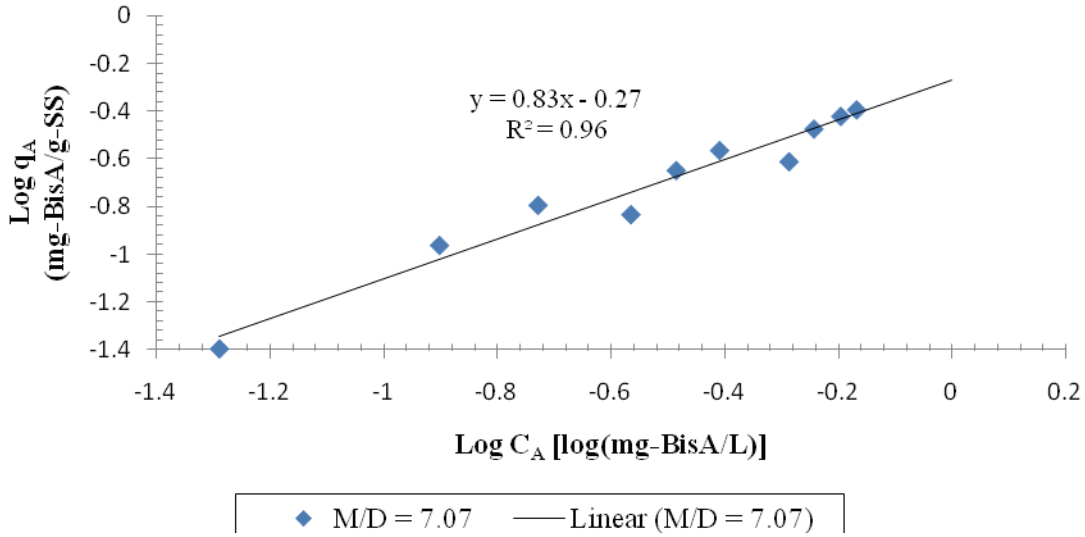


Figure 4.25. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 7.01 and 18.94 meq/L, respectively. The target M/D ratio and cationic strength were 6 and 20 meq/L, respectively.

Summary of Bisphenol A Isotherms

A summary of all the bisphenol A isotherms results can be seen in Table 4.7. The isotherm completed under extreme conditions with a target M/D ratio of 6 and a cationic strength of 20 meq/L had the lowest sorption capacity of any of the tests completed. Increases in the M/D ratio did tend to decrease sorption capacity, but the trends were often not statistically significant.

Table 4.7. Summary of Isotherms with Bisphenol A

Source	M/D Ratio	Cationic Strength (meq/L)	1/n	K [mg/g][L/mg]$^{1/n}$	R^2 %	No. of Data Points	1/n % Change from Low M/D	K % Change from Low M/D
MNWWRP	1.11	11.97	1.07	0.98	69	10	--	--
MNWWRP	2.33	13.00	0.80	0.83	87	10	-25	-15
MNWWRP	3.82	11.89	0.44	0.76	83	10	-59	-22
MNWWRP	0.92	7.47	1.18	1.10	94	10	--	--
MNWWRP	1.92	7.42	0.99	0.82	91	10	-16	-25
MNWWRP	4.72	9.18	0.90	0.63	90	10	-24	-43
MNWWRP	0.95	3.97	0.66	0.46	82	10	--	--
MNWWRP	1.84	3.99	0.86	0.56	89	10	30	22
MNWWRP	3.33	4.14	0.94	0.85	93	9	42	85
Azide-M	1.07	12.72	0.97	1.95	79	10	--	--
Azide-M	2.07	13.01	0.84	1.29	78	8	-13	-34
Azide-M	4.24	12.74	0.88	0.76	69	8	-9	-61
Salt-M	1.01	11.10	0.67	1.62	81	10	--	--
Salt-M	1.91	12.08	0.69	1.38	84	10	3	-15
Salt-M	3.40	11.57	0.72	1.74	85	10	7	7
KWRF	0.87	11.05	0.81	0.62	82	7	--	--
KWRF	1.79	10.83	0.77	0.56	85	8	-5	12
KWRF	3.49	11.20	0.84	0.53	71	7	4	35
MNWWRP	7.01	18.94	0.70	0.29	62	8	--	--

4.1.8 Comparing Isotherms with Same Target M/D Ratio

All isotherms with bisphenol A as the target compound were compared to each other with respect to cationic strength, water matrices, and biosolid source. The target M/D ratio was held constant during comparisons of isotherms that belonged to target cationic strength groups of 4, 8, and 12 meq/L. For example, all the isotherms with a target M/D ratio of 1 would be compared with different cation strengths, water matrices, and biosolid sources. Table 4.8 contains the results for the isotherms compared with a target M/D ratio of 1. Eleven out of 15 isotherms showed a statistically significant difference between them. Table 4.9 contains the statistical comparisons between isotherms performed with a target M/D ratio of 2. Again, 11 out of 15 isotherms showed a statistically significant difference between them. Similarly, there were 12 statistically significantly different isotherms with a target M/D ratio of 4 as seen in Table 4.10. A comparison of increasing M/D ratio and increasing cation concentration shows a significant decrease in sorption capacity for M/D ratios of 2, 4 and 6. This agrees with results by Higgins and Novak (1997) and represents a more realistic effect of salt addition from water softeners since both cation concentration and M/D ratio will increase. It is important the biosolids that were from MNWWRP were not labeled in the tables and only the KWRF biosolid was labeled because it was used only once.

Table 4.8. Isotherm Comparison with Target M/D Ratio of 1

Cationic Strength	t^*	t_c
12\8	2.248	1.833
12\4	3.023	1.833
8\4	2.862	1.833
12\12-KWRF	3.275	1.943
8\12-KWRF	2.295	1.943
4\12-KWRF	0.309	1.943
12\Azide	0.423	1.833
12\Salt	3.887	1.833
12K\Azide	2.638	1.943
12-KWRF\Salt	3.189	1.943
8\Azide	1.573	1.833
8\Salt	4.655	1.833
4\Azide	2.331	1.833
4\Salt	4.477	1.833
Azide\Salt	0.574	1.833

Table 4.9. Isotherm Comparison with Target M/D Ratio of 2

Cationic Strength	t^*	t_c
12\8	2.954	1.833
12\4	4.399	1.833
8\4	2.313	1.833
12\12-KWRF	3.042	1.860
8\12-KWRF	1.752	1.860
4\KWRF	0.770	1.860
12\Azide	0.443	1.860
12\Salt	2.178	1.895
12K\Azide	2.169	1.895
12-KWRF\Salt	4.258	1.833
8\Azide	1.717	1.895
8\Salt	4.297	1.833
4\Azide	1.806	1.895
4\Salt	5.242	1.833
Azide\Salt	1.014	1.895

Table 4.10. Isotherm Comparison with Target M/D Ratio of 4

Cationic Strength	t^*	t_c
12\8	8.49772	1.895
12\4	4.13691	1.833
8\4	3.18924	1.86
12\12-KWRF	7.61469	1.833
8\12-KWRF	3.67099	1.86
4\12-KWRF	4.33701	1.833
12\Azide	1.9779	1.895
12\Salt	0.87634	1.833
12K\Azide	2.12388	1.895
12-KWRF\Salt	4.98416	1.833
8\Azide	1.38336	1.895
8\Salt	3.76018	1.86
4\Azide	0.71971	1.895
4\Salt	3.78409	1.833
Azide\Salt	2.52502	1.895

4.2 EE2 ISOTHERM RESULTS

4.2.1 Target Cationic Strength = 12 Meq/L

Figures 4.26 to 4.28 contain the results of the isotherms performed at target M/D ratios of 1, 2, and 4 with a target cationic strength of 12 meq/L and with MNWWRP biosolids as the sorbate and clarifier effluent as the water source. Figure 4.26 contains the results for the isotherm with a measured M/D ratio of 0.95 and cationic strength of 12.03 meq/L. The intensity parameter for this isotherm is 0.61, and the capacity parameter is 0.46. Figure 4.27 contains the results of the isotherm with a measured M/D ratio of 2.30 and cationic strength of 10.65 meq/L. The intensity parameter is 0.69, and the capacity parameter is 0.46. Figure 4.28 contains the results for the isotherm with a measured M/D ratio of 3.96 and cationic strength of 10.11 meq/L. The intensity parameter is 0.49, and the capacity parameter is 0.38. The capacity and intensity parameters from the isotherms in this set were plotted using equation 4.2 (Figure 4.29). The paired *t* test for this set of isotherms is contained in Table 4.11. The statistics show a difference between the M/D ratio of 4 and the M/D ratio of 1 with less sorption at the higher M/D ratio.

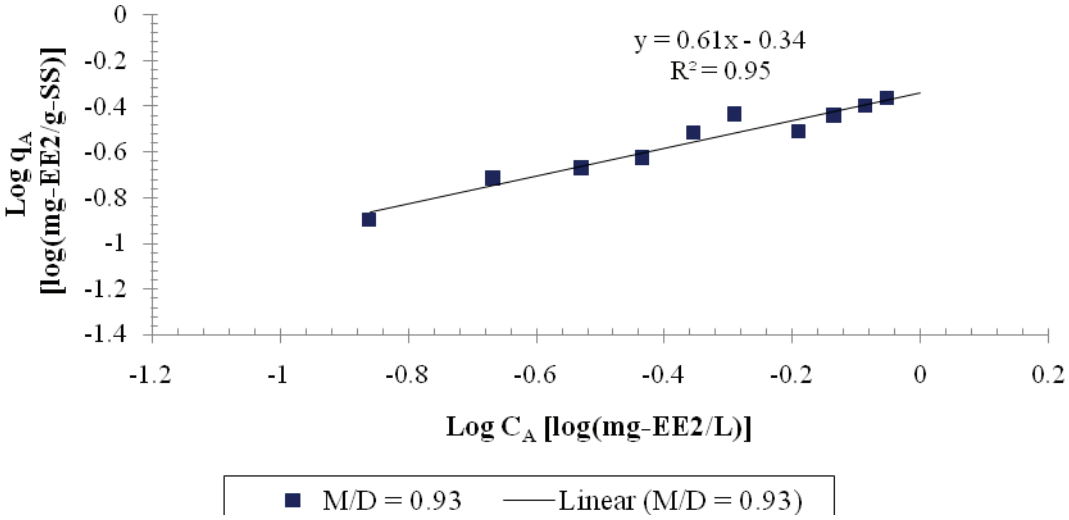


Figure 4.26. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 0.93 and 12.03 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

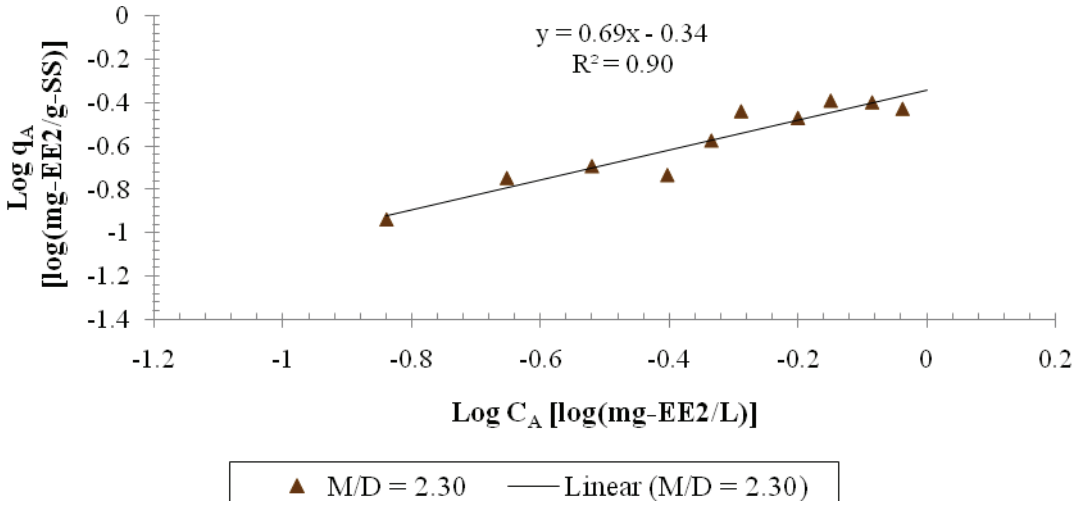


Figure 4.27. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 2.30 and 10.65 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

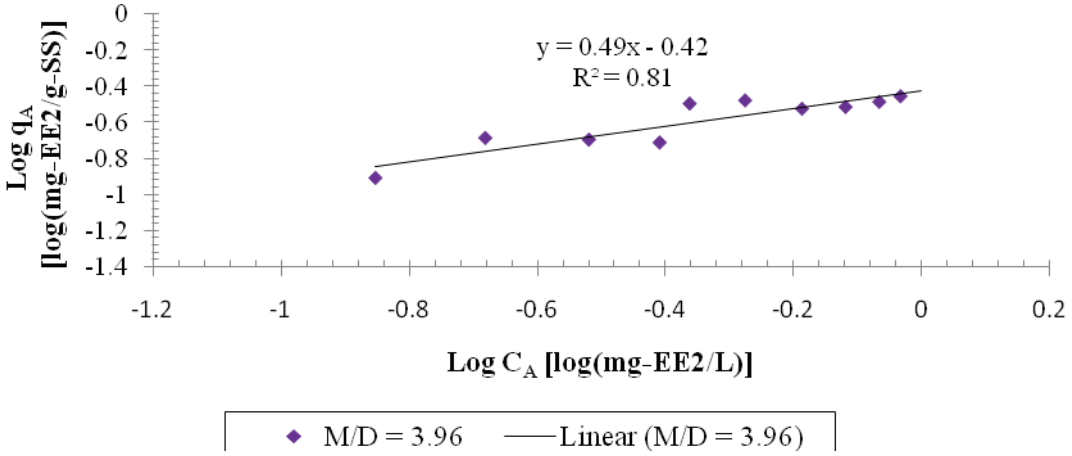


Figure 4.28. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 3.96 and 10.11 meq/L, respectively. The target M/D ratio and cationic strength were 4 and 12 meq/L, respectively.

Table 4.11. Paired *t* Test Results of the Isotherms with EE2 as the Target Compound, MNWWRP as the Biosolid Source, and Target Cationic Strength of 12 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* Test	*t**	t_c
Low	0.93	12.03	Low-Med	1.127	1.833
Med	2.30	10.65	Low-High	2.623	1.833
High	3.96	10.11	Med-High	1.126	1.833

[a]Pairing each isotherm using q_A and M/D ratio.

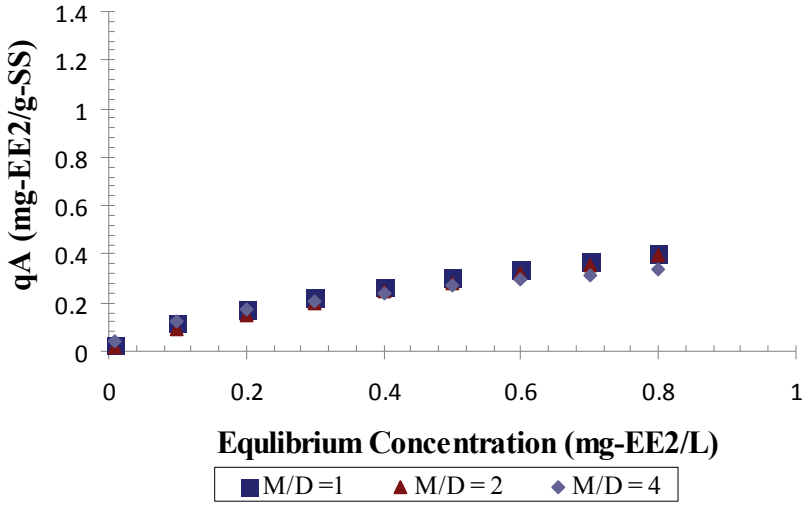


Figure 4.29. Combined Freundlich isotherm equations generated from the results of the isotherms with MNWWRP biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 12 meq/L.

4.2.2 Target Cationic Strength = 8 Meq/L

Figures 4.30 to 4.32 contain the results of the isotherms performed at target M/D ratios of 1, 2, and 4 with a target cationic strength of 8 meq/L, MNWWRP biosolids as the sor bate, and clarifier effluent as the water source. Figure 4.30 contains the results for the isotherm with a measured M/D ratio of 0.95 and cationic strength of 7.5 meq/L. The intensity parameter for this isotherm is 1.19, and the capacity parameter is 1.62. Figure 4.31 contains the results of the isotherm with a measured M/D ratio of 1.93 and cationic strength of 7.34 meq/L. The intensity parameter is 1.36, and the capacity parameter is 1.38. Figure 4.32 contains the results for the isotherm with a measured M/D ratio of 4.00 and cationic strength of 7.50 meq/L. The intensity parameter is 1.31, and the capacity parameter is 1.74. The capacity and intensity parameters from the isotherms in this set were used to predict the equilibrium relationship according to equation 4.2 (Figure 4.33). The paired *t* test for this set of isotherms is contained in Table 4.12. The results are somewhat contrary to the hypothesis, but there is no statistically significant difference between the low and high M/D ratios. The sorption was significantly lower at the target M/D ratio of 2 than at the other two M/D ratios.

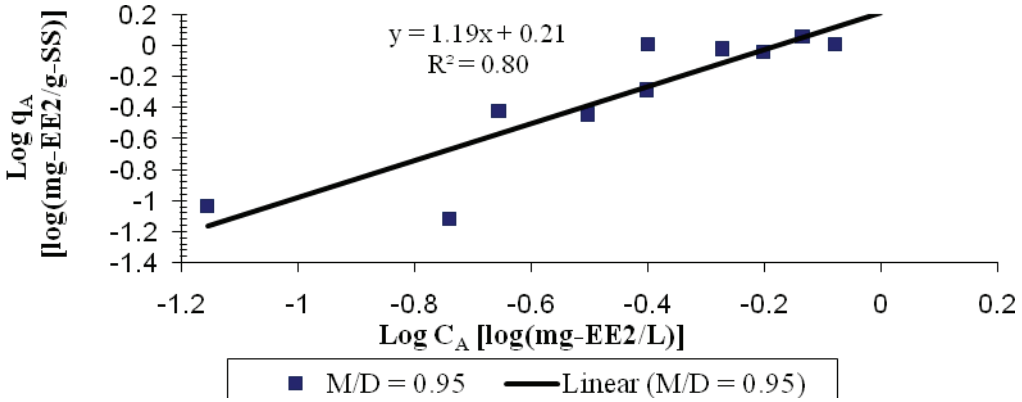


Figure 4.30. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 0.95 and 7.50 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 8 meq/L, respectively.

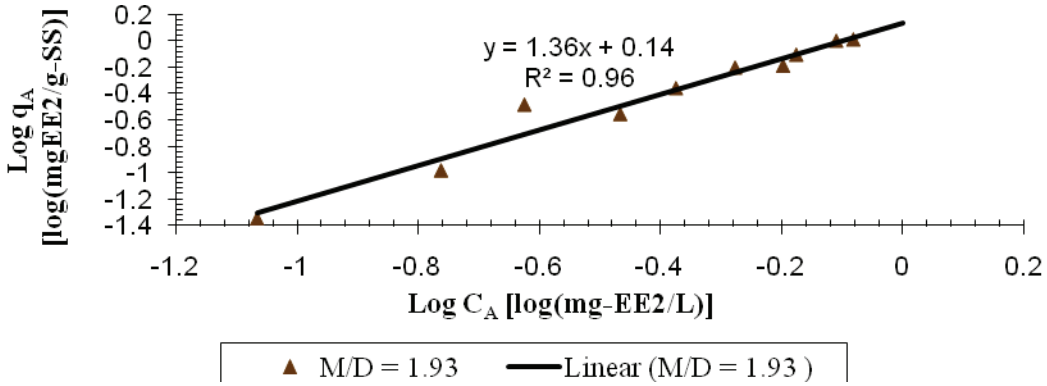


Figure 4.31. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 1.93 and 7.34 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 8 meq/L, respectively.

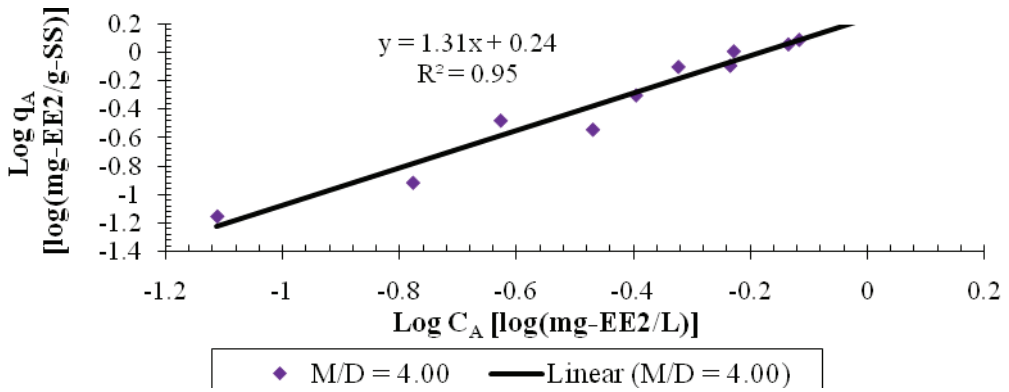


Figure 4.32. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 4.00 and 7.50 meq/L, respectively. The target M/D ratio and cationic strength were 4 and 8 meq/L, respectively.

Table 4.12. Paired *t* Test Results of the Isotherms with EE2 as the Target Compound, MNWWRP as the Biosolid Source, and Target Cationic Strength of 8 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* test	*t**	t_c
Low	0.95	7.50	Low-Med	2.819	1.833
Med	1.93	7.34	Low-High	0.401	1.833
High	4.00	7.50	Med-High	3.736	1.833

[a]Pairing each isotherm using q_A and M/D ratio.

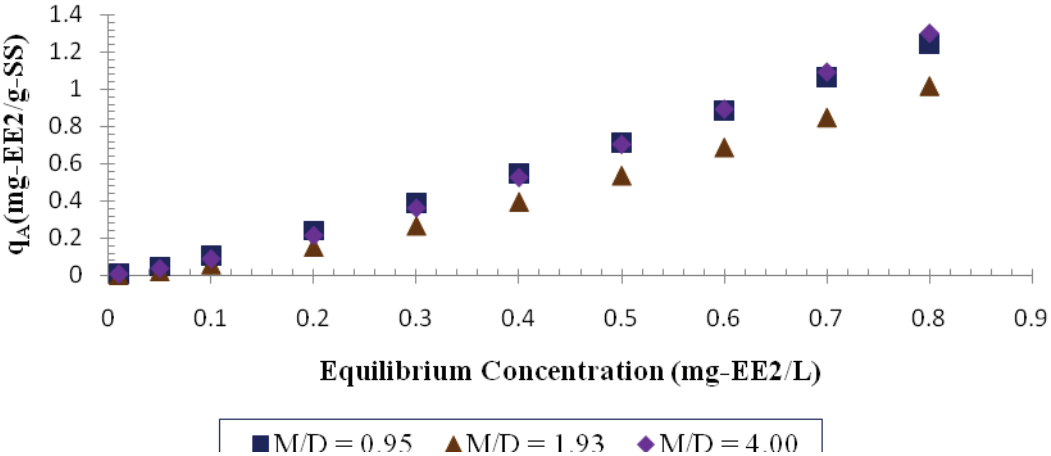


Figure 4.33. Combined Freundlich isotherm equations generated from the results of the isotherms with MNWWRP biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 8 meq/L.

4.2.3 Target Cationic Strength = 4 Meq/L

Figures 4.34 to 4.36 contain the results of the isotherms performed at target M/D ratios of 1, 2, and 4 with a target cationic strength of 4 meq/L and with MNWWRP biosolids as the sorbate and clarifier effluent as the water source. Figure 4.34 contains the results for the isotherm with a measured M/D ratio of 0.94 and cationic strength of 3.80 meq/L. The intensity parameter for this isotherm is 1.30, and the capacity parameter is 1.40. Figure 4.35 contains the results of the isotherm with a measured M/D ratio of 1.80 and cationic strength of 3.83 meq/L. The intensity parameter is 1.14, and the capacity parameter is 1.69. Figure 4.36 contains the results for the isotherm with a measured M/D ratio of 5.39 and cationic strength of 5.21 meq/L. The intensity parameter is 1.25, and the capacity parameter is 1.91. The capacity and intensity parameters from the isotherms in this set were used to predict the equilibrium relationship using equation 4.2 (Figure 4.37). The paired *t* test for this set of isotherms is contained in Table 4.13. The results are contrary to the hypothesis, as the sorption at the high M/D ratio is significantly greater than at the lower M/D ratios. These results are consistent with the bisphenol A results at the same cationic strength.

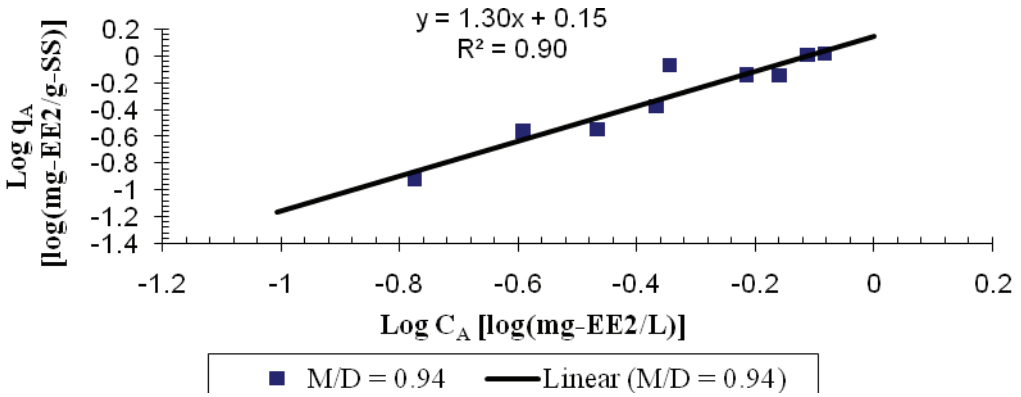


Figure 4.34. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 0.94 and 3.80 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 4 meq/L, respectively.

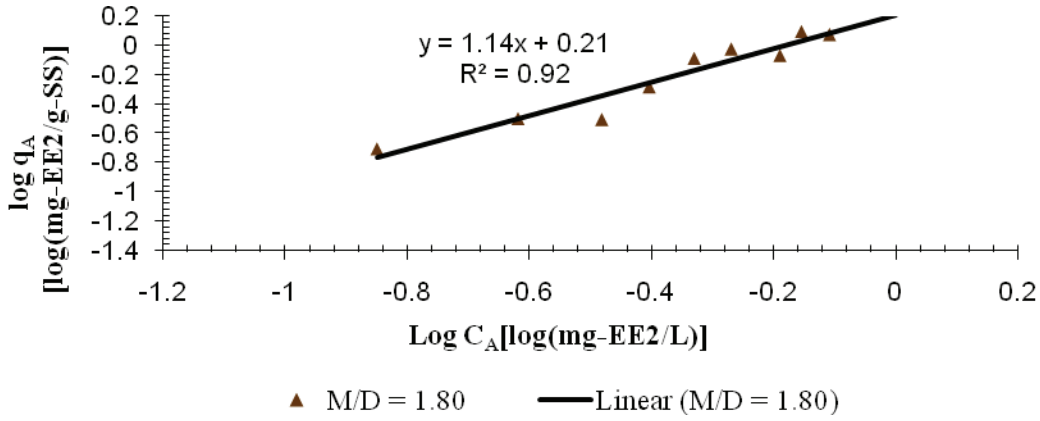


Figure 4.35. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 1.80 and 3.83 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 4 meq/L, respectively.

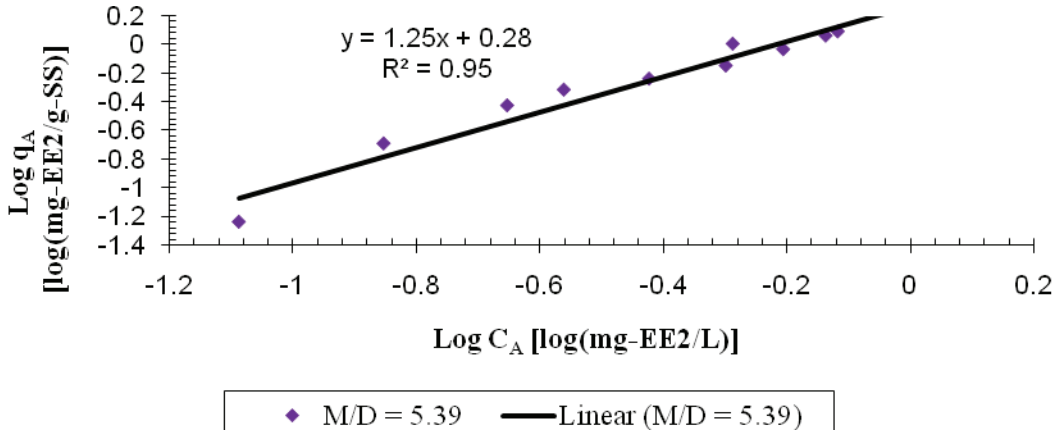


Figure 4.36. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 5.39 and 5.21 meq/L, respectively. The target M/D ratio and cationic strength were 4 and 4 meq/L, respectively.

Table 4.13. Paired *t* Test Results of the Isotherms with EE2 as the Target Compound, MNWWRP as the Biosolid Source, and Target Cationic Strength of 4 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* Test	*t**	t_c
Low	0.94	3.80	Low-Med	3.486	1.860
Med	1.80	3.83	Low-High	3.231	1.860
High	5.39	5.21	Med-High	1.169	1.860

[a]Pairing each isotherm using q_A and M/D ratio.

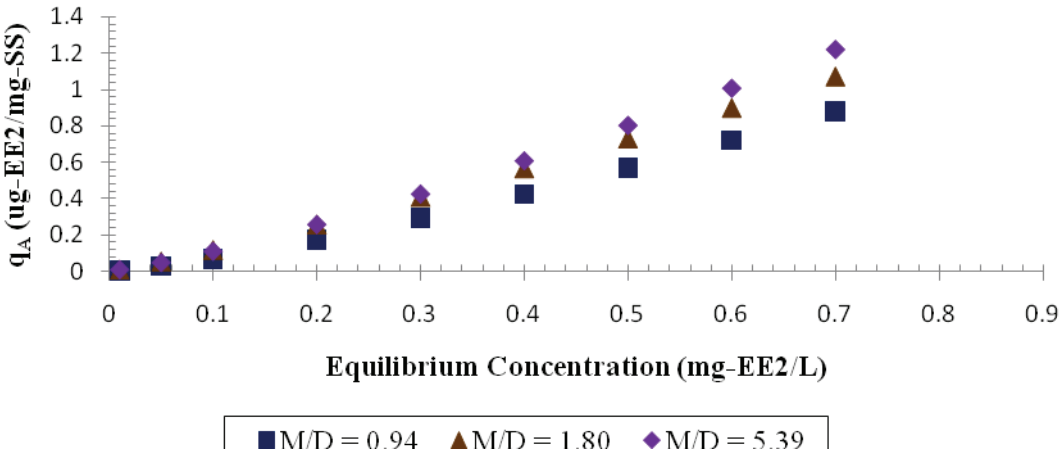


Figure 4.37. Combined Freundlich isotherm equations generated from the results of the isotherms with MNWWRP biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 4 meq/L.

4.2.4 Biological Control with Sodium Azide

Figures 4.38 to 4.40 contain the results of the isotherms performed at target M/D ratios of 1, 2, and 4 with a target cationic strength of 12 meq/L and with MNWWRP biosolids as the sorbate and sodium azide, calcium chloride, and magnesium sulfate as the water source. Figure 4.38 contains the results for the isotherm with a measured M/D ratio of 1.11 and cationic strength of 12.83 meq/L. The intensity parameter for this isotherm is 0.94, and the capacity parameter is 1.51. Figure 4.39 contains the results of the isotherm with a measured M/D ratio of 2.05 and cationic strength of 13.02 meq/L. The intensity parameter is 0.76, and the capacity parameter is 1.26. Figure 4.40 contains the results for the isotherm with a measured M/D ratio of 4.18 and cationic strength of 12.63 meq/L. The intensity parameter is 0.53, and the capacity parameter is 0.50. The capacity and intensity parameters from the isotherms in this set were plotted using equation 4.2 (Figure 4.41). The paired *t* test for this set of isotherms is contained in Table 4.14. There is a strong statistical correlation for a decrease in sorption with increasing M/D ratio, and the high M/D ratio has much lower sorption capacity. These results are similar to the bisphenol A results performed with sodium azide. The capacity parameters increased 228, 174, and 31% for M/D ratios of 1, 2, and 4, respectively, when compared with the isotherms performed with the clarifier effluent as the water source.

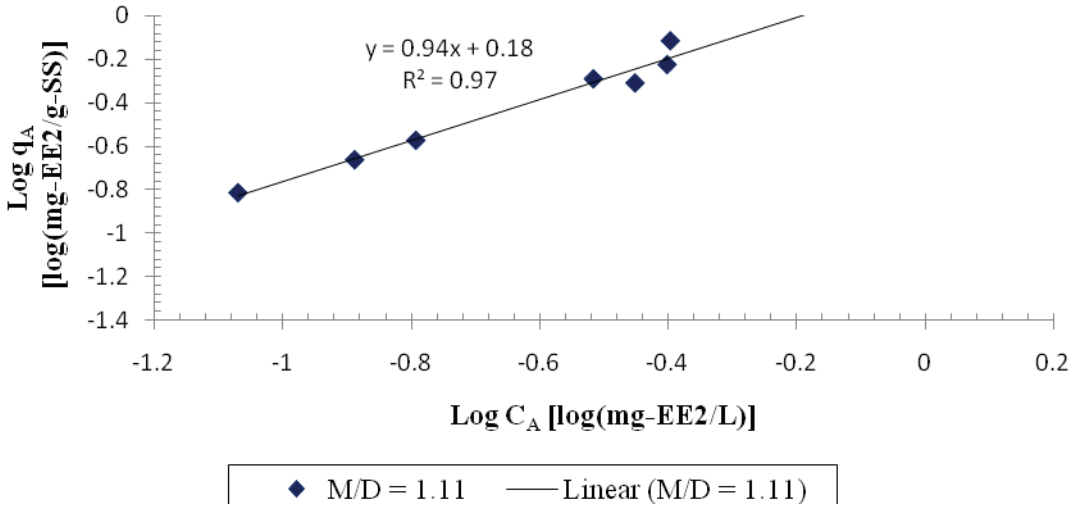


Figure 4.38. Freundlich isotherm to control biological activity by the presence of sodium azide. Isotherm performed with MNWWRP biosolids with an M/D ratio and cationic strength of 1.11 and 12.83 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

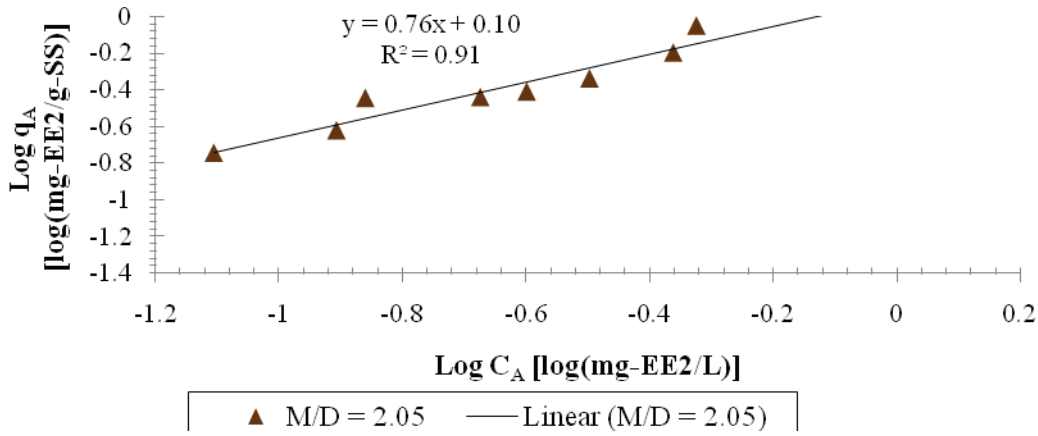


Figure 4.39. Freundlich isotherm to control biological activity by the presence of sodium azide. Isotherm performed with MNWWRP biosolids with an M/D ratio and cationic strength of 2.05 and 13.02 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

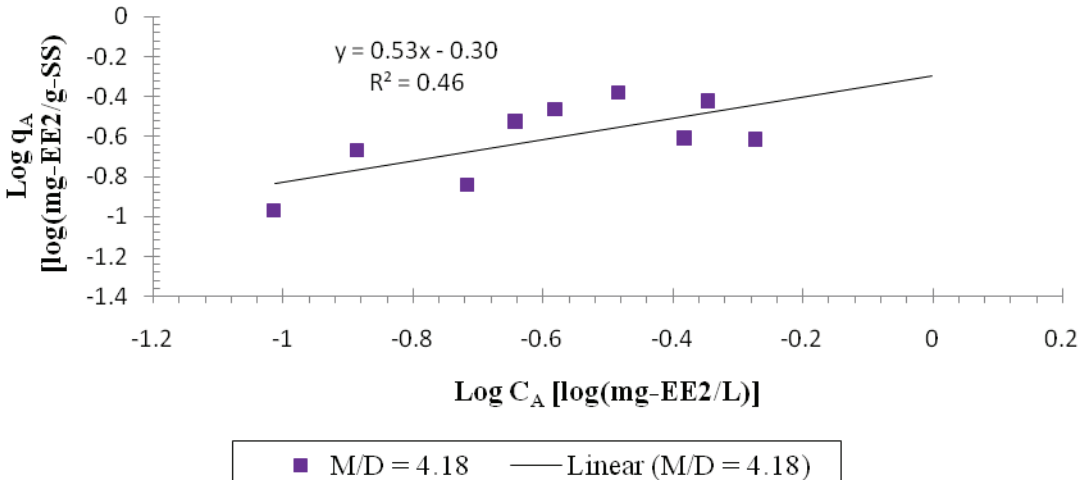


Figure 4.40. Freundlich isotherm to control biological activity by the presence of sodium azide. Isotherm performed with MNWWRP biosolids with an M/D ratio and cationic strength of 4.18 and 12.63 meq/L, respectively. The target M/D ratio and cationic strength were 4 and 12 meq/L, respectively.

Table 4.14. Paired *t* Test Results of the Isotherms with EE2 as the Target Compound, Sodium Azide to Control Biological Activity, MNWWRP as the Biosolid Source, and Target Cationic Strength of 12 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* Test	*t**	t_c
Low	1.11	12.83	Low-Med	1.335	1.943
Med	2.05	13.02	Low-High	2.712	1.943
High	4.18	12.63	Med-High	3.007	1.833

[a]Pairing each isotherm using q_A and M/D ratio.

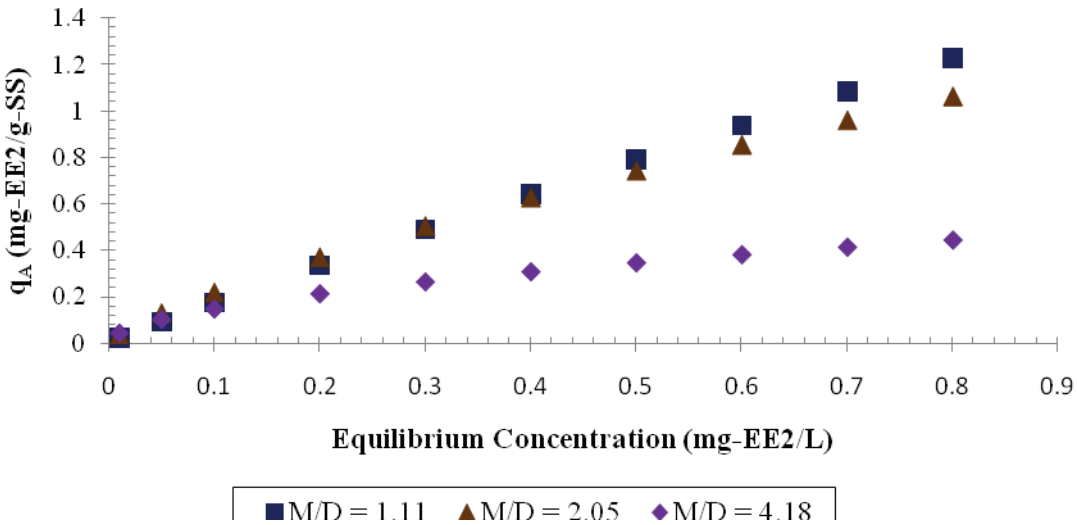


Figure 4.41. Combined Freundlich isotherm equations generated from the results of the isotherms with sodium azide to control biological activity, MNWWRP biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 12 meq/L.

4.2.5 Kyrene Biosolids at Target Cationic Strength of 12 Meq/L

Figures 4.42 to 4.44 contain the results of the isotherms performed at target M/D ratios of 1, 2, and 4 with a target cationic strength of 12 meq/L and with KWRF biosolids as the sorbate and KWRF permeate as the water source. Figure 4.42 contains the results for the isotherm with a measured M/D ratio of 1.02 and cationic strength of 11.22 meq/L. The intensity parameter for this isotherm is 0.92, and the capacity parameter is 1.38. Figure 4.43 has the results of the isotherm with a measured M/D ratio of 2.07 and cationic strength of 11.05 meq/L. The intensity parameter is 0.98, and the capacity parameter is 2.06. Figure 4.44 has the results for the isotherm with a measured M/D ratio of 4.02 and cationic strength of 11.14 meq/L. The intensity parameter is 0.82, and the capacity parameter is 1.55. The capacity and intensity parameters from the isotherms in this set were plotted using equation 4.2 (Figure 4.45). The paired *t* test for this set of isotherms is contained in Table 4.15. Although a statistically significant difference between the M/D ratios does exist, the trend is not consistent. The target M/D ratio of 2 has the highest sorption capacity, while the target M/D ratio of 1 has the lowest. The lack of a trend may be attributed to the poor settling characteristics of the KWRF sludge.

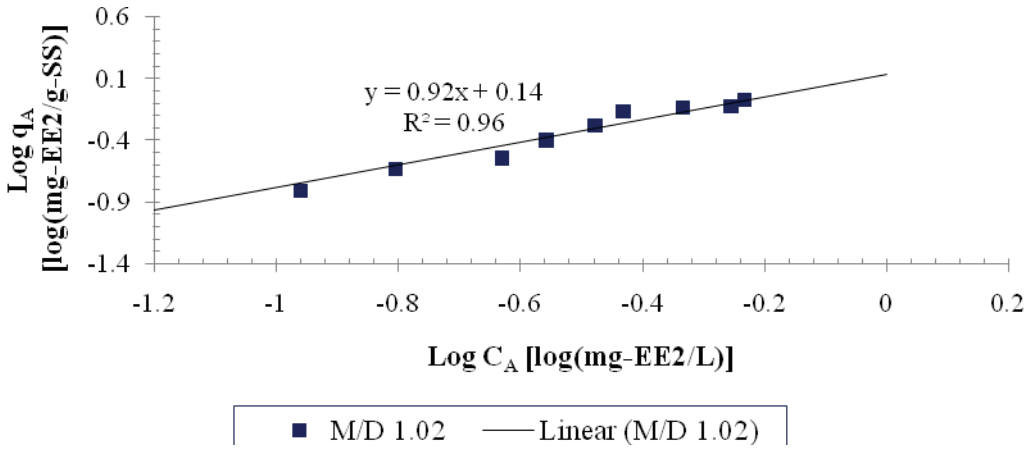


Figure 4.42. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 1.02 and 11.22 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

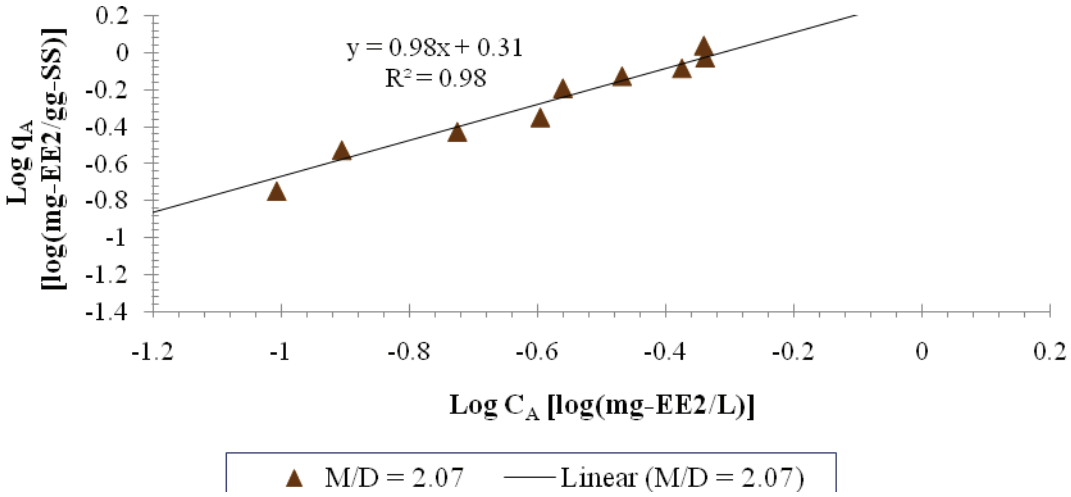


Figure 4.43. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 2.07 and 11.05 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

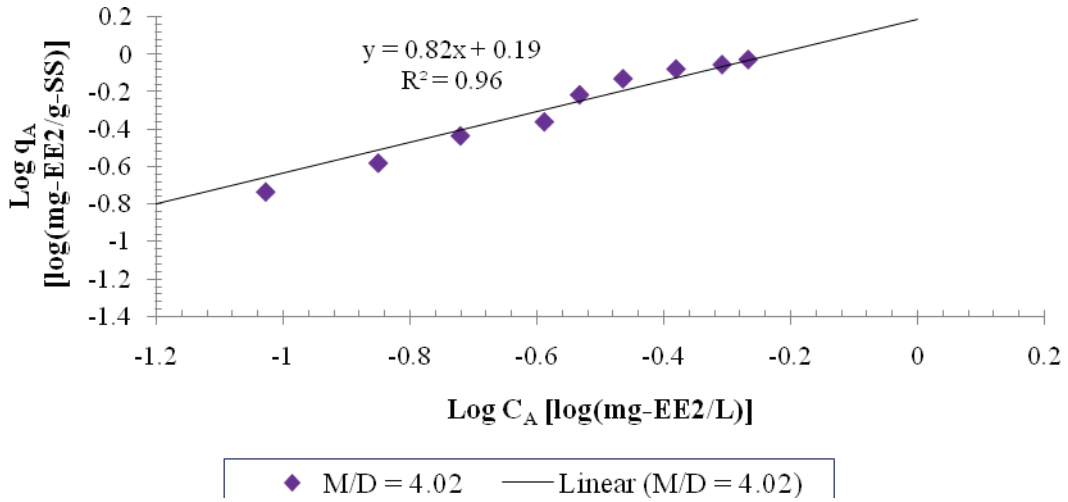


Figure 4.44. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 4.02 and 11.14 meq/L, respectively. The target M/D ratio and cationic strength were 4 and 12 meq/L, respectively.

Table 4.15. Paired *t* Test Results of the Isotherms with Bisphenol A as the Target Compound, KWRF as the Biosolid Source, and Target Cationic Strength of 12 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* test	*t**	t_c
Low	1.02	11.22	Low-Med	3.845	1.833
Med	2.07	11.05	Low-High	5.910	1.833
High	4.07	11.14	Med-High	1.686	1.833

[a]Pairing each isotherm using q_A and M/D ratio.

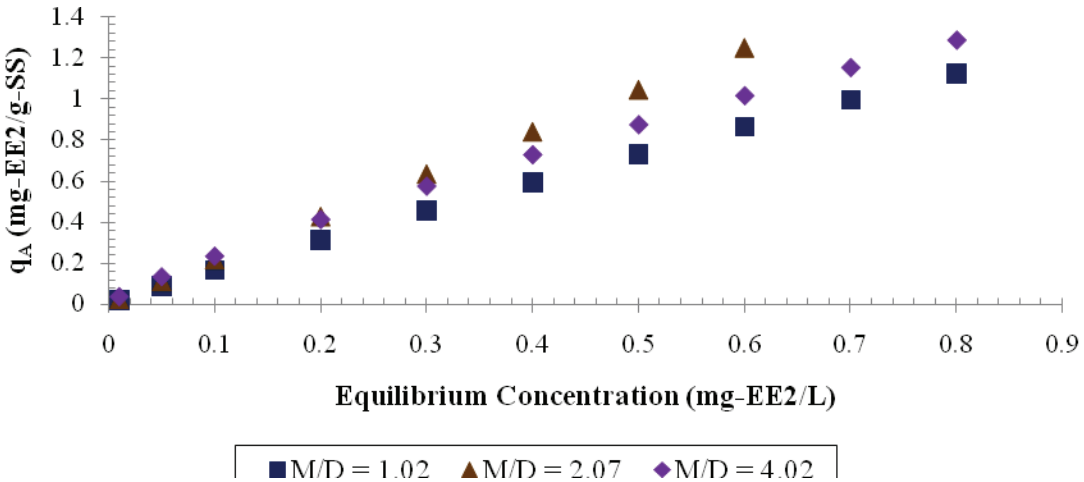


Figure 4.45. Combined Freundlich isotherm equations generated from the results of the isotherms with KWRF biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 12 meq/L.

The Kyrene sorption isotherm was performed a second time for EE2, and the results can be seen in Figures 4.46 to 4.49. The *t* test results are shown in Table 4.16. Although statistically significant, the results do not support the hypothesis of decreasing sorption with increasing M/D ratio.

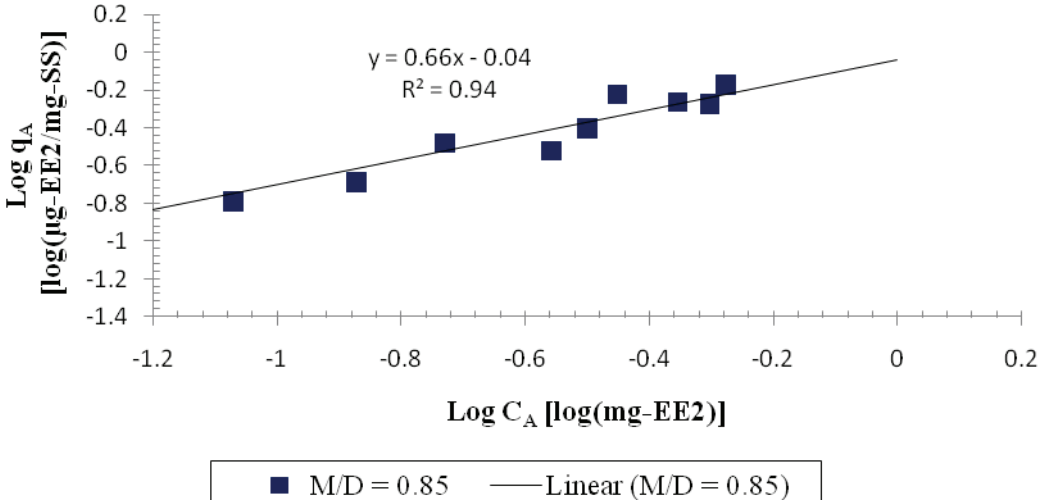


Figure 4.46. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 0.85 and 10.96meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

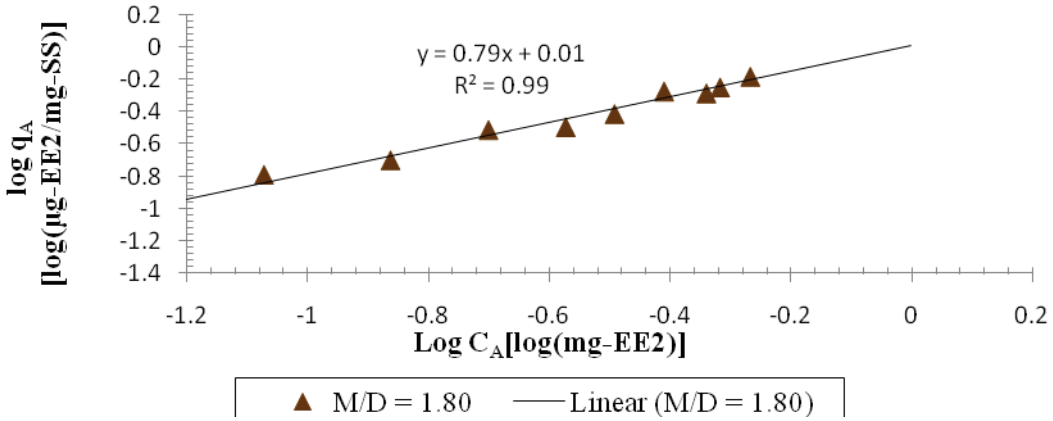


Figure 4.47. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 1.80 and 11.27 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

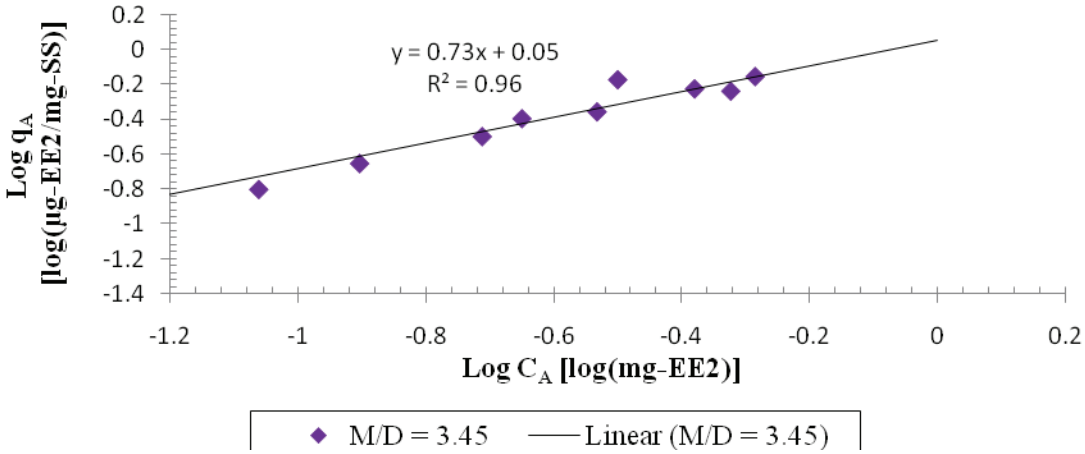


Figure 4.48. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 3.45 and 11.55 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

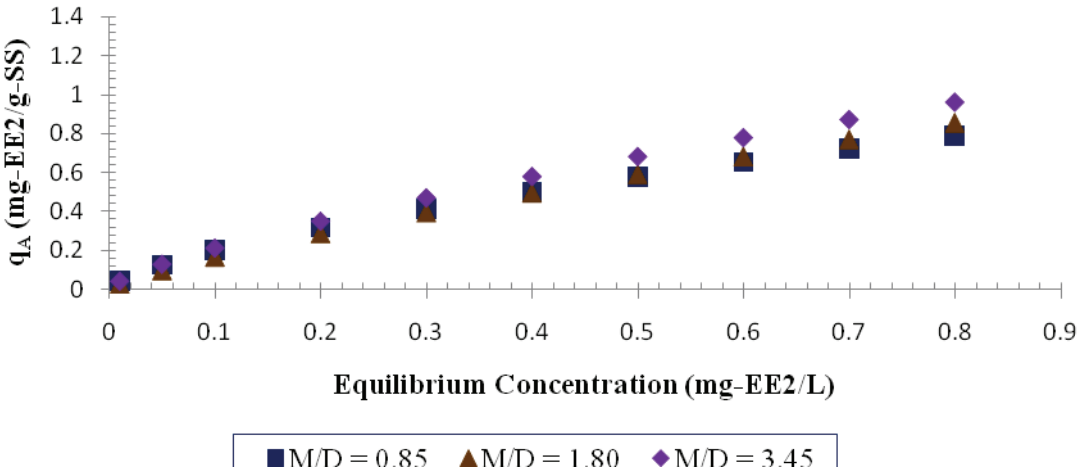


Figure 4.49. Combined Freundlich isotherm equations generated from the results of the isotherms with KWRF biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 12 meq/L.

Table 4.16. Paired *t* Test Results of the Isotherms with EE2 as the Target Compound, KWRF as the Biosolid Source, and Target Cationic Strength of 12 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* Test	*t**	t_c
Low	0.85	10.96	Low-Med	1.398	1.833
Med	1.8	11.27	Low-High	2.858	1.833
High	3.45	12.00	Med-High	3.255	1.833

[a]Pairing each isotherm using q_A and M/D ratio.

4.2.6 Target Cationic Strength = 20 Meq/L

Figure 4.50 contains the result for the isotherm that was performed with a target M/D ratio of 6 and target cationic strength of 20 meq/L. The measured M/D ratio was 6.57, and the cationic strength was 18.70 meq/L. The intensity and capacity parameters were 0.84 and 0.77, respectively.

Summary of EE2 Isotherms

Table 4.17 has the summary of the all isotherms performed with EE2. The only clear trend that is consistent with the hypothesis is with the sodium azide-inhibited tests. However, the high-cationic-strength samples with MNWWRP biosolids did have significantly lower sorption than did lower-ionic-strength samples, which disagrees with DLVO theory.

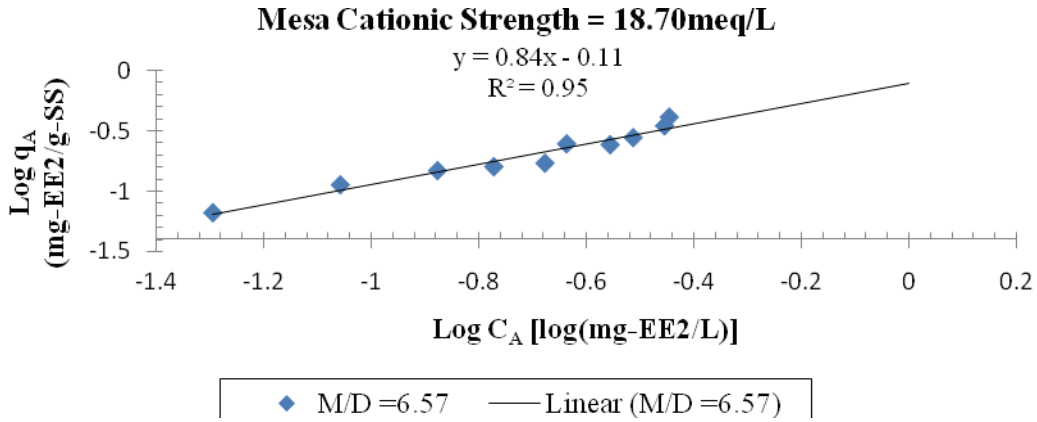


Figure 4.50. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 6.57 and 18.70 meq/L, respectively. The target M/D ratio and cationic strength were 6 and 20 meq/L, respectively.

Table 4.17. Summary of Isotherms with EE2

Source	M/D Ratio	Cationic Strength (meq/L)	1/n	K [mg/g][L/mg]$^{1/n}$	R^2 %	Data Points	1/n % Change from Low M/D	K % Change from Low M/D
MNWWRP	0.93	12.03	0.61	0.46	95	10	--	
MNWWRP	2.3	10.65	0.69	0.46	90	10	13	0
MNWWRP	3.96	10.11	0.49	0.38	81	10	-20	-17
MNWWRP	0.95	7.50	1.19	1.62	80	10	--	--
MNWWRP	1.93	7.34	1.36	1.38	96	10	14	-15
MNWWRP	4.00	7.50	1.31	1.74	95	10	10	7
MNWWRP	0.94	3.80	1.30	1.40	90	9	--	--
MNWWRP	1.80	3.83	1.14	1.61	92	10	-12	15
MNWWRP	5.39	5.21	1.25	1.91	95	10	-4	36
Azide-M	1.11	12.83	0.94	1.51	97	7	--	--
Azide-M	2.05	13.02	0.76	1.26	91	8	-19	-17
Azide-M	4.18	12.63	0.53	0.50	46	9	-44	-67
KWRF	0.85	10.96	0.66	0.91	94	10	--	--
KWRF	1.80	11.27	0.79	1.02	99	10	20	12
KWRF	3.45	12.00	0.73	1.13	96	10	11	24
KWRF	1.02	11.22	0.92	1.38	96	10	--	
KWRF	2.07	11.05	0.98	2.06	98	10	7	49
KWRF	4.02	11.14	0.82	1.55	96	10	-11	12
MNWWRP	6.57	18.70	0.84	0.77	95	10	--	--

4.2.7 Comparing Isotherms with Respect to Cationic Strength

All isotherms with EE2 as the target compound were compared to each other with respect to cationic strength. The target M/D ratio was held constant during comparison of isotherms that belonged to target cationic strength groups of 4, 8, and 12 meq/L. For example, all the isotherms with a target M/D ratio of 1 would be compared with different cation strengths, water matrices, and biosolids. Table 4.18 contains the results for the isotherms compared with a target M/D ratio of 1. Nine out of 10 isotherms showed a statistically significant difference between them. Table 4.19 contains the statistical comparisons between isotherms performed with a target M/D ratio of 2. This resulted in 9 out of 10 isotherms that showed a statistically significant difference. Similarly, there were 8 out of 10 statistically significantly different isotherms with the target M/D ratio of 4 as seen in Table 4.20. One trend that is apparent is that the sorption capacity decreases as the cation strength increases. Similar to the observation with bisphenol A, the sorption capacity for EE2 decreases as both the M/D ratio (1 to 4) and the cation strength increase (4 to 12 meq/L). Unlike what is found for bisphenol A, the sorption capacity for EE2 at the M/D ratio of 6 and at the cation strength of 20 meq/L is not the lowest sorption capacity.

Table 4.18. Isotherm Comparison with Target M/D Ratio of 1

Cationic Strength	t^*	t_c
12\8	3.534	1.833
12\4	2.842	1.833
8\4	3.376	1.860
12\12-KWRF	2.416	1.833
8\12-KWRF	3.414	1.833
4\12-KWRF	2.414	1.833
12\Azide	2.065	1.895
12-KWRF\Azide	0.156	1.895
8\Azide	2.729	1.895
4\Azide	1.787	1.895

Table 4.19. Isotherm Comparison with Target M/D Ratio of 2

Cationic Strength	t^*	t_c
12\8	3.102	1.833
12\4	3.417	1.833
8\4	3.842	1.860
12\12-KWRF	2.725	1.833
8\12-KWRF	2.860	1.833
4\KWRF	3.962	1.860
12\Azide	3.148	1.833
12-KWRF\Azide	1.478	1.833
8\Azide	1.580	1.833
4\Azide	2.817	1.860

Table 4.20. Isotherm Comparison with Target M/D Ratio of 4

Cationic Strength	t^*	t_c
12\8	3.220	1.833
12\4	3.802	1.833
8\4	1.242	1.833
12\12-KWRF	3.109	1.833
8\12-KWRF	2.881	1.833
4\12-KWRF	4.094	1.833
12\Azide	0.444	1.860
12-KWRF\Azide	2.155	1.860
8\Azide	2.597	1.860
4\Azide	3.112	1.860

4.3 ESTRIOL RESULTS

4.3.1 Target Cationic Strength = 12 Meq/L

Figures 4.51 to 4.53 contain the results of the isotherms performed with target M/D ratios of 1, 2, and 4 and cationic strength of 12 meq/L and MNWWRP biosolids. Figure 4.51 contains the results of the isotherm with a measured M/D ratio of 0.96 and cationic strength of 10.88 meq/L. The intensity parameter for this isotherm is 0.82, and the capacity parameter is 2.91. Figure 4.52 contains the results of the isotherm with a measured M/D ratio of 1.99 and cationic strength of 11.13 meq/L. The intensity parameter is 0.81, and the capacity parameter is 3.20. Figure 4.53 contains the results for the isotherm with a measured M/D ratio of 4.08 and cationic strength of 11.59 meq/L. The intensity parameter is 0.64, and the capacity parameter is 2.19. The capacity and intensity parameters from the isotherms in this set were plotted using equation 4.2 (Figure 4.54). The paired *t* test for this set of isotherms is contained in Table 4.21. There is a statistically significant difference between the high M/D ratio and the medium M/D ratio, with a clear decrease in sorption at the higher M/D ratio. However, there is no statistically significant difference between the low M/D ratio and the high M/D ratio. This is somewhat contrary to the hypothesis.

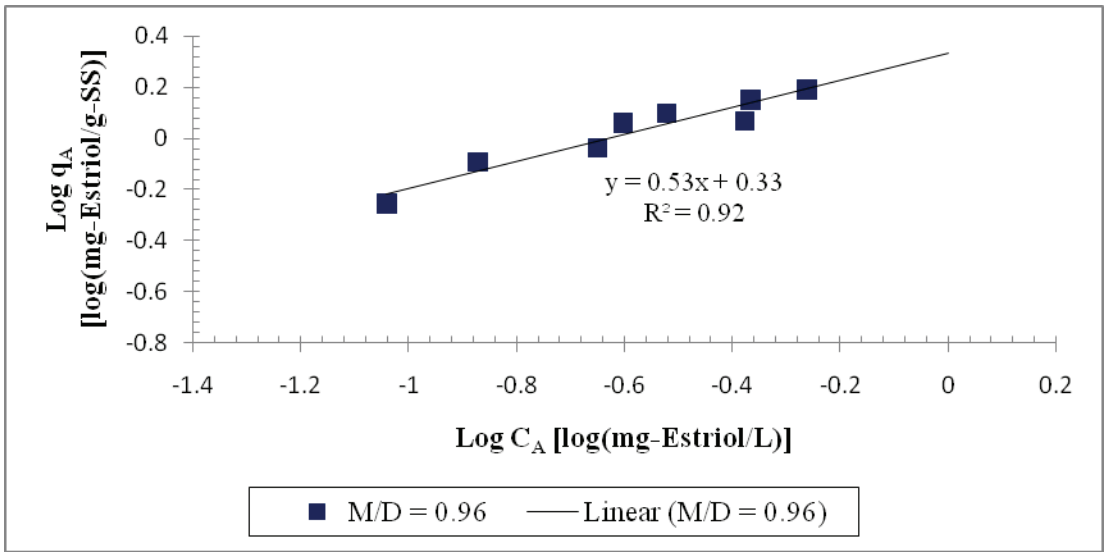


Figure 4.51. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 0.96 and 10.88 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

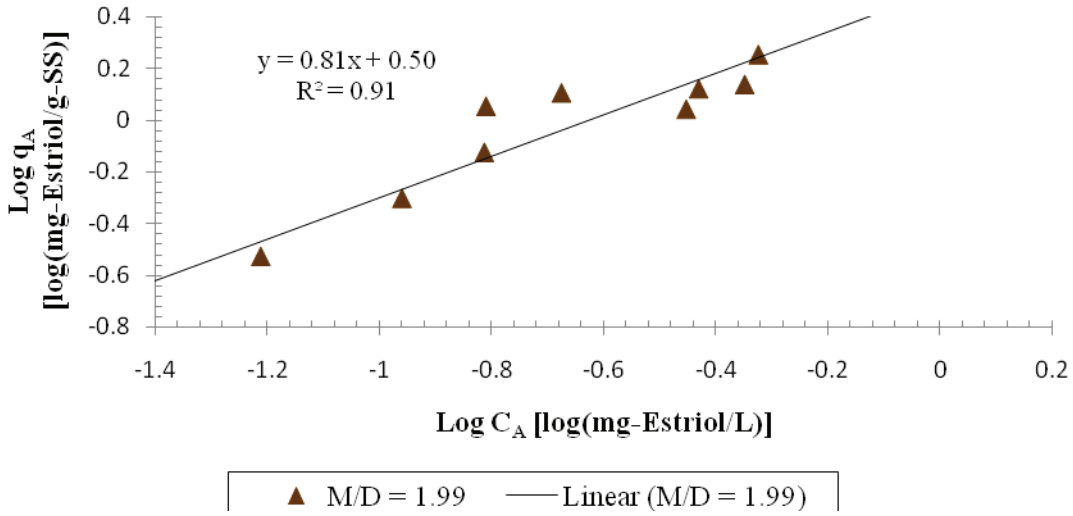


Figure 4.52. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 1.99 and 11.13 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

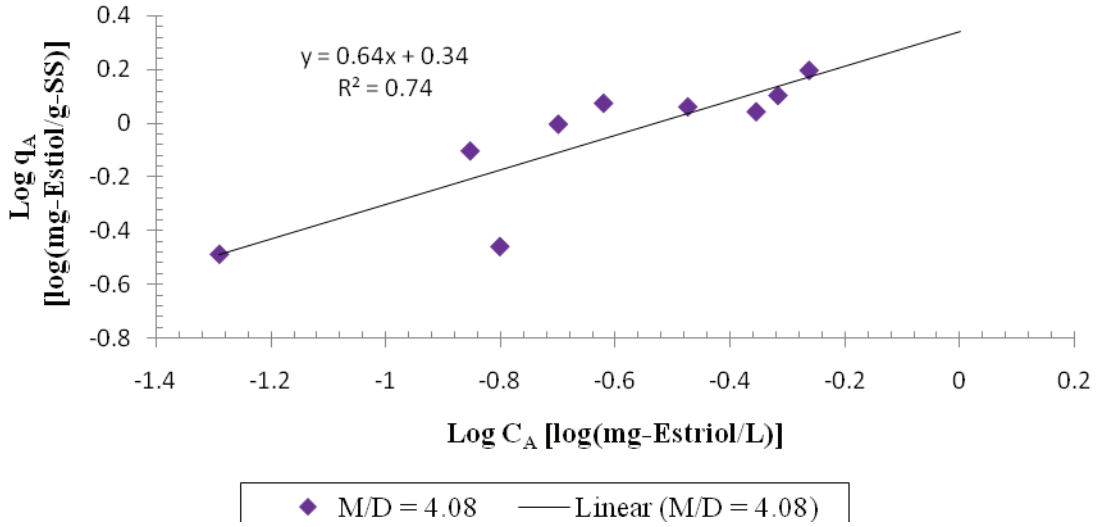


Figure 4.53. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 4.08 and 11.59 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

Table 4.21. Paired *t* Test Results of the Isotherms with Estriol as the Target Compound, MNWWRP as the Biosolid Source, and Target Cationic Strength of 12 meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* Test	*t**	t_c
Low	0.96	10.88	Low-Med	0.923	1.860
Med	1.99	11.13	Low-High	1.595	1.860
High	4.08	11.59	Med-High	2.465	1.860

[a]Pairing each isotherm using q_A and M/D ratio.

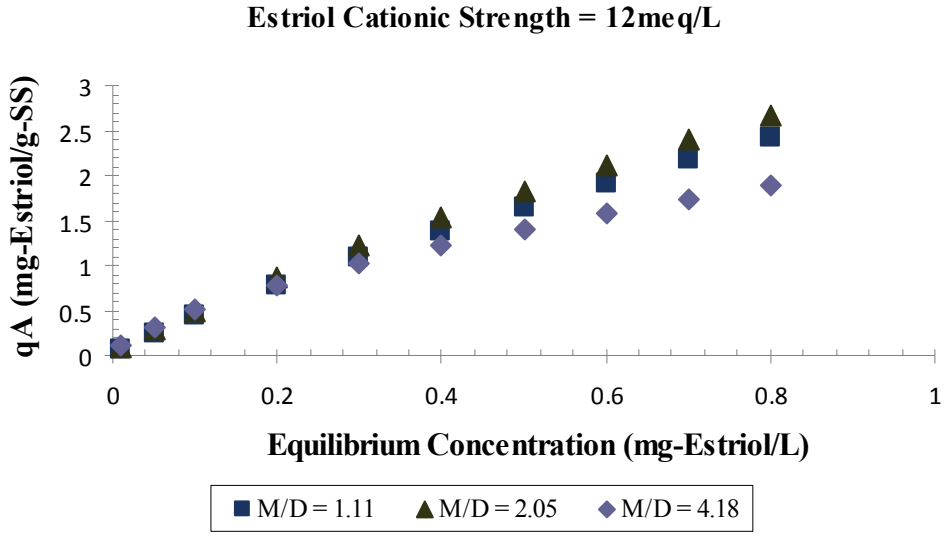


Figure 4.54. Combined Freundlich isotherm equations generated from the results of the isotherms with MNWWRP biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 12 meq/L.

4.3.2 Kyrene Biosolids at Target Cationic Strength of 12 Meq/L

Figures 4.55 to 4.57 contain the results of the isotherms performed with target M/D ratios of 1, 2, and 4 and cationic strength of 12 meq/L and KWRF biosolids. Figure 4.55 contains the results of the isotherm with a measured M/D ratio of 1.29 and cationic strength of 10.18 meq/L. The intensity parameter for this isotherm is 0.50, and the capacity parameter is 1.38. Figure 4.56 contains the results of the isotherm with a measured M/D ratio of 2.29 and cationic strength of 10.81 meq/L. The intensity parameter is 0.68, and the capacity parameter is 1.86. Figure 4.57 contains the results for the isotherm with a measured M/D ratio of 4.96 and cationic strength of 11.84 meq/L. The intensity parameter is 0.31, and the capacity parameter is 1.17. The capacity and intensity parameters from the isotherms in this set were plotted using equation 4.2 (Figure 4.58). The paired *t* test for this set of isotherms is contained in Table 4.22. Similar to the tests with NWWRP sludge, the M/D ratio of 2 had the highest sorption capacity.

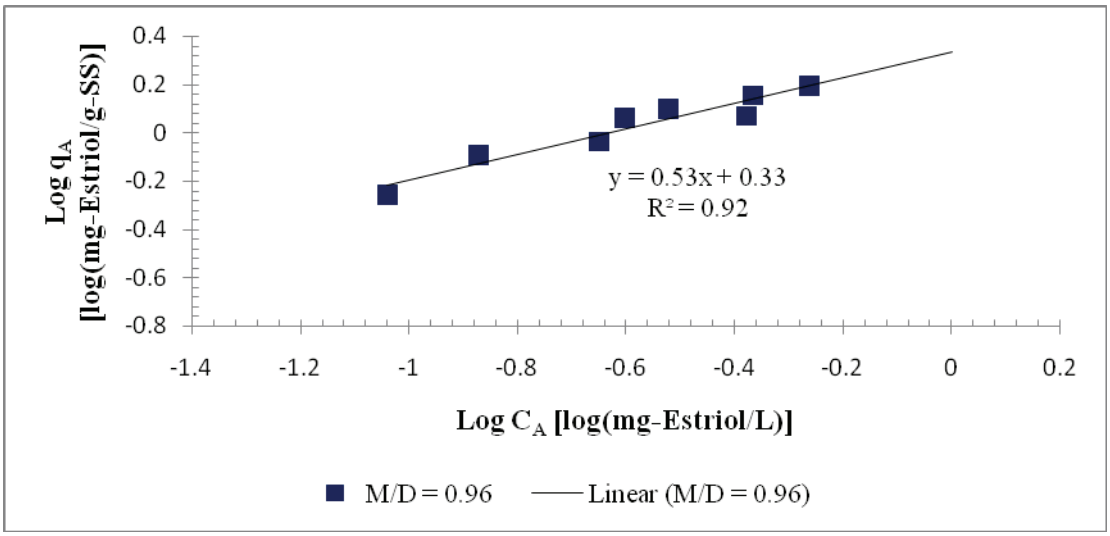


Figure 4.55. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 1.29 and 10.18 meq/L, respectively. The target M/D ratio and cationic strength were 1 and 12 meq/L, respectively.

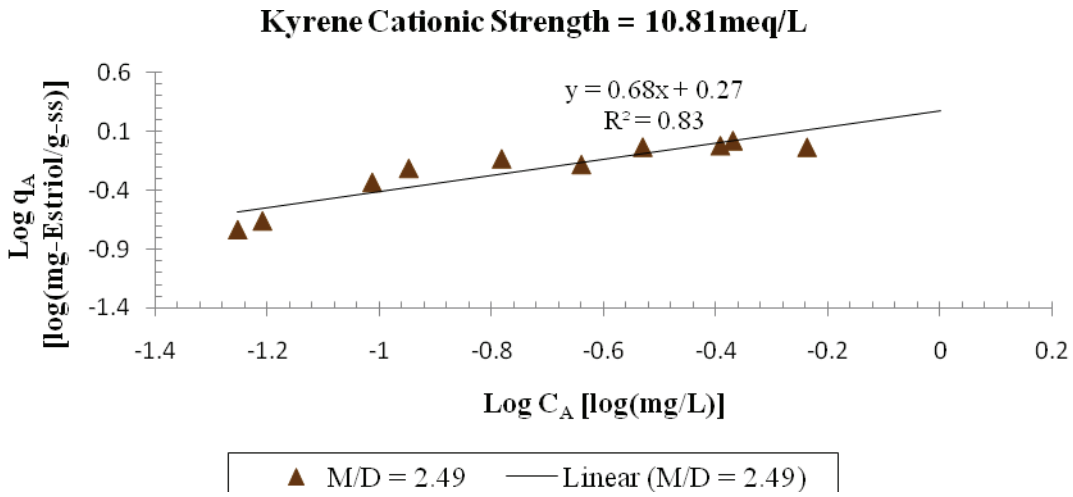


Figure 4.56. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 2.49 and 10.81 meq/L, respectively. The target M/D ratio and cationic strength were 2 and 12 meq/L, respectively.

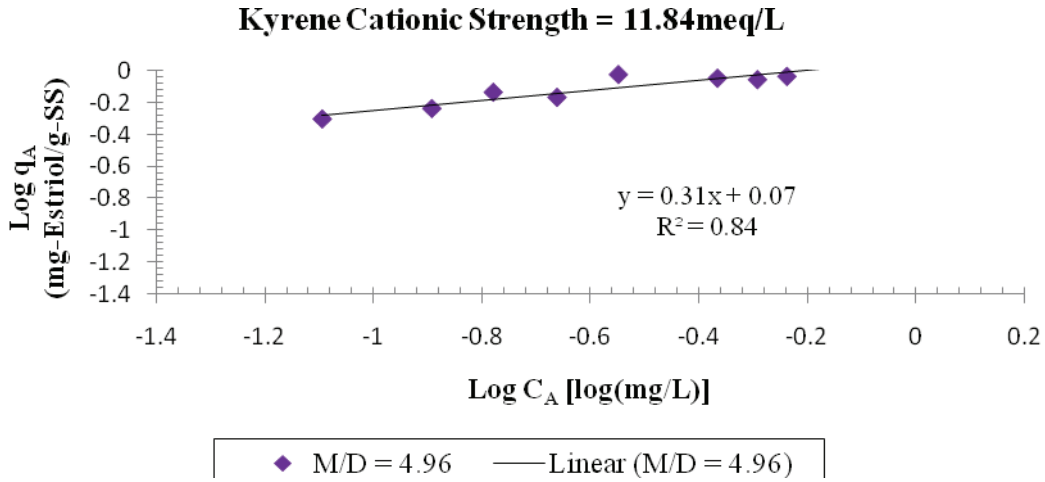


Figure 4.57. Freundlich isotherm performed with KWRF biosolids and M/D ratio and cationic strength of 4.96 and 11.84 meq/L, respectively. The target M/D ratio and cationic strength were 4 and 12 meq/L, respectively.

Table 4.22. Paired *t* Test Results of the Isotherms with Estriol as the Target Compound, KWRF as the Biosolid Source, and Target Cationic Strength of 12 Meq/L[a]

M/D	M/D Ratio	Cationic Strength (meq/L)	Paired *t* Test	*t**	t_c
Low	1.29	10.18	Low-Med	1.982	1.860
Med	2.49	10.81	Low-High	0.379	1.895
High	4.96	11.84	Med-High	1.048	1.860

[a]Pairing each isotherm using q_A and M/D ratio.

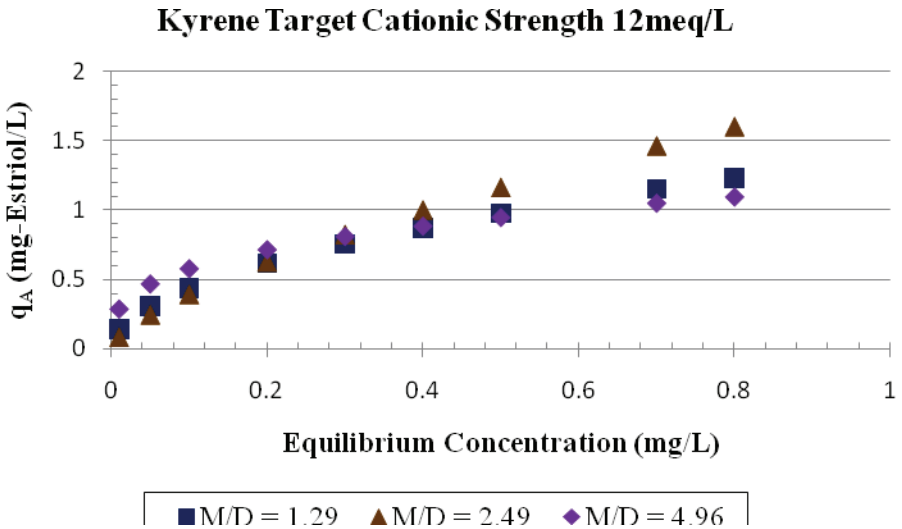


Figure 4.58. Combined Freundlich isotherm equations generated from the results of the isotherms with KWRF biosolids; target M/D ratios of 1, 2, and 4; and target cationic strength of 12 meq/L.

4.3.3 Target Cationic Strength = 20 Meq/L

Figure 4.59 contains the result for the isotherm that was performed with a target M/D ratio of 6 and a target cationic strength of 20 meq/L. The actual M/D ratio by AA was 6.90, and the cationic strength was 19.25 meq/L. The intensity and capacity parameters were 0.49 and 0.49, respectively.

Summary of Estriol Isotherms

Table 4.23 has the summary of the isotherms performed with estriol. Clearly, the KWRF sludge has a lower sorption capacity than does the MNWWRP sludge. Also, the high cationic strength and M/D ratio resulted in a significant decrease in sorption capacity as compared to other tests with MNWWRP sludge.

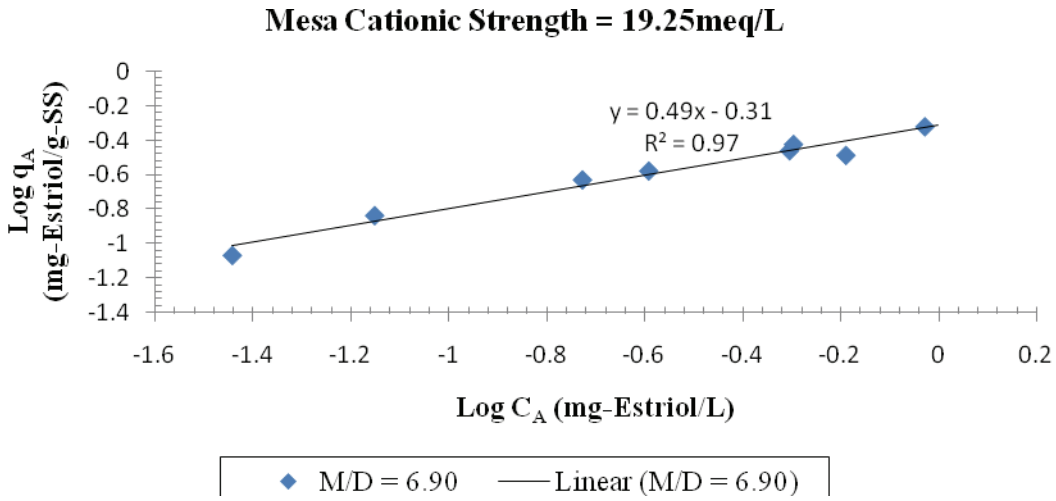


Figure 4.59. Freundlich isotherm performed with MNWWRP biosolids and M/D ratio and cationic strength of 6.90 and 19.25 meq/L, respectively. The target M/D ratio and cationic strength were 6 and 20 meq/L, respectively.

Table 4.23. Summary of Isotherms Performed with Estriol

Source	M/D Ratio	Cationic Strength (meq/L)	1/n	K [mg/g][L/mg]$^{1/n}$	R^2 %	No. of Data Points	1/n % Change from Low M/D	K % Change from Low M/D
MNWWRP	0.96	10.88	0.82	2.91	72	9	--	--
MNWWRP	1.99	11.13	0.81	3.20	91	10	-1	10
MNWWRP	4.08	11.59	0.64	2.19	74	9	-22	-25
KWRF	1.29	10.18	0.50	1.38	74	8	--	--
KWRF	2.49	10.81	0.64	1.86	83	10	28	35
KWRF	4.96	11.84	0.31	1.17	84	9	-38	-15
MNWWRP	6.90	19.25	0.49	0.49	97	8	--	--

4.3.4 Comparing Isotherms with Respect to Cationic Strength

The MNWWRP isotherm was compared to the KWRF isotherm while holding the M/D ratio constant. For example, the isotherms with a target M/D ratio of 1 would be compared to another with a different biosolid source. Table 4.24 contains the results for the isotherms compared with target M/D ratios of 1, 2, and 4. The KWRF biosolids consistently had lower sorption capacity than did the MNWWRP biosolids.

Table 4.24. Estriol Comparison between MNWWRP and KWRF Biosolids

M/D Ratio	t^*	t_c
1	3.504	1.895
2	3.386	1.833
4	3.372	1.860

4.4 COMBINED ISOTHERM AND KINETIC EXPERIMENTS

One isotherm was performed with all three target compounds together. This isotherm was performed at the highest target M/D ratio and cationic strength, which are 6 and 20 meq/L, respectively. A complication occurred in measuring the concentration of bisphenol A. This was because estriol was partially biodegraded into a compound that had a retention time similar to that of bisphenol A. Therefore, the peaks that were obtained from the estriol isotherm performed with a target M/D ratio of 6 and cationic strength of 20 meq/L were subtracted from the combined peaks of bisphenol A and the by-product of estriol to obtain the peak area for bisphenol A and, consequently, the concentration of bisphenol A for the combined experiment. Figures 4.60 to 4.62 contain the results of these isotherms. The intensity and capacity parameters obtained for EE2 were 0.63 and 0.38, respectively (Figure 4.60). The intensity and capacity parameters obtained for bisphenol A were 0.70 and 0.30, respectively (Figure 4.61). The intensity and capacity parameters obtained for estriol were 0.50 and 0.35, respectively (Figure 4.62). EE2 had the highest capacity parameter, followed by estriol and then by bisphenol A. EE2 was expected to have the highest capacity because it has the highest $\log K_{ow}$. When compared with the isotherms performed at the same cationic strength, there was a 51% reduction of capacity for EE2, a 29% reduction of capacity for estriol, and a 3% capacity increase for bisphenol A. It was expected that the capacity would drop for each of the target compounds; however, bisphenol A capacity increased 3%.

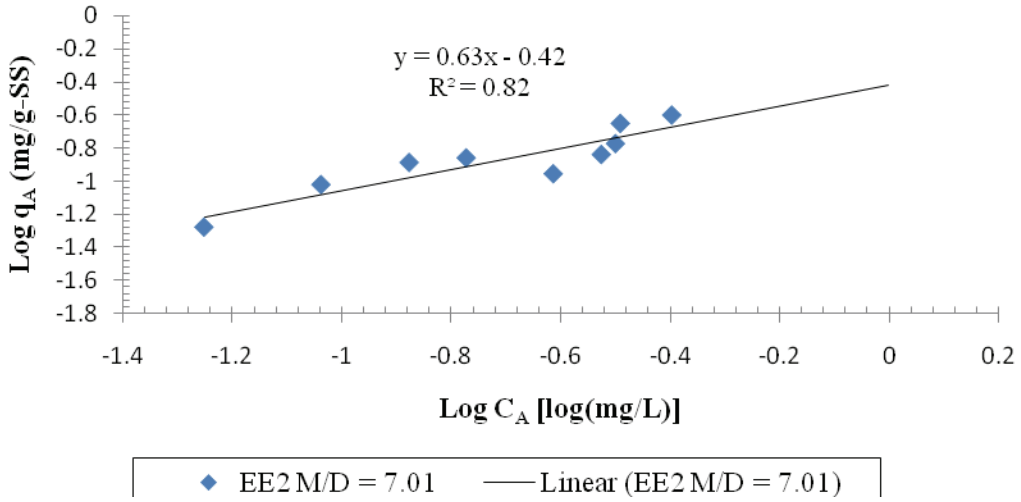


Figure 4.60. EE2 results from the combined isotherm that had an M/D ratio and cationic strength of 7.01 and 18.94 meq/L, respectively. The target M/D ratio and cationic strength were 6 and 20 meq/L, respectively.

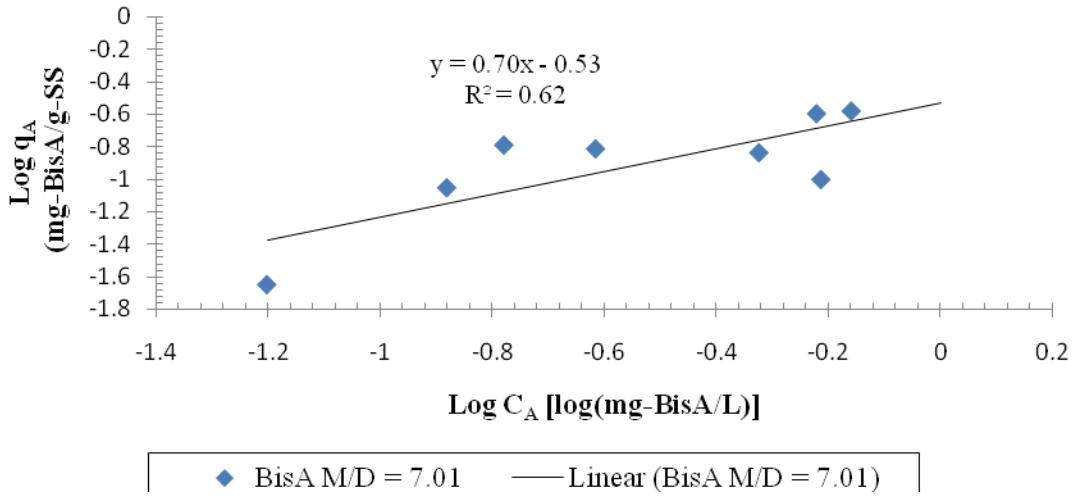


Figure 4.61. Bisphenol A results from the combined isotherm that had an M/D ratio and cationic strength of 7.01 and 18.94 meq/L, respectively. The target M/D ratio and cationic strength were 6 and 20 meq/L, respectively.

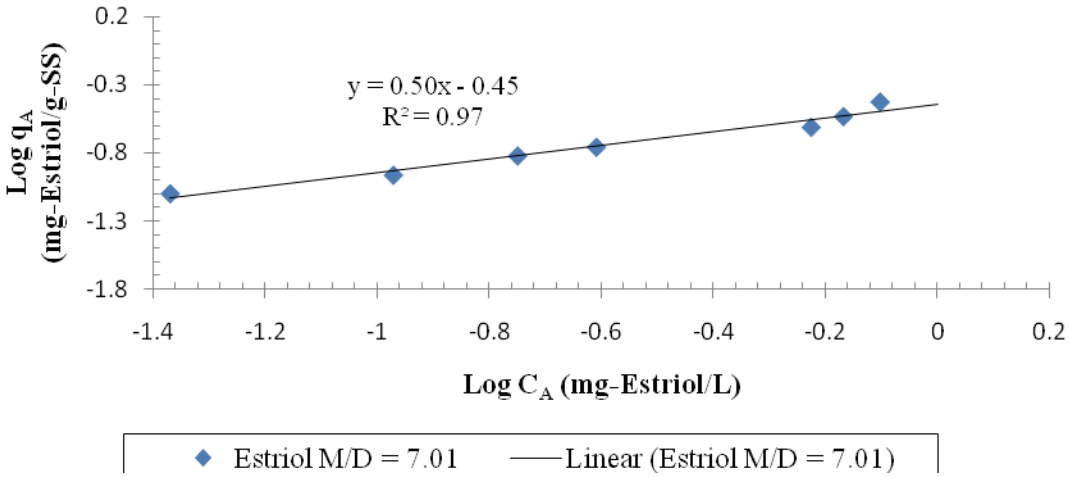


Figure 4.62. Estriol results from the combined isotherm that had an M/D ratio and cationic strength of 7.01 and 18.94 meq/L, respectively. The target M/D ratio and cationic strength were 6 and 20 meq/L, respectively.

Kinetic experiments were done to see if the 24-h period was long enough to obtain an equilibrium concentration. The kinetic experiments were done at a target M/D ratio of 4 and cationic strength of 12 meq/L. The first set of experiments involved bisphenol A and EE2 as the target compounds at the nominal initial concentration of 1000 µg/L and MNWWRP biosolids at a concentration of 333 mg/L. The solids were determined by the average of three volumes of the collected RAS as described in the experimental setup section of this report. The collection times were at each hour for the first 4 h and at the 24th h. These results are shown in Figure 4.63. A second set of experiments involved bisphenol A and EE2 as the target compounds with the nominal initial concentration of 1000 µg/L and MNWWRP biosolids at a concentration of 457 mg/L with collection times shown in Table 4.25. The results are shown in Figure 4.64. Both experiments show a rapid drop in concentration with equilibrium being reached by 24 h. However, the initial drop in concentration is below the equilibrium concentration, demonstrating an unexpected kinetic effect such as active transport. The rapid sorption could also be explained by a rapid sorption process from the water to the solids followed by a slow desorption process. This sorption–desorption phenomena may be due to competitive sorption where competing organic compounds such as soluble microbial products (SMPs) play an important role.

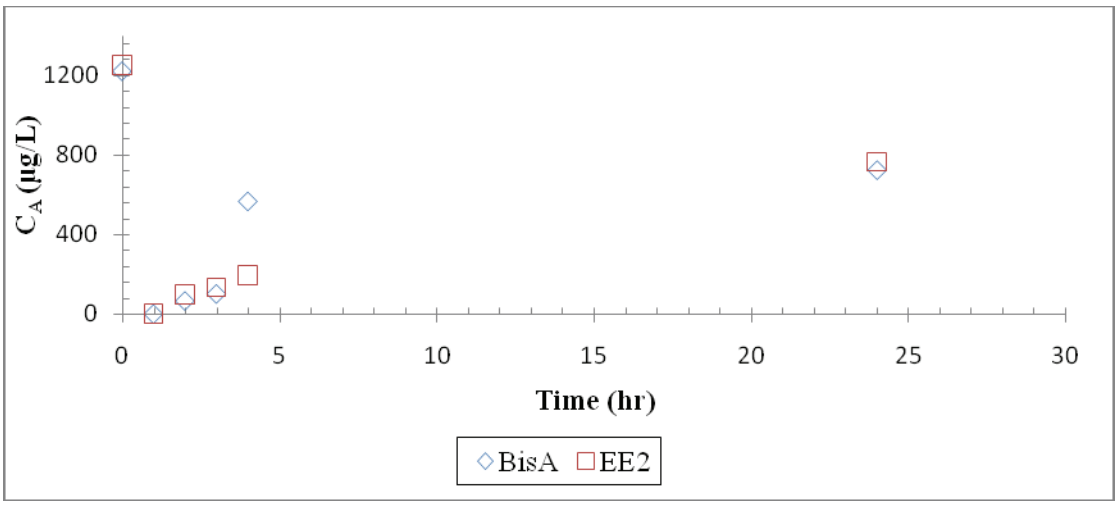


Figure 4.63. Kinetic experiment with bisphenol A and EE2 with 6 collection times.

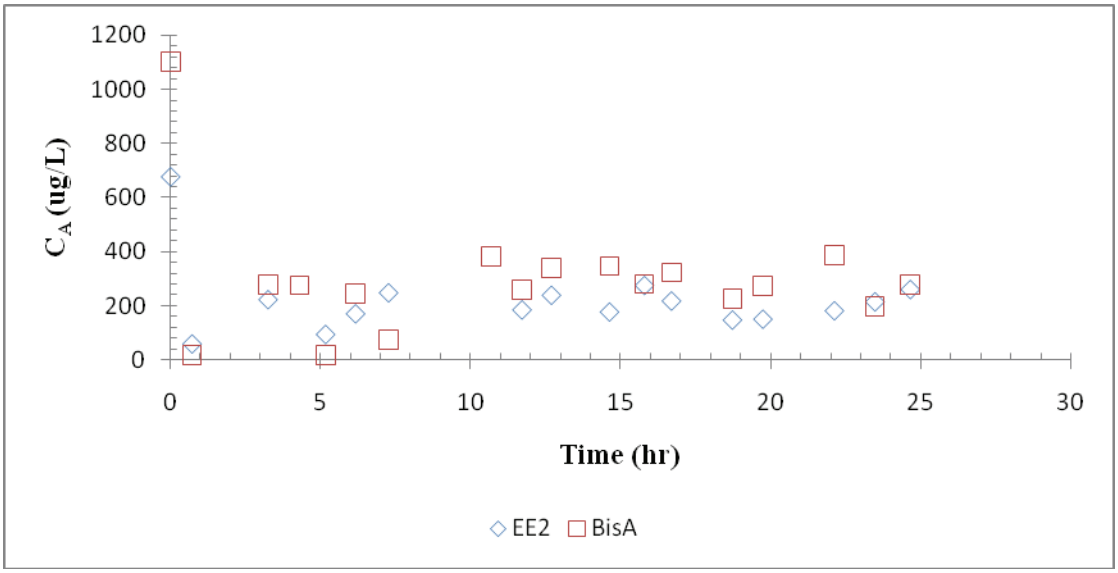


Figure 4.64. Kinetic isotherm with bisphenol A and EE2 with 21 collection times.

Table 4.25. Collection Times for the 2nd Kinetic Experiment

Collection	Time
Control and Initial Concentration	10.55 a.m.
1	11:33 a.m.
2	2:05 p.m.
3	3:08 p.m.
4	4:08 p.m.
5	5:05 p.m.
6	6:06 p.m.
7	9:32 p.m.
8	10:33 p.m.
9	11:32 p.m.
10	12:30 a.m.
11	1:28 a.m.
12	2:38 a.m.
13	3:32 a.m.
14	4:30 a.m.
15	5:34 a.m.
16	6:35 a.m.
17	8:03 a.m.
18	8:58 a.m.
19	10:32 a.m.
20 (includes controls)	11:30 a.m.

CHAPTER 5

EXPERIMENTAL DESIGN SEQUENCING BATCH REACTORS

5.1 REACTOR DESIGN

Three rectangular Plexiglas reactors (R1, R2, and R3) were designed to hold a working volume of 5 L (Figure 69). The reactors were seeded with 1 L of RAS collected from MNWWRP in a 20-L PE container. After the addition of RAS, 4 L of dechlorinated tap water was added to each reactor and each reactor was aerated with compressed air with a coarse stone diffuser. The air was humidified by bubbling the air though deionized water using a screw-tight humidifier with a plastic air diffuser to minimize the loss of water in each reactor and to trap oil that was in the air line from reaching the reactors. Each reactor was operated with a sludge age of 12 days by wasting 500 mL of SS 5 days a week.

Figure 5.1. Experimental setup of the sequencing batch reactors. R1 is on the left, R2 in the middle, and R3 on the right.

The reactors were operated as sequencing batch reactors by feeding each reactor with 3 L of synthetic feed on weekdays. After approximately 23 h of aeration, the aeration was turned off and the solids were settled for 30 min. Then 3 L of reactor supernatant was decanted from the reactors followed by feeding the reactors with 3 L of synthetic feed and aeration. DO was monitored and did not go under 4 mg/L during the feeding cycle, except when aeration stopped and solids were allowed to settle. The DO after settling for 30 min was between 0.5 and 0.0 mg/L.

5.2 FEED COMPOSITION

The first synthetic feed consisted of acetic acid as the electron donor and carbon source, ammonium as the nitrogen source, trace salts to provide essential minerals, and selected cations that consisted of sodium, calcium, and magnesium (Table 5.1). The trace salts were first dissolved in deionized water as shown in Table 5.2 and in a concentrated stock salt solution. These salts were diluted further as shown in Table 5.3 with the addition of phosphate, and the solution was labeled the trace stock salt solution. The cationic concentration of these salts was calculated to account for fewer than 10^{-3} meq of ions/L in the reactors and did not significantly affect the calculated M/D ratios.

The acetate feed was prepared by combining the compounds in Table 5.1 in a 2-L beaker and adding 800 mL of nanopure water. This solution was transferred to a 1-L volumetric flask, and nanopure water was added to fill the remaining volume up to 1 L. The acetate feed solution was transferred to a clear 1-L glass bottle and stored in the refrigerator at 4 ^{o}C. Ten milliliters of acetate feed was mixed with 3 L of nanopure water prior to transferring to the reactors during the feeding cycle. The resulting cationic composition was calculated to have 2 meq of Na^{+}/L, 1.5 meq of Ca^{2+}/L, and 0.5 meq of Mg^{2+}/L. The ammonium ion concentration was 12 mg of NH_4-N/L. The acetic acid had a final concentration of 200 mg/L.

Table 5.1. Acetate Feed Was Dissolved in 1 L, and 10 mL Was Added into a Feed Volume of 3 L

Substrate	Mass (g)
Glacial Acetic Acid	100
NH_4OH	13.75
$MgCl_2$–$6H_2O$	15.25
Na_2CO_3	31.8
$Ca(OH)_2$	16.65
Trace Salt Solution (150 mL)	--

Table 5.2. Stock Salt Solution in 1-L Volume

Stock Salt Solution Component	Mass (g)
$CoCl_2$–$6H_2O$	2.86
$CuCl_2$–$6H_2O$	2.05
$FeCl_3$	19.44
$ZnCl_2$	3.27
NH_4Mo–$7H_2O$	2.8

Table 5.3. Trace Salt Solution

Stock Trace Salt Solution	Mass (mg)
Stock Salt Solution (1 mL)	--
KH_2PO_4	27.2

After a few months of feeding of the reactors with this feed composition, the biomass bulked and would not settle below 3 L with an extended settling period. The biosolids were disposed of. The reactors were reseeded, and the feed was changed to allow for a more diverse population by adding more than one electron donor. Also, the feed concentration was increased to provide a food-to-mass ratio (F/M ratio) that is more consistent with AS systems that have good settling characteristics. The F/M ratio was below 0.1 with the acetate feed. The DOC results showed that the DOC reduction was between 200 and 300 mg/L. The second feed consisted of the acetate feed plus the addition of glucose and glutamic acid to the feed with concentrations of 600 and 400 mg/L, respectively (Table 5.4). The biomass depleted again to below 300 mg/L, and the reactors needed to be reseeded a third time as the pH dropped to below 3. Biomass depletion was thought to have been due to a trace nutrient deficiency, and yeast extract (10 mg/L) was added to the feed. The acetate feed was changed as well to add less acetic acid by adding the acetate salts as shown in Table 5.5; however, this did not solve the low-pH problem. The acetate feed was changed by removing glacial acetic acid entirely and just using the acetate salts as shown in Table 5.6 to provide the acetate electron donor substrate. The ammonium source was changed to ammonium chloride because no acid was being added with the synthetic feed. The ammonium chloride was kept separate from the acetic acid feed stock and was stored at a concentration of 55 g/L, and only 5 mL was added per 3 L of total feed. The ammonium concentration added was 14 mg of N/L.

Table 5.4. Glucose and Glutamic Acid Feed Were Dissolved in 1 L Separately, and 10 mL of Each Was Added into a Feed Volume of 3 L

Compound	Mass (g)
Anhydrous 96-α-D-Glucose	300
Monosodium Glutamic Acid Monohydrate	254

Table 5.5. Acetate Feed Was Dissolved in 1 L, and 10 mL Was Added into a Feed Volume of 3 L

Compound	Mass (g)
Glacial Acetic Acid	28.79
Sodium Acetate	49.22
Magnesium Acetate Tetrahydrate	16.85
Calcium Acetate–Hydrate	35.59
Stock Salt Solution (150 mL)	--

Table 5.6. Acetate Feed Was Dissolved in 1 L, and 10 mL Was Added into a Feed Volume of 3 L

Compound	Mass (g)
Sodium Acetate	49.22
Magnesium Acetate Tetrahydrate	16.85
Calcium Acetate–Hydrate	35.59
Stock Salt Solution (150 mL)	--

5.3 M/D RATIO

The initial start-up of the reactor with the first seeding was designed to have an M/D ratio of 1 with a cationic strength of 4 meq/L. This altered with the changing of the synthetic feed. The third seeding of the reactors had a design M/D ratio of 3.1 with a design cationic strength of 8.2 meq/L.

5.4 STORAGE AND ADDITION OF TARGET COMPOUNDS

The target compounds fed to the batch reactors were bisphenol A and EE2. Stock solutions of 10^{-2} M bisphenol A and EE2 were made by dissolving these compounds in methanol. These solutions were stored in the refrigerator at 4 ^{o}C.

Before addition of either bisphenol A or EE2 into the reactors, the stock solutions were removed from the refrigerator and allowed to warm to room temperature. Bisphenol A was the first target compound that was fed to the reactors. The concentration of bisphenol A in the 3 L of synthetic feed was 167 µg/L. This created a 100-µg/L nominal concentration of bisphenol A in each reactor when dilution by the residual volume in the reactor was considered. To obtain the desired concentration of 167 µg of bisphenol A/L in the feed solution, 219 µL of the stock 10^{-2} M bisphenol A was added to the synthetic feed. The synthetic feed was stirred with a magnetic bar for several minutes prior to sampling. A 1-mL sample of the synthetic feed for each reactor was taken every feed day and placed in an autosampler vial and stored in the refrigerator until analysis. After sampling, the synthetic feed was added to the reactors. EE2 was spiked into the reactor feed in a similar manner by adding 169 µL of the stock solution into the feed.

Bisphenol A was fed into the reactors for a period of 22 feed days. The average concentration of SS in the reactors during this period were 1130 mg/L, 1300 mg/L, and 1500 mg/L for R1, R2, and R3, respectively. Shortly after the final addition of bisphenol A to the reactors, each reactor developed a significant amount of biofilm that would not stay suspended with aeration. The SS mass was removed from the reactors, the biofilm was discarded, and the SS were added back to the reactors. This caused a drop in the concentration of SS to 400 mg/L.

After bisphenol A addition ceased, a period of 8 weeks was allowed to increase the SS in the reactor to above 1000 mg/L. During this period, solids were not wasted to allow for increased mass in the reactors. When the solids exceeded 1000 mg/L in each reactor, EE2 was added to the reactors and wasting of SS started again. EE2 was added to each reactor for a period of 26 feed days. The average concentrations of SS in the reactors in this period were 840, 1250, and 1000 mg/L for R1, R2, and R3, respectively.

5.5 FILTERING AND STORAGE OF SAMPLES

Effluent was collected each feed day in a 30-mL beaker. Ten milliliters of effluent from each reactor was filtered first with a glass fiber filter (Whatman GF/A or GF/C). The filtrate was transferred back to the beaker, and the vacuum flask was rinsed with nanopure water. This was followed by a second filtration of the effluent with a 0.45-µm-pore-size cellulose membrane filter. The filtrate was transferred to a clean 30-mL beaker, and a 1-mL sample was placed in an autosampler vial and stored in the refrigerator until analysis by HPLC with fluorescence detection. Analysis by HPLC occurred within 2 weeks of storage.

5.6 MASS BALANCE

A mass balance was used to determine the mass of the target compound sorbed on the solids and the mass accumulated in the system. The following set of equations was used to determine the mass balance of the reactors. Because the target compounds were assumed not to be biodegraded, the mass change due to reaction is not included in the mass balance.

Mass In – Mass Out – ~~Mass Reaction~~ = Mass Accumulated =
Mass in Residual Liquid + Mass Sorbed (5.1)

Mass Sorbed = Mass In – Mass out – Mass in residual liquid (5.2)

The 1st day of accumulation in the reactor is shown by equation 5.3, and the mass sorbed is shown in equation 5.4.

$$C_{in,1}V_{in,1} - C_{ef,1}V_{ef,1} = C_{ef,1}V_{res,1} + C_{S,1}M_{SS,1} = \text{Mass Accumulated} \quad (5.3)$$

$$C_{in,1}V_{in,1} - C_{ef,1}V_{ef,1} - C_{ef,1}V_{res,1} = C_{S,1}M_{SS,1} = \text{Mass Sorbed} \quad (5.4)$$

C_{in} is the influent concentration [µg/L], V_{in} is the influent volume [L], C_{ef} is the effluent concentration [µg/L], V_{ef} is the effluent volume [L], V_{res} is the residual volume in reactor [L], C_{SS} is the sorbed concentration [µg/g], M_{SS} is the mass of SS in the reactor [g], and the numeric subscript represents the feed day.

The mass out on subsequent days must include the mass that was sorbed onto the solids that were removed from each reactor. Assuming a complete mixed reactor with 500 mL of SS being removed from the 5-L volume of the reactor, 10% of the solids were removed every feed day. The mass balance for subsequent days must include the mass that accumulated the 1st day as well as the mass that was wasted with the solids leaving the reactor. Thus, equation 5.5 is obtained for the mass accumulated on the 2nd day. The mass sorbed on the 2nd day is shown in equation 5.6.

$$C_{ef,1}V_{res,1} + C_{S,1}M_{SS,1} + C_{in,2}V_{in,2} - C_{ef,2}V_{ef,2} - 0.1C_{S,1}M_{SS,1} = C_{ef,2}V_{res,2} + C_{S,2}M_{SS,2} \quad (5.5)$$

$$C_{ef,1}V_{res,1} + C_{S,1}M_{SS,1} + C_{in,2}V_{in,2} - C_{ef,2}V_{ef,2} - 0.1C_{S,1}M_{SS,1} - C_{ef,2}V_{res,2} = C_{S,2}M_{SS,2} \quad (5.6)$$

This pattern will continue, and the summation of mass accumulation is shown in equation 5.7. Then the summation for the mass sorbed follows the same pattern and is shown in equation 5.8.

$$\Sigma C_{in,i}V_{in,i} - C_{ef,i}V_{ef,i} - 0.1C_{SS,i-1}M_{SS,i-1} = \text{Mass Accumulated} = C_{ef,i}V_{res,i} + C_{SS,i}M_{SS,I} \quad (5.7)$$

$$\Sigma\, C_{in,i}V_{in,i} - C_{ef,i}V_{ef,i} - 0.1C_{SS,i-1}M_{SS,i-1} - C_{ef,i}V_{res,i} = \text{Mass Sorbed} = C_{SS,i}M_{SS,i} \quad (5.8)$$

The subscript "i" represents the feed day.

CHAPTER 6

SEQUENCING BATCH REACTOR RESULTS

6.1 REACTOR pH, SVI, SS, DOC, N-NH_4, AND SALTS

6.1.1 pH

The pH was monitored daily on each reactor daily after the 24-h aeration period. The pH was generally between 7.5 and 8.5 as shown in Figure 6.1. During one period, the pH was seen to drop to 4. It was during this period that 1 N NaOH was used to raise the pH above 7 and pH paper was used to determine the impact of NaOH addition. Tap water was added to reactor R1, which had the most persistent pH problem. It was determined that glacial acetic acid should be removed from the synthetic feed, and only the acetate salts were used to prevent any further pH problems.

The pH of the reactors was periodically monitored just after feeding. It ranged from between 6 and 7. The effluent pH range was between 7.5 and 8.5. The pH of the reactor may have changed because of the activity of the biomass reducing the electron donors to inorganic carbon. This pH change may be due to insufficient buffer in the synthetic feed.

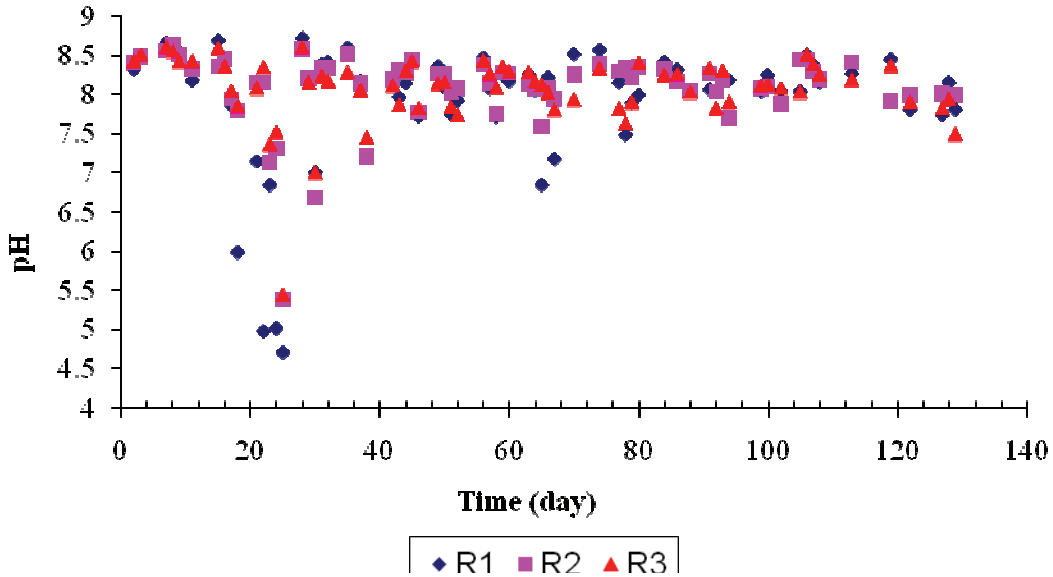


Figure 6.1. pH of the reactors starting at the third seeding and continuing throughout the use of the reactors.

6.1.2 SVI and SS

SVI and SS were monitored weekly. Initially, the SVI was below 100, and this lasted 35 days for R1, 40 days for R3, and 50 days for R2; however, as the SS decreased, the SVI dramatically increased (Figure 6.2 and Figure 6.3). The average SVI for the period that

bisphenol A was added to the feed was 79, 64, and 88 mL/g for R1, R2, and R3, respectively. The average SVI during the period that EE2 was added to the feed was 156, 132, and 171 mL/g for R1, R2, and R3, respectively.

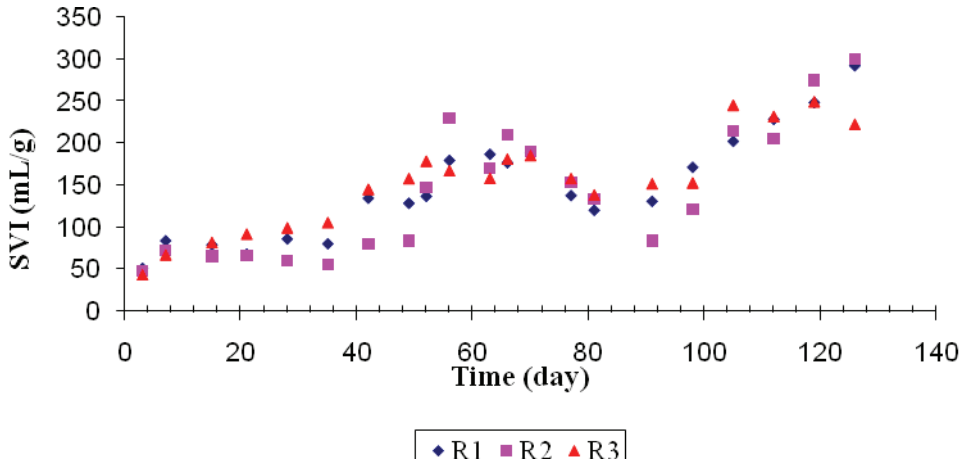


Figure 6.2. SVI of each reactor starting at the third seeding and continuing throughout the use of the reactors.

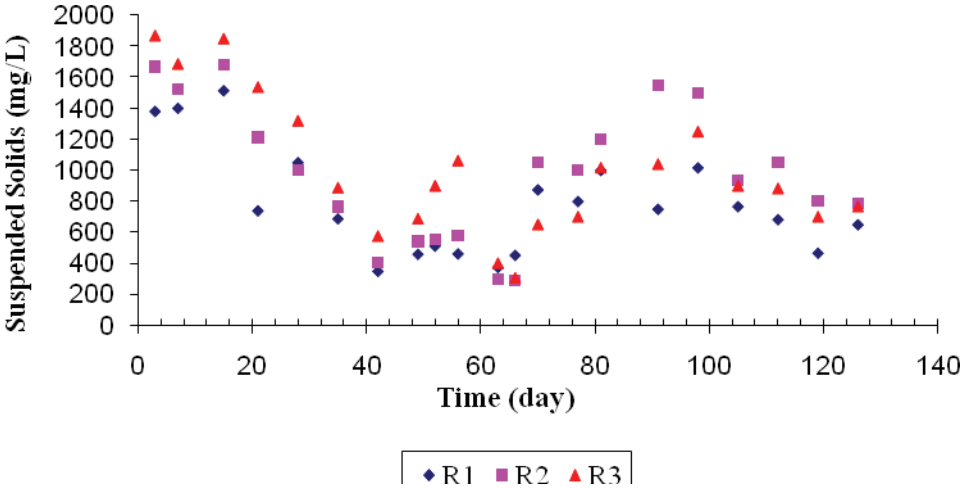


Figure 6.3. SS of each reactor starting at the third seeding and continuing throughout the use of the reactors.

6.1.3 DOC

The effluent DOC was monitored weekly. The electron donors glucose, glutamic acid, and acetate had a theoretical DOC concentration of 800 mg of DOC/L. Initially, the DOC was reduced from its theoretical value of 800 mg/L to below 10 mg/L (Figure 6.4). This occurred for the first 20 days for R2 and R3. Then the effluent DOC ranged between 100 and 550 mg/L (Figure 6.4) for all reactors. The influent DOC was monitored biweekly, and it ranged between 460 and 800 mg/L. Generally, the DOC decreased approximately 200 to 300 mg/L from the influent DOC and the effluent DOC in each reactor after the initial start-up period.

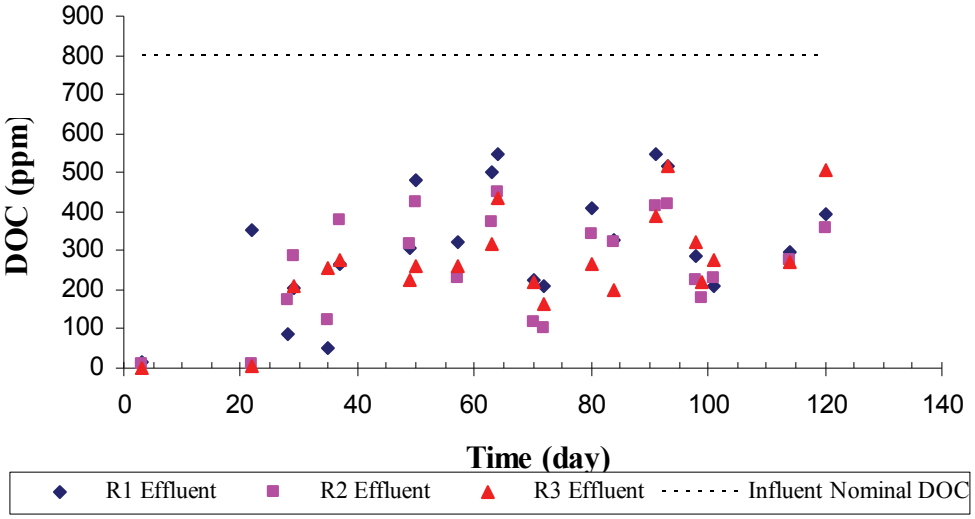


Figure 6.4. DOC in each reactor starting at the third seeding and continuing throughout the use of the reactors.

6.1.4 Ammonium

The effluent ammonium concentration was measured once during the time that bisphenol A was spiked into the reactors. The sample was taken during the last week that bisphenol A was spiked. The ammonium concentration was 36.7, 35.5, and 35.5 mg of N-NH_4/L for R1, R2, and R3, respectively, which results in an increase of the monovalent cations by approximately 2.6 meq/L. The increase in ammonium ion was from the degradation of glutamic acid.

The ammonium concentration was measured twice during the time that EE2 was spiked into the reactors. The average ammonium concentration was 10.4, 13.9, and 15.8 mg-N-NH_4/L for R1, R2, and R3, respectively. The lower ammonium concentration was achieved by adding a lower volume of ammonium stock to the feed.

6.1.5 Salts

Sodium, magnesium, and calcium in the reactors were analyzed only once during the time that bisphenol A was spiked in the reactor (Table 6.1). The M/D ratios were 3.75, 2.03, and

2.08, and the cationic strengths were 8.20, 6.10, and 6.24 meq/L for R1, R2, and R3, respectively (Table 6.2).

Table 6.1. Cationic Composition of R1, R2, and R3 During the Time Bisphenol A Was Spiked in Reactors

Findings for:											
Sodium (meq/L)			Calcium (meq/L)			Magnesium (meq/L)			Avg. N-NH_4 (meq/L)		
R1	R2	R3	R1	R2	R3	R1	R2	R3	R1	R2	R3
6.48	4.09	4.2	1.3	1.55	1.55	0.48	0.46	0.47	2.62	2.5	2.5

Table 6.2. M/D Ratio and Cationic Strength during the Time Bisphenol A Was Spiked in Reactors

Findings for:							
M/D Ratio of:			Cationic Strength (meq/L)			Nominal M/D	Nominal Cationic Strength (meq/L)
R1	R2	R3	R1	R2	R3		
5.26	3.28	3.33	11	8.6	8.74	3.75	9.49

Sodium, magnesium, and calcium in the reactors were analyzed weekly during the time that EE2 was spiked in the reactor (Table 6.3). The average M/D ratios were 2.94, 2.76, and 2.73, and the average cationic strengths were 6.85, 6.97, and 6.76 meq/L for R1, R2, and R3, respectively (Table 6.4).

Table 6.3. Cationic Composition of R1, R2, and R3 in Meq/L

Findings for:											
Sodium (meq/L)			Calcium (meq/L)			Magnesium (meq/L)			Avg. N-NH_4 (meq/L)		
R1	R2	R3	R1	R2	R3	R1	R2	R3	R1	R2	R3
5.57	5.87	5.61	1.20	1.55	1.50	0.53	0.56	0.53	0.74	1.00	1.13
4.87	4.48	4.43	1.30	1.35	1.30	0.40	0.39	0.37	0.74	1.00	1.13
5.00	4.39	4.30	1.25	1.35	1.30	0.43	0.39	0.38	0.74	1.00	1.13
5.26	5.65	5.35	1.45	1.30	1.45	0.44	0.46	0.44	0.74	1.00	1.13
4.87	5.17	5.04	1.30	1.50	1.35	0.40	0.43	0.41	0.74	1.00	1.13

Table 6.4. M/D Ratio and Cationic Strength during the Time EE2 Was Spiked in Reactors[a]

Findings for:							
M/D Ratio			Cationic Strength (meq/L)			Nominal M/D	Nominal Cationic Strength (meq/L)
R1	R2	R3	R1	R2	R3		
3.65	3.26	3.31	8.03	8.98	8.77		
3.29	3.15	3.33	7.31	7.22	7.24		
3.42	3.10	3.24	7.42	7.13	7.11		
3.18	3.78	3.42	7.89	8.41	8.37		
3.29	3.20	3.50	7.31	8.10	7.94		
3.37	**3.30**	**3.36**	**7.59**	**7.97**	**7.89**	3.75	9.49

[a]Boldfaced values are averages of their columns.

6.2 BISPHENOL A RESULTS

The effluent concentration of bisphenol A increased for 14 feed days that bisphenol A was fed, similar to a classic breakthrough curve for 45 L of treated water volume (Figures 6.5 to 6.7). The effluent concentration stabilized at approximately 100 µg/L and then dropped rapidly after bisphenol A was removed from the feed. The mass balance showed a logarithmic relationship between the mass sorbed and the effluent concentration, as depicted in Figure 6.8. A Freundlich isotherm curve was generated (Figure 6.9) by using the calculated mass sorbed from the mass balance and effluent concentration. The resulting capacity parameter was $K = 1.09(mg/L)(L/mg)^{1/n}$, while the intensity parameter was $1/n = 2.07$. In a comparison of the reactor isotherm generated from this study with the other isotherms containing bisphenol A, the reactor had a capacity that is higher than those of the experiments performed with the clarifier effluent and lower than those of the experiments with the controlled water matrix and sodium azide. The capacity was predicted to be similar to the capacity of the water matrix control because it was being fed with a synthetic feed; however, it was 31% lower, but it is within the same range as the isotherms performed at a cationic strength of 8 meq/L. These differences may be due to the difference in the concentration of the salts and M/D ratio, the type of biomass, and the concentration of bisphenol A being fed being the same as the concentration of the lowest nominal isotherm point. When comparing the intensity parameter of the reactor isotherm with that found in the other experiments with bisphenol A, we see the intensity is more than double in many cases (Table 4.7).

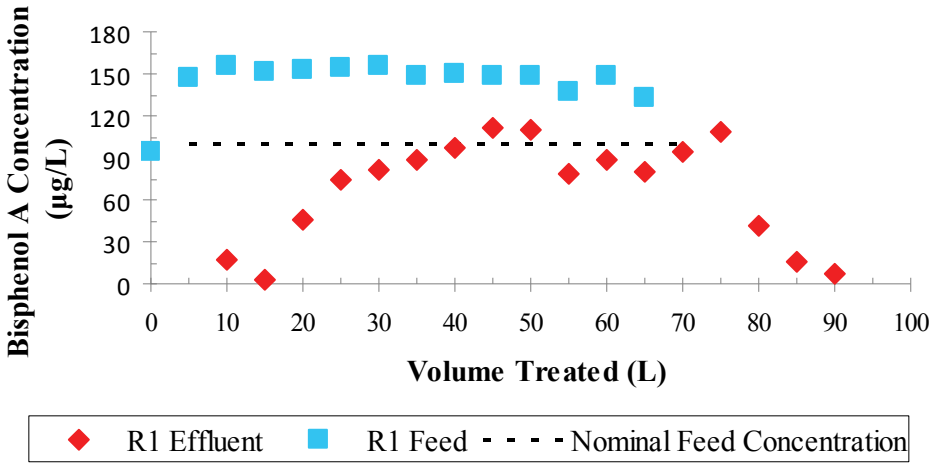


Figure 6.5. Feed and effluent concentration of bisphenol A for reactor R1.

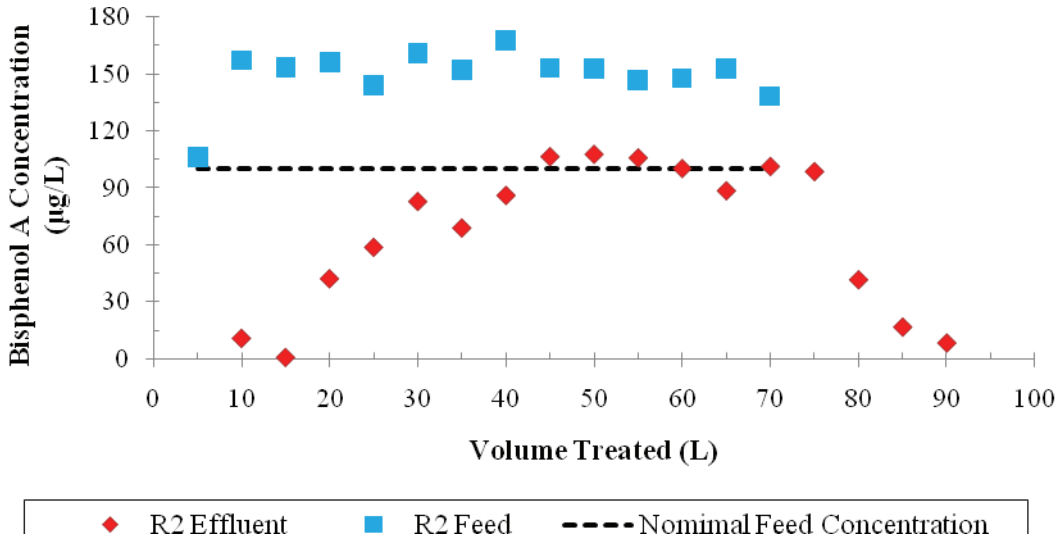


Figure 6.6. Feed and effluent concentration of bisphenol A for reactor R2.

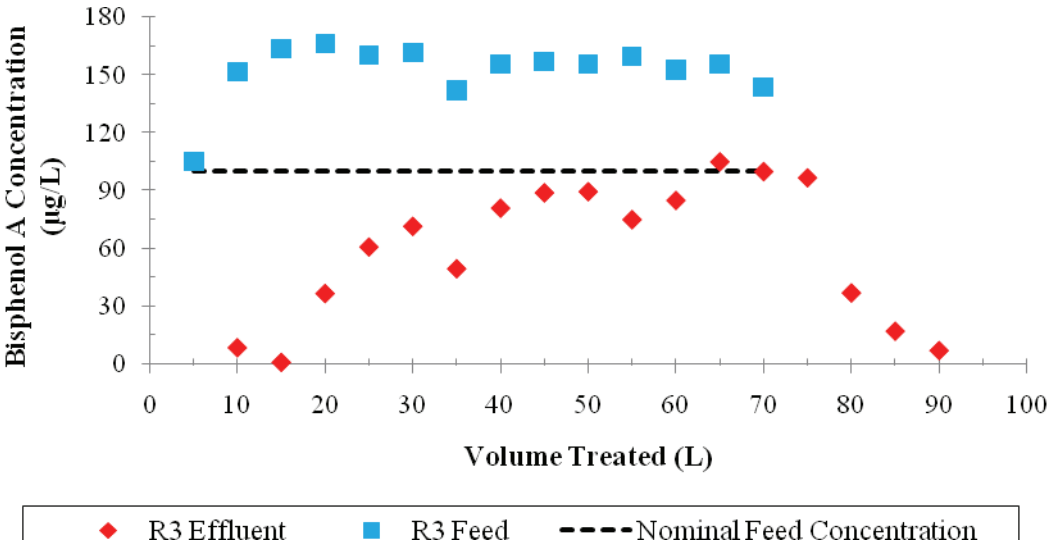


Figure 6.7. Feed and effluent concentration of bisphenol A for reactor R3.

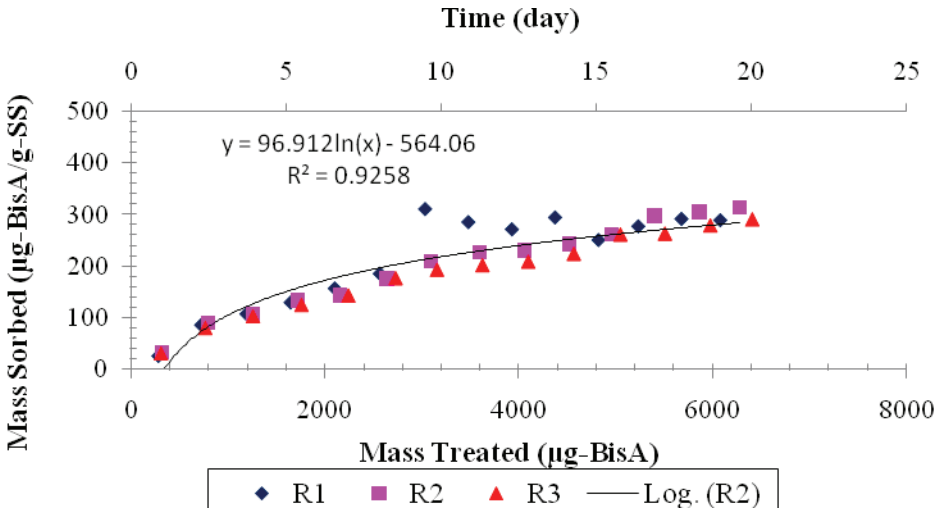


Figure 6.8. Mass of bisphenol A sorbed on the SS of each reactor. Logarithmic regression used with best R^2 value that occurred in reactor R2.

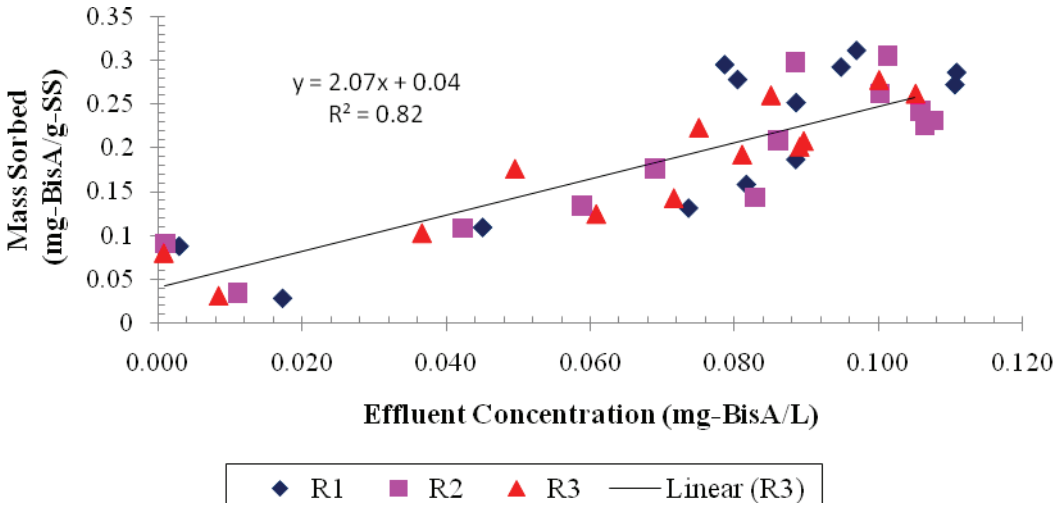


Figure 6.9. Freundlich isotherm fit for bisphenol A in each reactor. Mass balance was used for the sorbed concentration and effluent liquid concentration as the equilibrium concentration.

6.3 EE2 Results

The effluent concentration of EE2 was similar to a sorption breakthrough curve (Figures 6.10 to 6.12) but generally stabilized between 80 and 90 µg/L and then dropped rapidly after EE2 was removed from the feed. The mass sorbed was calculated by the mass balance (Figure 6.13). A logarithmic relationship between the mass sorbed and the effluent concentration was observed. A Freundlich isotherm was used to analyze (Figure 6.14) the relationship between the mass sorbed and effluent concentration. The resulting capacity parameter was K = $1.55(mg/L)(L/mg)^{1/n}$, the intensity parameter was 1/n = 1.06, and R^2 was 37%. The capacity is in the range of the isotherms performed at the cationic strength of 8 meq/L as shown in Table 4.17. The intensity parameter is lower than those of the isotherms that were performed at a cationic strength of 8 meq/L. However, the sorption parameters are in the same range, so it appears that the results from the batch reactor experiments and the isotherms are consistent, being in the same range in many cases.

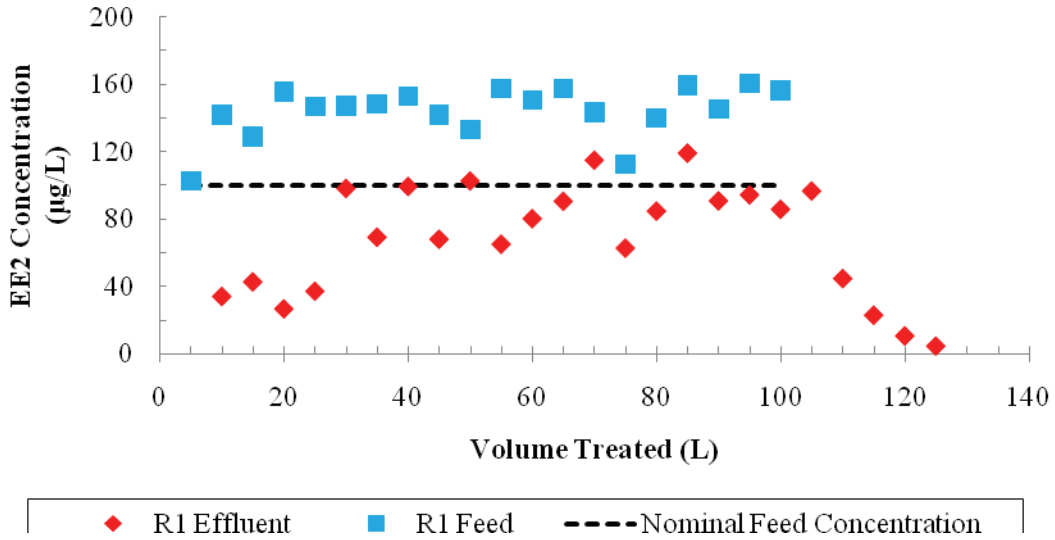


Figure 6.10. Feed and effluent concentration of EE2 for reactor R1.

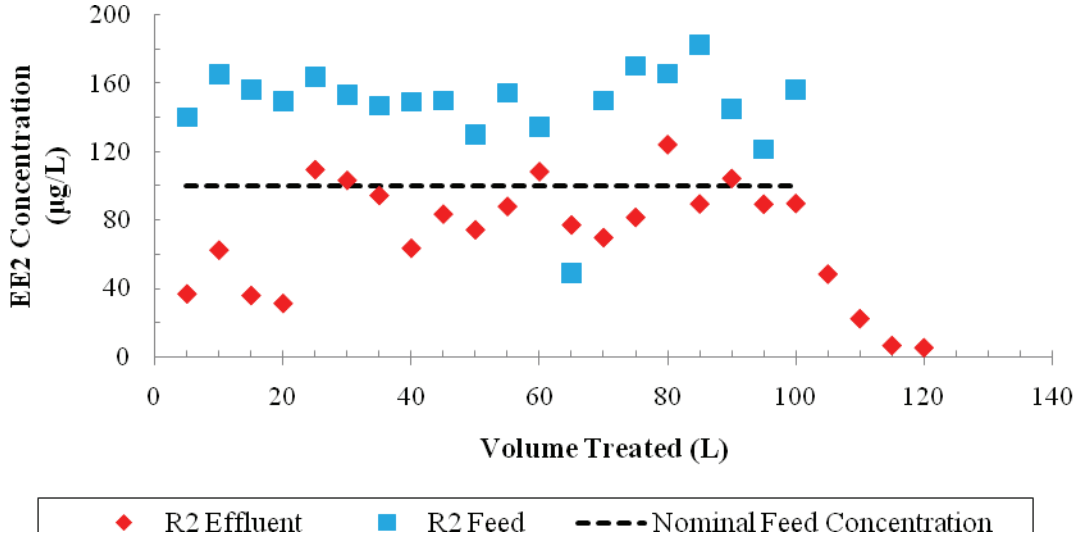


Figure 6.11. Feed and effluent concentration of EE2 for reactor R2.

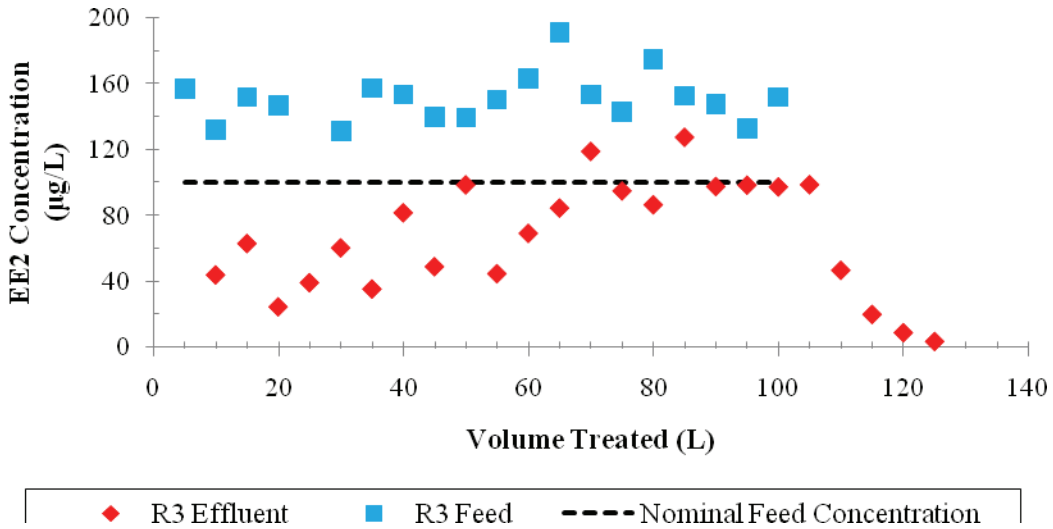


Figure 6.12. Feed and effluent concentration of EE2 for reactor R3.

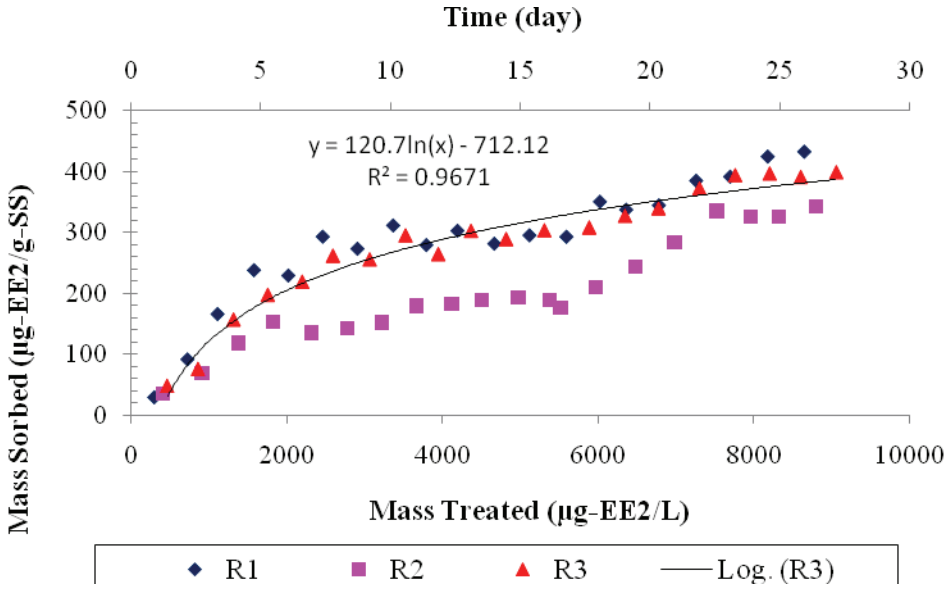


Figure 6.13. Mass of EE2 sorbed on the SS of each reactor. Logarithmic regression used with best R^2 value, which occurred in reactor R3.

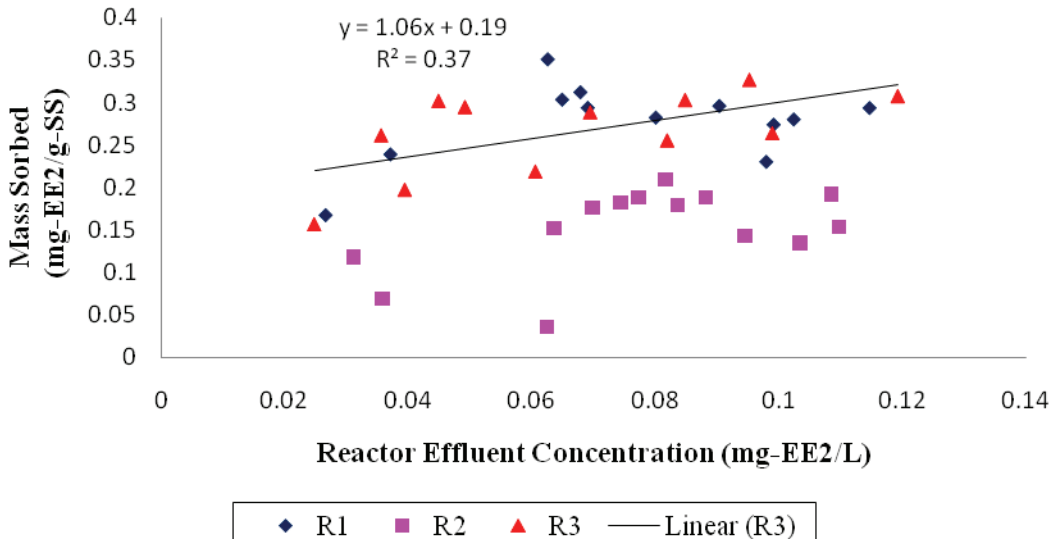


Figure 6.14. Freundlich isotherm fit for EE2 in each reactor. Mass balance was used for the sorbed concentration and effluent liquid concentration as the equilibrium concentration.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

- Complete breakthrough of bisphenol A and of EE2 was observed in the sequencing batch reactors. The elevated concentrations necessary for the analytical methods made studying the impact of the M/D ratio impractical since the steady-state influent concentrations would equal the effluent concentrations.

- For M/D ratios of 1 to 4 in abiotic isotherms, there was a statistically significant trend of decreasing sorption capacity with increasing the M/D ratio. This was consistent with the DCBT and the hypothesis of this study.

- For M/D ratios of 1 to 4, there was no statistically significant relationship between the M/D ratio and sorption capacity with biologically active biosolids in a wastewater effluent matrix and a laboratory salt matrix.

- The difference between the biotic and abiotic isotherms could not be attributed to the water matrix.

- Isotherms completed with an M/D ratio of 6 and a cation concentration of 20 meq/L had statistically significantly lower sorption capacity for bisphenol A, EE2, and estriol than did isotherms with an M/D ratio of 1 to 4 and cation concentrations of 4 to 12 meq/L. This is consistent with the DCBT and the hypothesis of this study. The elevated ionic strength could increase bioflocculation according to the classical theory on bioflocculation, where the double layer compresses as the ionic strength increases.

- A comparison of isotherms with increasing M/D ratios and increasing cation concentrations revealed a statistically significantly lower sorption capacity for bisphenol A and EE2. The effects were most pronounced with M/D ratios between 2 and 4 and with cation concentrations between 8 and 12 meq/L. Water reclamation plants influenced by water softeners are in this range.

- The majority of isotherms with KWRF biosolids had lower sorption capacity than did MNWWRP solids. KWRF is a membrane bioreactor. The SVI of its biosolids was almost approximately 150% that of the MNWWRP biosolids. The poor bioflocculating properties of the KWRF biosolids could limit sorption capacity; however, other factors such as microbial populations may play a role.

- Competitive sorption was observed when EE2, bisphenol A, and estriol were added in the same isotherm. Sorption capacity decreased for both EE2 and estriol.

- Kinetic experiments revealed that concentrations decreased to near detection limits 1 h after the addition of EE2 and bisphenol A. The concentrations increased to equilibrium concentrations in fewer than 20 h. The decrease in concentration may be attributed to microbial activity. This activity may be responsible for the lack of statistically significant relationships between the M/D ratio and sorption capacity in many of the experiments.

RECOMMENDATIONS AND PRACTICAL SIGNIFICANCE

Water softeners have a clear impact on reclaimed water quality by increasing the concentration of monovalent cations. This impact has become most pronounced when reclaimed water is used for irrigation, and the high salt content has a negative impact on plants and soil properties. This research demonstrates that water softeners may also be affecting the ability of water reclamation plants to remove hydrophobic compounds that are difficult to biodegrade. Many known estrogenic compounds are in this category, and estrogenic compounds were used as model compounds in this study.

Future research should use bench-scale or pilot-scale AS systems to determine if the effects observed during this study are important in actual water reclamation systems. The research should use analytical techniques capable of measuring environmental concentrations (nanograms per liter) to avoid the problem of breakthrough that was observed in this study. In addition, a complete mass balance to determine potential losses by biodegradation should be done and the compounds chosen for study should be known to resist biodegradation.

Field studies will be very difficult, since there will be limited ability to control the inputs. If one can find a set of satellite treatment plants along the same sewer line with different salt concentrations, then the data might be suitable for a field study.

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1199 North Fairfax Street, Suite 410
Alexandria, VA 22314 USA
(703) 548-0880
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