Investigation of Activated Sludge Properties under Different Electrical Field and in the Presence of Calcium

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Abstract

The purpose of this research was to study the impact of direct current (DC) application on activated sludge (AS) properties. A control reactor without an electrical field and a series of 1.5L batch reactors were filled with activated sludge at two levels of mixed liquor suspended solid concentrations (LR MLSS: 5000-7000 mg/L and HR MLSS: 10000-12000 mg/L) and were subjected to four electrical modes (continuous, 5ON:5OFF, 5ON:10OFF and 5ON:15OFF) for 48 hours. Experiments were performed for both AS alone and AS mixed with different concentrations of calcium salt (250 and 750 mg/L). The sludge volume index (SVI), time to filtration (TTF), particle sizes, specific oxygen consumption rate, soluble microbial products (SMP) and phosphate concentrations were measured before and after the experiments. Designed reactors' parameters permitted the microorganisms to preserve their bioactivity. Results showed that the continuous electrical mode achieved the highest reduction in SVI. At all electrical modes, over 75% reduction in phosphate concentration was achieved. For most of the AS properties, the impact of EC at LR MLSS was higher than that at HR MLSS. A longer exposure time to DC resulted in smaller particle sizes. As the exposure time to DC decreased, the amount of SMP deposited on the anode surface increased. More calcium was deposited on the cathode surface at a longer exposure time. Furthermore, the addition of 250 mg Ca^{2+}/L to AS, in the absence of an electrical field, resulted in 33% and 63 % higher SMP and phosphate removal efficiency. The results can be applied to better control electrocoagulation processes within various wastewater treatment system including MBR and SMEBR.

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A special thank to my amazing brother and aunt, Ali and Elham, for their continuous support and endless encouragement and a special thank to my beloved fiancé, Nima, for being a tremendous source of inspiration for me and believing in me.

I am grateful to dedicate this work to my dear parents,

Hadi and Mahboubeh

Table of Contents

List of Figures

List of Tables

Chapter 1 Introduction

1.1. Problem Statement

The discharge of low quality effluents to surface water has created severe water pollution, which has affected the aquatic life and decreased the availability of water resources. Therefore, efficient and effective wastewater treatment technologies have become the main challenge all over the world in order to increase the quality of the effluent obtained from wastewater treatment plants (WWTP). Moreover, WWTP design should follow sustainable development principles. Therefore, there is a tendency to decrease the consumed energy, footprint and emission of waste materials from different parts of the operational units within WWTP. As a result, new approaches to improve the performance of wastewater treatment units are required. One of the modern approaches is the introduction of electrokinetic systems such as electrocoagulation processes (EC) instead of conventional chemical coagulation. The other modern approach is the application of membranes to overcome the disadvantages of secondary clarifiers in conventional activated sludge process and achieve higher effluent quality.

Electrocoagulation process has been proven to be highly effective in the removal of impurities and nutrients from wastewater. The short operation time, minimum chemical requirement, easy operation and low sludge production are the advantages of EC technology over chemical coagulation. EC has been applied to a variety of wastewaters with different characteristics. Furthermore, EC has also been implemented as a separate unit before or after activated sludge process in order to achieve higher effluent quality.

The most common compounds that can be removed by EC are colloidal particles, metals and soluble inorganic compound present in the wastewater.

EC is the in situ generation of metallic ions (coagulant) by electro-oxidation of a proper sacrificial anode for coagulation/flocculation processes. Moreover, during the electrocoagulation process several electrokinetic phenomena take place: electrodissolution, electroosmosis, electrophoresis and electromigration, which have a direct impact on the EC performance and the media which is being treated. However up to date, investigations have been devoted to the physical/chemical aspect of electrocoagulation process and not sufficient research was performed regarding the impact of electrical field on major wastewater components (e.g. microbial by). Therefore, studying the impact of direct application of DC on the media which is being treated is an essential need.

The introduction of EC within activated sludge process, to enhance the performance of the system, could be one of the approaches to reach the sustainable development in wastewater treatment units. However, since microbial community are generally negatively charged, their behaviour might be affected in the presence of an electrical field. Furthermore, electrical field could also have impact on the components of activated sludge. Therefore, direct application of DC current to aerobic activated sludge might influence the activated sludge characteristics and its performance. EC system within biological processes can be improved by investigating the impact of direct application of DC on aerobic activated sludge. This would result in better control over its performance even within the application of various wastewater treatment technologies including membrane bioreactors.

The integration of membrane module into conventional activated sludge process (membrane bioreactor-MBR) is a notable innovation in the field of biological wastewater treatment. However, the major drawback of MBR is the membrane-fouling phenomenon, which has significantly limited its applications. One of the most principal parameters that affect the permeability of membranes are the activated sludge components and properties such as mixed liquor suspended solids, particle size, sludge volume index, microbial by-products (SMP and EPS), sludge retention time, hydraulic retention time, soluble inorganics and etc. Overall, membrane fouling has been characterized as bio-fouling and inorganic fouling. The membrane biofouling is due to a formation of biofilm on the membrane surface and the inorganic fouling is due to the formation of inorganic precipitates (e.g. calcium carbonate) on the surface or in the pores of membrane. Furthermore, divalent cations such as calcium, as one of the components of wastewater and activated sludge, have been reported to have the potential to reduce the membrane biofouling. Therefore, knowing that the characteristics of activated sludge have a direct impact on membrane fouling, the integration of electrocoagulation process into MBR system can permit to achieve the most successful results. As current study of Elektorowicz's Research Team on submerged membrane electro-bioreactor (SMEBR system, Patent No. 12/553,680) demonstrated this combination could achieve a high reduction in membrane fouling and an excellent effluent quality. In order to optimize SMEBR system and due to lack of adequate studies on wastewater component's behavior under electrical field, an investigation to fully understand the impact of DC field on activated sludge properties should be performed.

1.2. Study Objectives

1.2.1. Main Objective

The scope of this research was defined to focus mainly on variations in activated sludge properties through the application of different electrical modes and in the presence of different concentrations of salt. The overall objective of this research was investigating the impact of different operational conditions (electrical parameters, wastewater composition and MLSS) on the activated sludge characteristics. The specific research objectives are listed in section 1.2.2.

1.2.2. Detailed Objectives

- Observation of the impact of electrocoagulation process on activated sludge properties
- Assessment of electrocoagulation process in the removal of inorganic substances present in wastewater which cause irreversible fouling of membranes in SMBR systems
- Studying the impact of divalent cations such as calcium on the removal of soluble microbial product from wastewater
- Evaluating EC process at higher conductivities for removal of soluble microbial products and inorganic pollutants
- Achieving better sludge characteristics and conditioning properties through the addition of calcium salt

- Analysing electrodes' surface for the deposition of organics and inorganics

1.3. Thesis Organization

In this section an overview of the contents of various parts of this research has been presented. This thesis has been organized into five chapters and the subject matters discussed in each chapter are as follow:

Chapter One: This introductory chapter covers the statement of problem and objectives of this study.

Chapter Two: A review of the existing relevant literature on the topic has been presented. This chapter demonstrates the available information and fundamentals of MBR and EC process and their advantages/disadvantages. Furthermore, it reveals the gaps in the knowledge related to the topic under study.

Chapter Three: This chapter details the experimental approaches and methodologies followed throughout this research work.

Chapter Four: This chapter represents and discusses the results obtained from different experimental works performed in the laboratory.

Chapter Five: This conclusive chapter is a summary of the entire research performed. Moreover, recommendations for the future works have also been presented.

Chapter 2 Literature Review

2.1. Wastewater Treatment

Nowadays, legislative laws, regarding the effluent wastewater, are becoming extremely stringent and restricted. In addition, due to the discharge of many pollutants into the water resources such as rivers, estuaries, etc., there is an absolute need of reuse of wastewater around the world. A variety of biological (as secondary treatment) and physico-chemical processes (as primary and tertiary treatment) have been applied for wastewater treatment such as activated sludge process, filtration, chemical coagulation, ion-exchange, membranes, carbon adsorption and etc. (Mollah et al. 2001). One of the most common biological wastewater treatment used in the world is the activated sludge process that was first presented back in 1880s. This process involves the oxidation of organic matters present in wastewater by an activated mass of microorganisms. There are several activated sludge processes, which among them, the more common and applied one is the conventional activated sludge (CAS) process.

After the primary treatment, approximately 60% of total solids (TS) and 40% of biological oxygen demand (BOD) are removed and wastewater enters the activated sludge process.

Activated sludge processes involve several components, which the basics consist of:

- Biological reactor where microorganisms, kept in suspension by mixing, are responsible for the treatment of wastewater

- Settling tank where the liquid and solid fractions of activated sludge would be separated
- Return activated sludge line which recycles a mass of activated microorganisms from the bottom of settling tank to the biological reactor to perform further treatment

The supply of air or pure oxygen to microorganisms in the reactor enhances the removal of organic content present in wastewater. The mixture of raw wastewater with the suspended biomass present in the reactor is commonly known as Mixed Liquor Suspended Solids (MLSS).

Figure 2-1 illustrates the primary treatment and CAS processes. Moreover, due to the importance of nutrient removal, CAS was improved by designing a staged reactor which combines several complete-mix reactors in series where some of the reactors are not aerated (anaerobic or anoxic), some are aerated and also some internal recycle activated sludge flows are used (Metcalf and Eddy 2003). However, there are several operational problems that exist in conventional activated sludge process such as high operational costs (e.g. labor), high sensitivity against shock toxic loads, and production of large amount of sludge, which requires disposal and long treatment times.

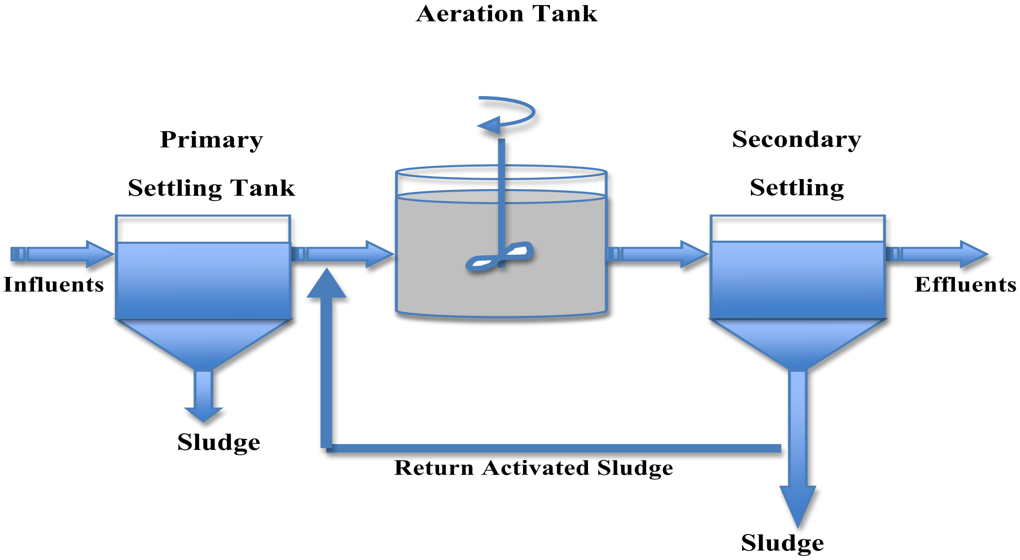


Figure 2-1 Conventional Activated Sludge process

2.2. Overview of Membrane Bioreactor (MBR)

Conventional activated sludge treatment systems are widely used in wastewater treatment and it has achieved a high removal efficiency of organic matters. Despite its advantages, CAS process has several disadvantages. Due to sensitivity of CAS process, its performance would be highly affected by sudden changes in physical or chemical nature of wastewater, such as changes in pH or organic loading rate. Consequently, high amount of suspended solids would be present in the effluent, which results in turbidity, lower organic removal efficiency, lower biomass activity and settling characteristics (Lerner et al. 2007). Other studies have also indicated that one of the most important operational issues in CAS is the biomass washout during the process (Yoon et al. 2000). To solve this problem, recently membranes have been used as a replacement for conventional clarifiers as solid/liquid separators. Membrane bioreactors (MBR) are the combination of conventional activated sludge process and membrane technology. By applying this process, the settling characteristics of biomass do not have impact on the effluent quality (Song et al. 2008). Moreover, this system is capable to adopt itself to a wide range of fluctuations in influent quality; therefore, it can be applied to any kind of wastewater without affecting the quality of the effluent. In addition, complete solids–liquid separation, small footprint and production of high-quality effluent has eliminated the weakest link in the conventional activated sludge process (Choi and Yong Ng 2008).

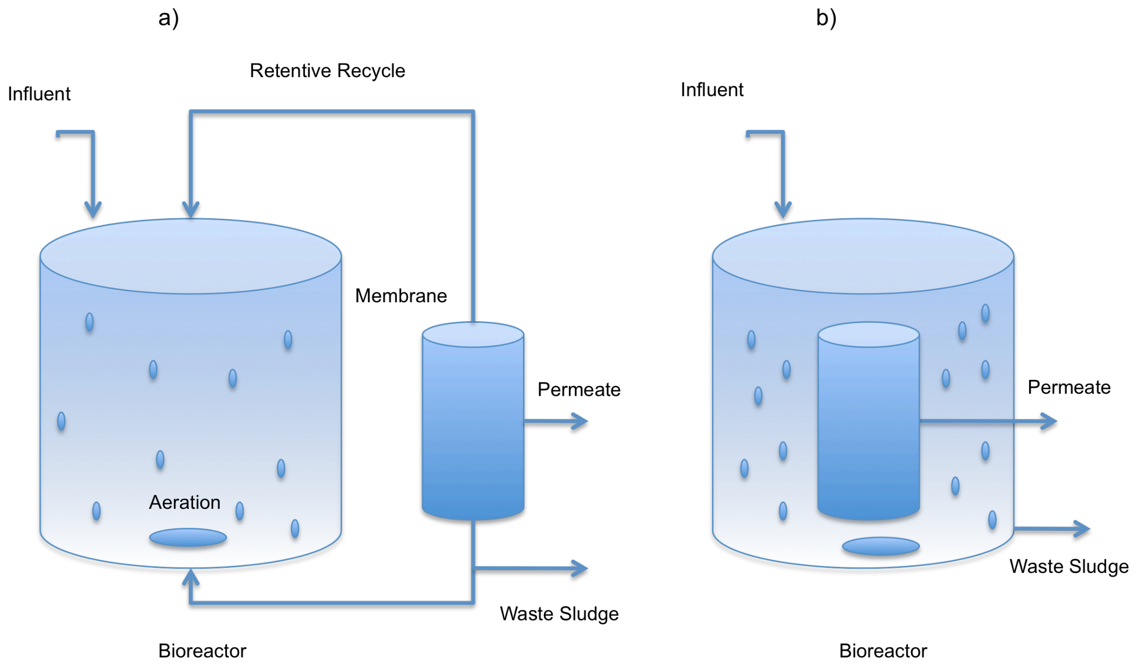


Figure 2-2 a) Side-stream membrane bioreactor b) Submerged membrane bioreactor

The effluent produced by MBR has been found to have excellent quality that can be discharged to coastal, surface waters or be reclaimed. MBR was first introduced in 1960s by Dorr-Olivier Inc., which they used an activated sludge process combined with a cross flow membrane filtration loop. Due to the high cost of membranes its application was limited but in 1989 an immersed membrane in the bioreactor was introduced which gain a lot of attention. (Yamamoto et al. 1989) and recently, MBR has been widely exploited. It was reported that, based on the increasing number of products and their capacity, the MBR market had a value of US$ 216 million in 2006 and it is expected to reach US$ 363 million in 2010 (Atkinson 2006). There are two configurations to this technology, which are side stream membrane bioreactor where the membrane module is placed after the activated sludge process and submerged membrane bioreactor (SMBR), which the membrane module is immersed in the activated sludge reactor (Figure 2-2).

SMBR are preferred over side-stream configuration due to the advantages of its design. In mid 90s, the exponential decrease in membrane costs and high effluent quality increased the application of this technology. Mixing is performed by aeration in SMBR, which creates coarse bubbles that also decrease membrane fouling. The energy required for SMBR is half the energy consumed for side stream membrane. Aeration in SMBR is one of the most important parameter that affects the performance of the system. Following is the tasks performed by aeration in SMBR:

- Keep the solids in suspension
- Decrease membrane fouling by scouring the surface of membrane and
- Provide oxygen for biomass present in the reactor for maximum biodegradation.

The membrane module can consist of hollow fibers or flat sheets. The idea in MBR is to use two-phase bubbly flow to control membrane fouling (Lerner et al. 2007).

The following points represent the characteristics of MBR, which has dominated this technology over conventional activated sludge process:

1. Superior effluent quality. The typical removal efficiency of chemical oxygen demand (COD), biological oxygen demand (BOD) and total suspended solids (TSS) are higher than 95% (Manem and Sanderson 1996). Nitrification efficiency may be very high as well.
2. Sludge retention time (SRT) and hydraulic retention time (HRT) can be controlled separately resulting in manageable biological treatment (Manem and Sanderson 1996).
3. Due to high removal rates, MBR can treat high volumetric loads. An amount of 5.7 kg COD/m^3 was reported for an aerobic MBR treating dairy effluent (Bouhabila et al. 2001).
4. Long SRT (10-60 days) and high MLSS concentrations (10-30 g/L).
5. Low food to microorganisms (F/M) ratio resulting in lower sludge production since microorganisms are in endogenous phase and MBR acts as aerobic sludge digester.
6. Since membrane is used to separate biomass from liquid phase, the concerns regarding settleability and sludge bulking have been solved (Ramphao et al. 2005).

Figure 2-3 indicates the separation of biomass from the liquid phase by membranes.

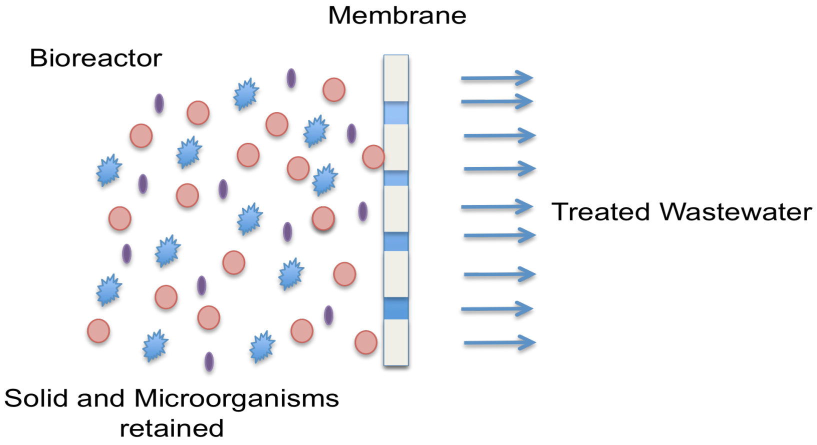


Figure 2-3 Biomass/Liquid separation in membrane processes

Membrane bioreactors have higher energy consumption in comparison to CAS, which is attributed to the recirculation of mixed liquor and air supply in SMBR (Van Dijk and Roncken 1997).

However, membrane fouling has been one the most major technical issues which has limited the MBR application for wastewater treatment.

2.2.1. Membrane Fouling

Fouling has been defined as "Membrane resistance as a result of adsorption of substances on the surface or in the pores of membrane". Factors affecting the fouling are as follow (Figure 2-4): biological parameters, which affect the efficiency of MBR, membrane parameters, which affect the treatment ability of MBR, environmental and technological parameters (temperature, SRT, etc.). Exocelluar polymeric substances (EPS) and soluble microbial products (SMP) are the macromolecules produced as a result of biological processes. They can form a microbial biofilm (gel layer) on membrane surface by forming colloidal groups that can accumulate on membrane surface and reduce the efficient pore diameter (Liao et al. 2004; Sombatsompop et al. 2006). The impact of MLSS on fouling was also studied for different MLSS ranges. It was found that the direct impact of MLSS concentration between 2 to 24 g/L on membrane filterability is minimal. However, MLSS have destructive secondary effects on membrane fouling (Rosenberger et al. 2005; Rosenberger and Kraume 2002). Furtheremore, the impact of particle size on filterability of sludge was also studied. Some researchers believe that a larger size particle can be easily deatached from membrane surface whereas smaller paritcles have higher permanent fouling characteristics. Mikkelsen and Keiding 2002 state that floc size increases when the concentration of EPS is high; therefore it improves the sludge dewaterability.

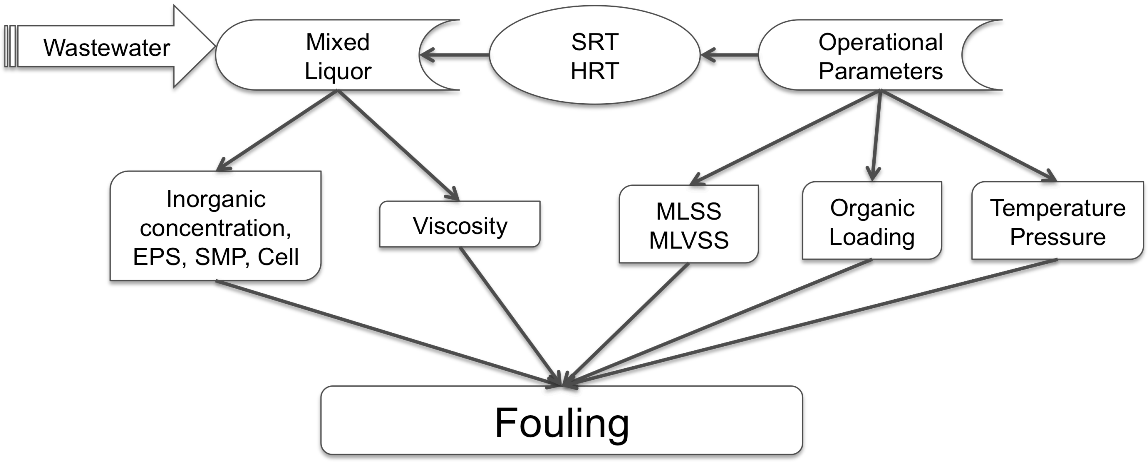


Figure 2-4 Different parameters affecting fouling

Membrane fouling is mainly defined as the decline in permeate flux or increase in Trans Membrane Pressure (TMP) due to the accumulation of foulants on the membrane pores and surface (Hong et al. 2002). In pressure driven membranes like MBR, the permeate production capacity is an important factor affecting the process since it illustrates the membrane fouling. Under steady state conditions, permeate flux can be calculated by dividing permeate volumetric flow rate by the membrane surface area. This flux is proportional to the pressure drop, which takes place across the membrane surface, and is called trans membrane pressure (TMP). In other words, fouling or membrane clogging is the increase of membrane hydraulic resistance that leads to higher energy consumption and frequent membrane cleaning. Therefore, in order to be able to present fouling control strategies, understanding the fouling mechanisms are the first step that has to be taken.

There are two different forms of fouling: 1) reversible, which can be eliminated by simple physical cleaning since the bonds that exist between the foulants and membrane surface are week 2) irreversible fouling. In the latter form of fouling, the foulants are attached to the membrane surface and inside the pores therefore, intensive chemical cleaning should be applied in order to be able to remove them. Van Bentem et al. (2001) indicate that there are four major fouling mechanisms that lead to the decrease in membrane performance. These fouling mechanisms are shown in Table 2-1. Biofouling is mainly due to the microbial cells aggregation and their bio-product on membrane surface, which mainly result in irreversible fouling. Organic adsorption can be prevented by pretreatment of wastewater. Scaling is caused by deposition of mineral precipitates on membrane surface or in its pores. In other words, membrane fouling can be as a result of internal fouling or external fouling of membrane. External fouling is the formation of a cake/gel layer on the membrane surface by solutes due to concentration gradient, where as internal fouling is due to pore blocking since the fine colloids, which have the same size of the membrane pores, can clog the pores. Figure 2-5 indicates the mechanisms of fouling on membrane surface.

Table 2-1 Fouling mechanisms in MBR

Fouling	**Description**
Biofouling	Biofilm formation of membrane surface due to microorganisms accumulation
Organic Adsorption	Deposition of dissolve organic matters
Scaling	Deposition of dissolved minerals due to excess in solute
Particle and Colloidal Fouling	Deposition of particulate matters

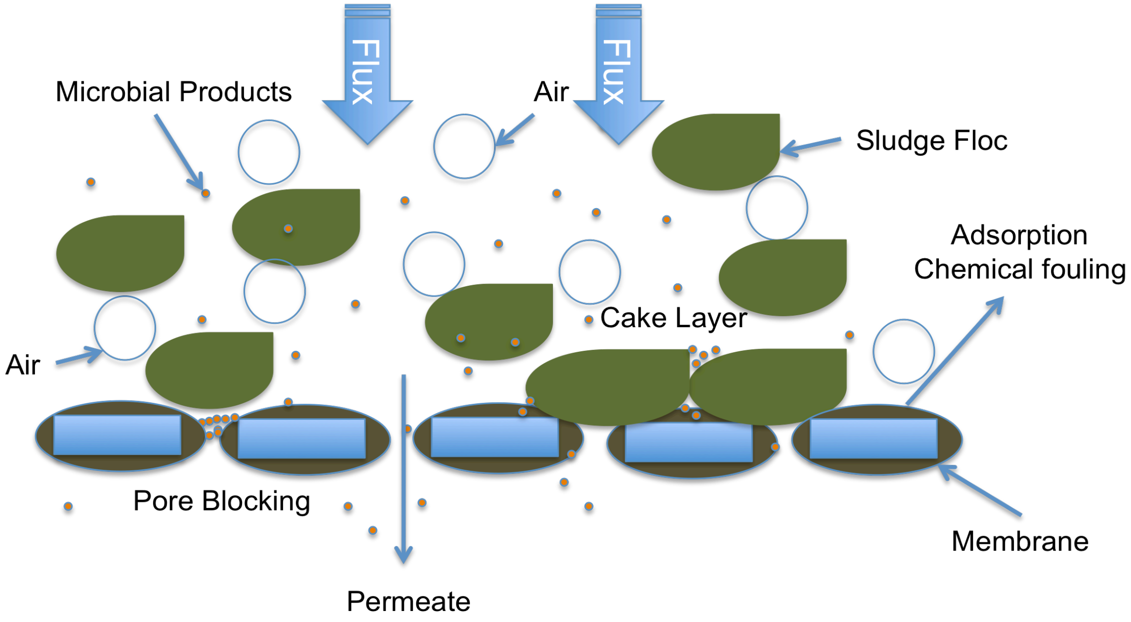


Figure 2-5 Fouling mechanism on membrane surface

2.2.2. Membrane Biofouling

Due to high concentration of microbial organisms in activated sludge, biofouling is the predominant fouling mechanism that takes place on membrane surface. Ridgway and Flemming (1996) reported that bacterial bonding to membrane surfaces is enhanced and mediated by extracellular polymeric substances. These substances are microorganism's products, which are released to the exo-cellular environment due to cell metabolisms and autolysis (Lee et al. 2001). They contain protein, carbohydrate, polysaccharides, lipids and also humic substances. The concentration of EPS is affected by different operational factors such as sludge retention time, MLSS concentration, wastewater type and microbial growth rate (Drews et al. 2006). Liao, et al. (2004) report that EPS is first adsorbed to membrane surface following the adsorption of microorganisms on the surface of membrane, which results in formation of sludge cake. EPS acts as nutrient for microorganisms and protect them from adverse environmental changes by forming a protective buffer zone around them.

Soluble macromolecules, colloids and slimes are called soluble EPS or soluble microbial products (SMP). These compounds can also originate from the influent feed substrate (Le-Clec et al. 2005). SMP adsorb on membrane surface and after blocking the membrane pores, they create a gel structure on membrane surface, which provide the necessary nutrients for microorganisms to grow and form a biofilm (Rosenberger et al. 2005). In the study conducted by Cabassud et al. (2004) for MBR, SMP levels in the effulent remained the same while the fouling was increasing. They concluded that the parameter which is responsible for membrane fouling is SMP components. Same conclusion was obtained by other reseraches that SMP concentration have a considerable impact on the memrbane fouling and performance (Ng and Hermanowicz 2005). Furtheremore, Lesjean et al. (2005) performed a comparison between the mixed liqour supernatant and the permeate obtained from MBR. They revealed that the subtances present mixed liquor supernatant are the ones responsible for MBR fouling.

2.2.3. Divalent Cation Bridging Theory

Bioflocculation is one the most important phenomenon in wastewater treatment since it determines the solid/liquid separation due to microbial colloids aggregation. The higher the bioflocculation, the better the settling and separation properties of activated sludge. The mechanism of bioflocculation has been under study by many researchers in order to improve separation of solids from liquid (Sobeck and Higgins 2002). EPS form a matrix that can trap microbes and help the aggregation of microorganisms and therefore form bioflocs. It was found that 80% of the mass of bioflocs is EPS (Frolund et al. 1996). Therefore, it can be concluded that the interactions taking place between EPS are very important with regards to bioflocculation. It has been widely reported in the literature that EPS carry a negative charge due to the functional groups within EPS such as carboxyl groups (Sobeck and Higgins 2002; Kim and Jang 2006; Arabi and Nakhla 2008). With respect to the latter statement, the role of cations in bioflocculation becomes an important parameter to be investigated.

Three theories that were proposed regarding this matter are double layer theory or the DLVO theory, Alginate theory and Divalent Cation Bridging (DCB) theory. Sobeck and Higgins (2002) compared these theories to better undertand the model, which applies to biofloc formation in the presence of cations. DLVO theory, based on the fact that colloidal particles have a counter ion double layer surrounding them, describes that addition of cations to the solution would decreases the size of double layer and repulsive forces between the particles and therefore improve bioflocculation. DLVO theory includes all cations (monovalent and divalent). Alginate theory is only limited to calcium which describes that Alginate (a kind of polysaccharide), due to its specific composition, can form a gel layer in the presence of calcium and promote bioflocculation where as DCB suggests a non-specific binding of divalent cations with EPS. The latter theory demonstrates that high concentration of sodium (monovalent cation), results in deterioration of floc properties. Due to ion exchange phenomenon, Na in high concentrations displaces Ca bonded to bioflocs. Consequently, due to the lack of bridging with monovalent cations, resulting in reduction of the floc strength, floc structure would be loosed. Higgins and Novak (1997a) showed that ratios of monovalent (Na^+, NH_4^+, K^+) to divalent cation (concentrations expressed in meq/L) higher than 2 would deteriorate the floc properties.

Several conclusions were achieved as follow: addition of calcium and magnesium separately with the same concentration improved the floc properties and increasing their concentrations lead to further improvements. The opposite results were found for sodium, which indicated its detrimental effects on flocculation. DCB was found to be the best theory to describe this phenomenon. Furthermore, it was found that continuous flow would lead to more accurate results than batch experiments. The Dupont company applied this theory to the treatment plant by displacing NaOH (which is used for pH control) with $Mg(OH)_2$. They had significant improvement in their floc properties;

subsequently, their chemical requirement for further clarification was decreased due to better flocculation in the presence of Mg instead of Na (Sobeck and Higgins 2002).

Murthy and Novak (2001) also investigated the impact of inorgnic cations on effluent quality of an activated sludge process. It was found that as the concentration of biopolymers in effluent increases, soluble COD in effluent would also increase and the ratio between them is 1:1. Morover, addition of cations affected the quality of effluent: higher monovlant concentrations promoted the release if biopolymers whereas higher concentration of divalent cations improved the settling and dewatering characteristics of activated sludge and resulted in less amount of biopolymers in the effluent. Another research was also performed on activated sludge to investigate the impact of Na^+ and Ca^{2+} on the floc structure. Batch reactors were filled with waste acitvated sludge and were exposed to different Ca/Na ratios (0, 0.5, 1, 1.5, 2 and 2.5) for 15 minutes. It was observed that Ca/Na > 1 resulted in less small flocs and more larger microbial flocs. Addition of calcium caused an initial defloculation in the activated sludge but as Ca/Na > 1, the floc sizes started to increase as well. They also stated that Na can also increase the floc size (Cousin and Ganczarczyk 1999), which is in contradiction with the work of Sobeck and Higgins (2002) who revealed that Na has detrimental impacts on floc struture and will deteriorate it. Cousin and Ganczarczyk (1999) also described the behaviour of calcium and sodium in activated sludge. They assumed that interactions between calcium and sodium (at Ca/Na > 1) would result in higher ionic strenght and subsequent compression of electrical double layer. Consequenly larger flocs would be formed due to calcium bridging with mirobial flocs.

Sludge dewaterability is also one of the most important properties of activated sludge that was studied by some researchers. Time to filtration (TTF) is one of the parameters that indicate this property. Lo et al. (2001) studied the impact of salinity on sludge dewaterablity and found out that as the concentration of salts in activated sludge increases, the TTF would decrease. Addition of coagulant in the presence of salinity slightly increased the TTF. In addition, they stated that higher final solid content represents lower bound water content. In this regard, 27% and 34% in final solid content was obsereved when salinity alone and salinity with conditioner was applied respectively. On the other hand, the study performed by Wu et al. (2008) for a sequencing batch reactor revealed that addition of NaCl to the reactor resulted in better sludge volume index (SVI) value but higher suspended solids were present in the effluent. Futheremore, it was concluded that salinity did not have any significant impact on organic matter removal. Impact of salinity was also studied for nitrogen removal from wastewater. Salinity at higher coencentration than 2% (w/v) inhibited the nitrite oxidizing bacteria and caused their activity rate to decrease above 1%. On the other hand, salinity effect on ammonia oxidizing bacteria,when the concentration of ammonia was higher than 2% (w/v), reduced their viability by half in comparison to their activity when medium concentration of salt was present in the wastewater. In this study sodium chloride (NaCl) was added to wastewater to increase the salinity (Ye et al. 2009).

Impact of salinity was further studied for submerged membrane bioreactors (SMBR). In a research conducted by Reid et al. (2006) effect of salinity shocks on a pilot scale SMBR performance was scrutinized. SMBR was exposed to high concentration of NaCl (30 g/L) in a period of 10 minutes. Initially COD and NH_3 removal efficiency was reduced but after the concentration of salt was reduced, their efficiency was restored. Same behavior was observed for SMP and EPS. Higher SMP resulted in less membrane permeability, which was confirmed by previous researches. Kim and Jang (2006) studied membrane fouling with respect to biomass characteristics based on EPS and SMP. Due to the fact that smaller particles result in higher fouling rates, the conditions where bioflocculation would take place would be a beneficial to membrane permeability. As described above, bioflocculation has been described by three different theories in which divalent cation bridging theory best describes the bioflocculation phenomenon with divalent cations. Bioflocculation can be attributed to membrane fouling based on EPS and SMP characteristics; therefore in this study the effect of calcium on membrane biofouling has been under investigation. A bench scale submerged membrane bioreactor was fed with synthetic wastewater with two different calcium concentrations. The concentrations were chosen to be 0.026 mM (LC) and 2.86 mM (OC) in order to obtain the monovalent to divalent ratio of 33 and 1.3 respectively. Higgins and Novak (1997a) had reported that M/D ratio higher than 2 will result in floc deterioration and higher fouling rates. Experimental results indicated that SVI was lower for OC than LC, which reveals that better bioflocculation had taken place in OC, resulting in denser sludge formation. As expected, EPS concentration obtained from OC was lower than LC sludge had settled better. FTIR analysis was also performed to specify which type of foulants is dominant in membrane fouling. Results indicated that protein and carbohydrates were the major foulants but intensities were lower for OC i.e. less biofouling for OC membrane. Scanning electron microscopy (SEM) pictures of virgin membrane and fouled membrane showed that the LC membrane was fully covered with a biofilm (gel layer) whereas OC membrane pores were partially blocked. Low hydrophobicity of SMP and lower concentration of SMP resulted in lower fouling rate for OC membrane. It was assumed that due to higher calcium concentration in OC, more SMP and EPS were bind with calcium through calcium bridging and therefore better bioflocculation had taken place. Moreover, calcium can act as a coagulant and form colloidal flocs by charge neutralization. It is assumed in this work that these SMP would aggregate through calcium bridging and form larger flocs that are not able to block the membrane pores. On the other hand, alkalinity and phosphates present in wastewater can react with calcium and form calcium carbonates and phosphate scales, subsequently reducing the permeability of membrane due to inorganic fouling. These authors did not investigate this aspect of fouling.

Arabi and Nakhla (2008) investigated the impact of calcium on membrane bioreactors to better understand the cation induced bioflocculation phenomenon and their effect on fouling either biofouling and inorganic fouling of membranes. Calcium was added to influent in concentration of 250 mg/L and 800 mg/L. SMP analysis revealed that when higher calcium concentration was added, 52% reduction was obtained while lower concentration reduced SMP by only 37% in comparison to control sample. Therefore, it can be concluded that higher calcium concentrations resulted in improvement of bioflocculation. However, when higher concentration was applied, the permeability of membrane decreased. This was due to the formation of $CaCO_3$ scaling on the membrane surface as a result of inorganic fouling. These results were confirmed by particle size analysis which indicated that in lower concentration of calcium, larger particles are formed where as in higher concentrations of calcium, the size of particles were almost the same as the control reactor. In the latter case, they postulated that this behavior is due to the formation of calcium carbonates precipitates since they have a smaller size than microbial flocs. Inorganic fouling was mainly due to calcium carbonate precipitation on the membrane surface, which is said to be an irreversible fouling due to the cohesive characteristic of this compound (Ould-Dris et al. 2000). MINTEQ modeling results gained comparable results with experimental data (Arabi and Nakhla 2008). Modeling indicated around 8% of calcium is in the form of calcium bicarbonate and calcium sulfate. Also calcium phosphate and magnesium phosphate are well presented as inorganic foulants in MBR but these are only present when pH is higher than 7. Since magnesium is also a divalent cation, same analysis was performed with Mg for SMBR (Arabi and Nakhla 2009). Therefore, the inoganic fouling of membrane bioarectors is also an important factor affecting membrane perfomance.

2.2.4. Membrane Inorganic Fouling

The membrane resistant (R_f) can be attributed to organic and inorganic fouling and is calculated base on the following equation:

$$R_f = R_m + R_c + R_{organic-f} + R_{Inorganic-f} \qquad \text{(Eq. 1)}$$

Where R_m is the intrinsic resistant of membrane, R_c is the cake resistance, $R_{(organic\text{-}f)}$ is the organic fouling of membrane whereas $R_{(inorganic\text{-}f)}$ is the resistance caused by inorganic scales and requires chemical cleaning of membrane. EDTA and/or an acidic solution with air flushing are usually used to clean the membrane for inorganic fouling whereas NaOCl and air flushing is used for organic removal. The EPS present in wastewater bears a negative charge whereas carbonate compounds are slightly positive. Therefore, the bioflocs formed by EPS can be adsorbed onto carbonate crystals and reduce the potential for fouling resulting in bioflocculation (Yoon et al. 1999). Inorganic fouling of membrane have been studied by some authors but still requires further research to fully undestand the behaviour of inorganics in MBR. You et al. (2006) operated two different configurations of membranes (SMBR and external membrane module) to study the effect on fouling mechanism. Analysis of membrane surface was also performed by SEM-EDS and X-ray diffraction. Two different concentrations of calcium were added (50 and 350 mg/L). The concentration of calcium in the permeate flow was 20 and 80 mg/L respectively. During the operation the variation in flux and TMP were measured, before addition of calcium the TMP and flux were fairly stable but after the addition of calcium:

1) SMBR: the increase in TMP occurred in two different phases, in the first phase, a gradual increase was observed in TMP (and decrease in flux), whereas in the second phase an abrupt increase in TMP and a sudden decrease in flux appeared (more than 70% reduction of flux)
2) External membrane: no significant effect were detected in flux due to the presence of calcium

These results revealed that when there is a concern regarding scale formation on membrane surface, the application of the external membrane systems is more effective. Scaling can be a result of two mechanisms: crystallization (which itself have two mechanisms) and hydrodynamic transportation. In the crystallization process, “bulk crystallization” refers to the supersaturated systems where the agglomeration of scale forming ions is promoted due to random collisions of ions in motion. The cluster of ions coalesces to form a crystal inducing precipitation upon reaching a critical size. On the other hand, “surface crystallization” is caused by foreign bodies such as membrane surface, which creates a surface for deposition of crystals, therefore, promoting scale formation of membrane surface. It can be concluded that the scale formation on membrane surface is either as a result of inorganic crystal formation in the bulk phase and/or the lateral growth of crystals on the membrane surface. In order to prevent the fouling caused by metal ions present in wastewater, the cluster of ions or free ions should be free of contact from each other (You et al. 2006). Moreover, calcium carbonate precipitates are cohesive, which means they seek for a surface to deposit on. Therefore, they have a high potential to be attached to membrane surface and cause irreversible fouling. At the initial stage of MBR operation, crystallization takes place on membrane surface, which later would be developed, tending to form larger crystals with a deformed shape. The scale will grow in all directions resulting in thick deposit, which is mainly on the membrane surface due to its cohesive nature. T-EDXA, FT-IR, SEM-EDS and XRD analysis confirms that Ca is the predominant element present in the external part of membrane scale (Lee and Kim 2009; You et al. 2006; Arabi and Nakhla 2008). Scales formed by calcium are mainly in the form of $CaCO_3$ and $CaSO_4$, which cause irreversible pore plugging (Choi et al. 2009). The fouling caused by calcium carbonate is due to the fact that their size is larger than membrane pores resulting in external fouling of membrane. Scaling has also been observed in anaerobic MBR systems due to high partial pressure of CO_2 in the reactor, which intensify the formation of scales. It is known that the concentration of solutes increase in the direction of feed flow, therefore, it can exceed the solubility limit and promote the formation of precipitates, either in bulk or on membrane surface by depositions (Lee and Kim 2009). Other reported inorganic foulants are $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$, which have the ability to affect the structure of membranes and shear off the active layer of membrane surface (Cicek et al. 1999). In addition, the main inorganic foulant for anaerobic MBR have been reported to be Struvite ($MgNH_4PO_4.6H_2O$), which it appears as white precipitates on membrane surface (Choo and Lee 1996). Figure 2-6 depicts the membrane surface while being fouled by calcium deposition on its surface and inside its pores. Accordingly, the control of membrane fouling to prevent a decrease in membrane efficiency, while treating wastewater, is essential.

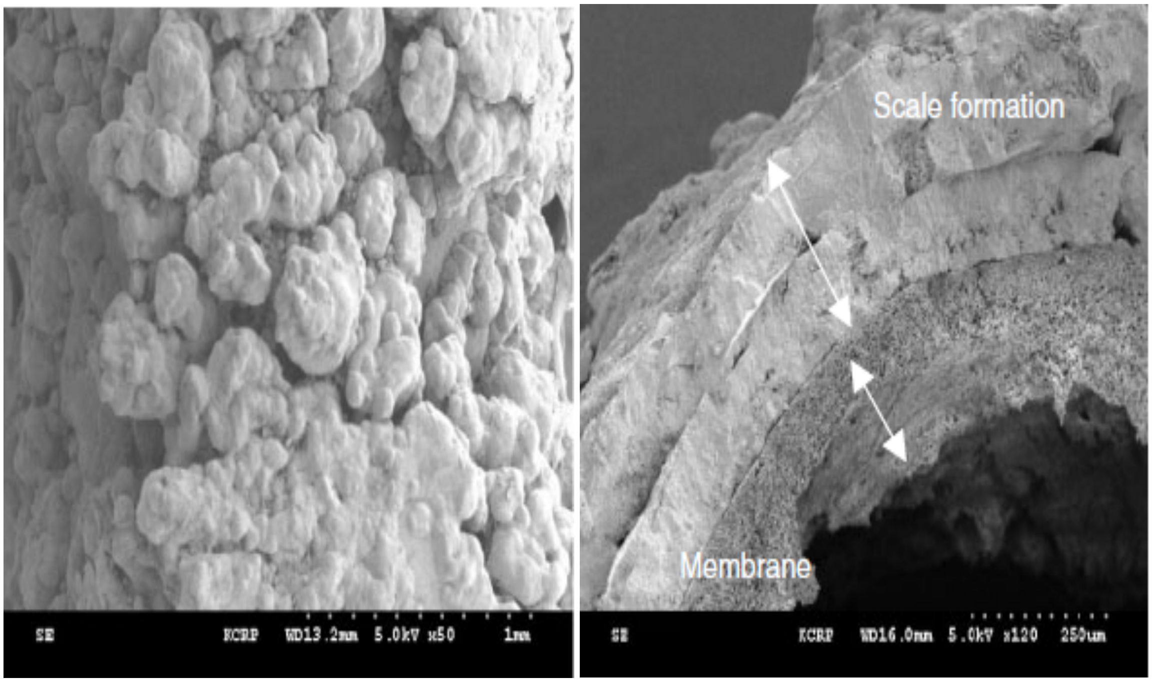


Figure 2-6 Calcium carbonate scales on membrane surface and inside the pores (Lee and Kim 2009)

2.2.5. Fouling Prevention and Control Strategies

Membrane fouling has been one of the major issues confronting the application of MBR for wastewater treatment. As mentioned before, the colloidal and soluble substances, particulates, inorganic and organic materials, present in either influent or activated sludge, are important factors affecting the membrane performance by blocking membrane pores. Several conventional methods have been proposed to prevent membrane fouling such as coagulation, flocculation, adsorbents and filtration techniques. Wastewater pretreatment have also been performed in order to eliminate the membrane scaling. The adjustment of pH (by addition of acid) and using antiscalants or scale inhibitors products are the common pretreatments under research (Choia et al. 2009; Lee and Kim 2009).

Addition of adsorbents and coagulants has been widely reported to be an effective method in reducing membrane fouling (Le-Clech et al. 2006). One of the most common adsorbent used is powdered activated carbon (PAC). PAC reduces membrane fouling either by up taking soluble organic matters or by adsorbing EPS on its surface (Seo et al. 2005). Furthermore, coagulation process has been widely reported to enhance phosphorus removal from wastewater and membrane filtration performance (Lee et al. 2001). Colloidal fraction in wastewater has a net negative surface charge and their size is in the range of 0.01 to 1 μm. They create stable suspension conditions and it is not possible to remove them by sedimentation. Coagulation is a process where these particles would be destabilized so that particles' collision can take place and larger floc can be formed (Metcalf and Eddy 2003). In other words, the neutralization of charged colloidal particles in suspension by mutual collision with counter ions in wastewater provokes coagulation which later results in colloids' aggregation. This process is due to the reduction of the net surface charge on colloidal particles (reduction of repulsive characteristic of the electrical double layer) and allowing the van der Waal's forces to bring them together (Mollah et al. 2001). Coagulant is the chemical, which is added to wastewater in order to destabilize the colloidal particles. The most common coagulants added are usually organic polymers or metal salts such as alum and ferric sulphate. The destabilization and aggregation of colloidal particles through coagulation can be described in steps: charge neutralization and adsorption of particles to metal hydroxides, the inter-particle bridging and enmeshment of colloidal particles in the floc and sweep. In these processes, free Al^{3+} and Fe^{3+} (as coagulants) are not the only elements causing the particles aggregation and metal hydroxides, which are formed during coagulation process, have a significant impact on floc formation (Metcalf and Eddy 2003). It has been shown that alum addition has resulted in 25% reduction in SMP and further membrane hydraulic performance. However, the optimization of alum was performed for precipitating phosphate and not for membrane filterability (Holbrook et al. 2004). Song et al. (2008) investigated the membrane fouling and removal efficiency of phosphorus for a submerged membrane bioreactor by addition of the chemical inorganic coagulants. In order to analyze the particle size in the reactor, due to addition of coagulant, the MLSS sampling was grabbed from the inside of the reactor. They concluded that the fouling have significantly decreased since the permeate flow increased. Also high phosphate removal efficiency was achieved when alum or ferric chloride was used as coagulants. When coagulant was added in concentration above 200 mg/L, the permeate flow was twice the amount obtained from the reactor where no coagulant was added. Since addition of ferric chloride resulted in a decrease in pH, they did not recommend its application, although a high efficiency of the phosphorus removal was obtained. No significant effect was observed regarding nitrogen removal by alum but fouling was minimized due to aggregation of small particles that could cause blockage of membrane pores. Lee et al. (2001) studied the impact of zeolite and alum as coagulants on membrane fouling and phosphorus removal and optimized the alum concentration based on phosphorus removal. They kept the molar ratio of Al/P to 1.5 and attributed the effective decrease in membrane fouling to higher particle size distribution in MBR. In another study ferric chloride was used as coagulant since it was found to have higher efficiency than alum; unfortunately, it was more expensive. Furtheremore, among ferric chloride, alum and organic polymers, the latter was found to be more effective in increasing the MLSS particle size and obtaning more efficient time to filtration (Le-Clech et al. 2006; Fan et al. 2007). Wu et al. (2006) conducted research on the impact of four types of coagulants (alum, ferric chloride, polymeric aluminum sulfate and polymeric ferric chloride) on the properties of activated sludge. Polymeric coagulant gained much more effective results compared to monovalent coagulant since they produced more positive charges and longer chain supplies. It was stated that the decrease in mambrane fouling, when adding coagulants, can be attributed to three subsequent processes: preventing the gel layer formation on membrane surface, decreasing the rate of foulant development in the reactor, and eliminating the foulants formed on membrane surface. It was also concluded that it is better to add the coagulant to wastewater before entering the MBR in order to obtain higher efficiency in reduction of foulants from MBR. Ferric chloride has been shown to be slightly more effective in the removal of SMP and EPS compared to alum. It was found that $FeCl_3$ concentrations higher than 250 mg/L yields a significant decrease in membrane resistancy. Addition of ferric choride to MBR resulted in 92% and 97% removal in phophorus and COD removal respectively (Mishima and Nakajima 2009).

Although, chemical coagulation has achieved good efficiency in removal of colloidal particles, addition of chemicals has negative effects as well. Addition of chemicals to wastewater generates products and even by-products, which eventually result in large volume of sludge in the reactors (Clark and Stephenson 1998). The following are the disadvantages of chemical coagulation:

1. Considerable consumption of chemicals
2. Production of voluminous and large amount of sludge
3. High operating costs (Patterson 1989)
4. Generation of secondary pollutant as a result of chemical addition (Adhoum et al. 2004)
5. Generation of solid sludge which results in severe environmental issues (Parga et al. 2005)

In this regard, electrocoagulation processes has been proposed as an alternative solution for chemical coagulation (Bani-Mehlem and Elektorowicz 2010). Chen et al. (2007) investigated the impact of electrical field on membrane flux (wastewater flow passing the membrane surface). They designed a reactor with two compartments, one containing the electrocoagulation system (having 5 cm gap between the electrodes) and the other holding the hollow fiber membrane. Using direct current (DC), applying 15 to 20 V/cm achieved significant increase in membrane flux in comparison to the system without electrocoagulation process. The optimal value for voltage gradient obtained was 20 V/cm, where there was no concern regarding membrane flux decline. In this condition, 80% reduction in wastewater COD accomplished and the layer deposited on membrane surface was much more thinner. They concluded that electrical field is an effective technology to improve membrane performance was reducing membrane resistancy. Furthermore, combination of electrocoagulation with SMBR system as one unit was proposed by Elektorowicz et al. (2009) which was named submerged membrane electro-bioreactor (SMEBR).

2.3. Electrocoagulation (EC)

2.3.1. Introduction to the EC

A variety of physico-chemical processes have been applied for wastewater treatment such as filtration, chemical precipitation, ion-exchange, membranes, carbon adsorption and etc. (Mollah et al. 2001). Electrochemical techniques (e.g. electrocoagulation, electroflotation) have been widely under study due to the fact that they do not require the addition of chemicals. Among them electrocoagulation (EC) process has received a lot of attention due to the improvement of electrochemical technologies and the reduction in its capital cost. There is a high potential for EC to be applied to various wastewater treatments and other water related topics, based on economical and environmental values (Kobya and Delipinar 2008). Electrocoagulation has proven to be very effective in removal of impurities without the need of addition of chemicals while minimum sludge is produced. Commercially, it has been very profitable but in the scientific way, it requires further research.

In general, EC is the in situ generation of coagulant by electro-oxidation of proper anode electrode, therefore no chemicals are added and minimum sludge is produced. The colloidal particles in wastewater are either removed by binding with opposite charges ions or by adsorption to metallic hydroxides which are generated in the solution. The most common compounds that can be removed by EC are colloidal particles, metals and soluble inorganic compound present in wastewater (Mollah et al. 2001). One of the differences between chemical coagulation and electrocoagulation processes is in the form which metallic ions are presented to wastewater. In electrocoagulation metallic ions, which can be referred as coagulants, are delivered to the wastewater by electrical processes. As the base of EC, the supplied electrical field in EC process affects the negative surface charge of colloidal particle and their stability. If high electrical current is applied, more charge would be neutralize and more particles can agglomerate and form efficient flocs (Ogutveren and Koparal 1997). EC has been proven to be a cost effective and reliable technology that can be applied to wastewater treatments (Hu et al. 2003). The short operation time, no addition of chemicals, easy operation and low sludge production are the parameters that have brought the attention of industry to this technology. In addition, the sludge produced by EC is a metallic sludge and therefore the flocs are larger and have less bound water. As a consequence, the volume of the sludge generated is modest and much more easier to handle (Mollah et al. 2001). It was found that EC has higher potential in removal of suspended soilds (SS) and COD in comparison to conventional chemical coagulation (Jiang et al. 2002). Therefore, in order to be able to improve the efficiency of the EC process, deep understanding of the EC mechanisms and processes is required.

2.3.2. Principle Mechanisms in EC

In general, EC is consisted of three consecutive steps. Electrolytic oxidation of sacrificial anode generates coagulants and the particles present in bulk solution destabilize and further aggregate to form flocs. Due to the passage of electrical current through the solution and formation of coagulant, the diffuse double layer around the suspended charges particles compresses. In addition, the electrostatic interparticle repulsion reduces due to the interactions taking place between the ionic species and the counter ions generated from the sacrificial anode. Furthermore, the flocs formed create a sludge blanket that can enmesh the remaining pollutions in wastewater (Mollah et al. 2001). There are several major phenomena taking place during EC:

a) Electrophoresis; when particles migrate toward the oppositely charged electrode and as a consequence of charge neutralization, adhere to each other and form larger flocs.
b) Electroosmosis; movement of water under the influence of imposed electric gradient. Due to the presence of more cations than anions in the water, the flow of water is toward the cathode.
c) Electromigration; transport of ions and polar molecules in the direction of the opposite electrode under electrical field.
d) Metallic cations released from anode material and hydroxyl ions generated from cathode can react with impurities such as metals present in wastewater, form precipitates and settle.

e) The metallic ions generated from anode material reacts with OH^- and forms hydroxide compounds providing a high adsorption surface for impurities including soluble organic compounds.

f) Sweep coagulation: the generated metallic hydroxides form long chains, which can trap the impurities such as colloidal particles within the chain and sweep them (Kobya et al. 2006)

g) Oxidation of organic impurities and formation of less toxic compounds (Kobya and Delipinar 2008)

h) Removal by settling, adhesion to bubbles generated during the EC process (electroflotation) (Chen 2004; Canizares et al. 2005)

The two metals, which have been widely used as an anode in EC process, are aluminum and iron which are cheap, easily accessible and effective (Mouedhen et al. 2006; Mollah et al. 2001; Kurt et al. 2008). Canizares et al. (2007) performed several EC tests to compare these two electrodes. They found that in electrocoagulation processes, which are not continuous, aluminum anode is preferred upon iron anode since iron can easily oxidizes and further corrode when the cell is not connected to electricity. The mechanisms of removal of ions and particles by EC process have been described as follow in Section 2.2.3.

2.3.3. Reactions at the Electrodes

The electrochemical reactions at the electrodes during EC process are explained in this section.

Reactions at the cathode:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (Eq. 2)

Due to the generation of OH^- and hydrogen evolution (bubble formation), the pH of the vicinity around cathode increases and the solution becomes alkali. Reactions that take place at the sacrificial anode are as follow, which M represents the material of anode:

$M \rightarrow M^{3+} + 3e^-$ (Eq.3)

When the M^{3+} is generated, several complex mechanisms occur and result in metal hydroxide floc production. General simplified mechanisms are shown further (Kobya and Delipinar 2008):

M^{3+} → monomeric species → polymeric species → Amorphous $M(OH)_3$ (Eq. 4)

Treatment of wastewater by aluminum electrode results in generation of monomeric and, at appropriate pH, polymeric species of aluminum:

$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-$ (Eq. 5)

Due to spontaneous hydrolysis of the aluminum ion produced, monomeric compound are formed: (Mouedhen et al. 2006)

$Al^{3+}_{(aq)} + H_2O \rightarrow Al(OH)^{2+}_{(aq)} + H^+_{(aq)}$ (Eq. 6)

$Al(OH)^{2+}_{(aq)} + H_2O \rightarrow Al(OH)_2{}^+_{(aq)} + H^+_{(aq)}$ (Eq. 7)

$Al(OH)_2{}^+_{(aq)} + H_2O \rightarrow Al(OH)_{3\,(s)} + H^+_{(aq)}$ (Eq. 8)

At low pH, Al^{3+} and $Al(OH)_2{}^+$ is generated but when the pH becomes more suitable, these species convert to $Al(OH)_3$. Due to the fact that diametric and polynuclear hydrolysis of aluminum can also occur, the following reaction can also emanate which results in formation of $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$ and etc. and finally polymerized $Al_n(OH)_{3n}$:

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \qquad \text{(Eq. 9)}$$

Furthermore, it has also been postulated that if the anode potential is sufficiently high, secondary reactions might take place too. These reactions can be evolution of oxygen, direct oxidation of organic compounds and also oxidation of Cl^- by the following reactions (Mouedhen et al. 2006; Kobya et al. 2006):

$$2H_2O \rightarrow O_2 + 2H^+ + 4e^- \qquad \text{(Eq. 10)}$$

$$2\,Cl^- \rightarrow Cl_2 + 2e^- \qquad \text{(Eq. 11)}$$

As indicated above, generation of H^+ in anode vicinity results in low pH, therefore, acidic region around anode area is created while pH increases in the cathode vicinity. The generation of these hydroxo cationic complexes depends on the pH of the medium. Both compounds, cationic hydrolysis products and amorphous $Al(OH)_3$, can remove the pollutants from the aqueous medium. The charges hydroxo cationic complexes have a adsorptive gelatinous nature and can remove the colloidal impurities either by surface charge neutralization or by adsorption. It is also possible that the amorphous aluminum hydroxides entrap the impurities within themselves (Mouedhen et al. 2006; Mollah et al. 2001).

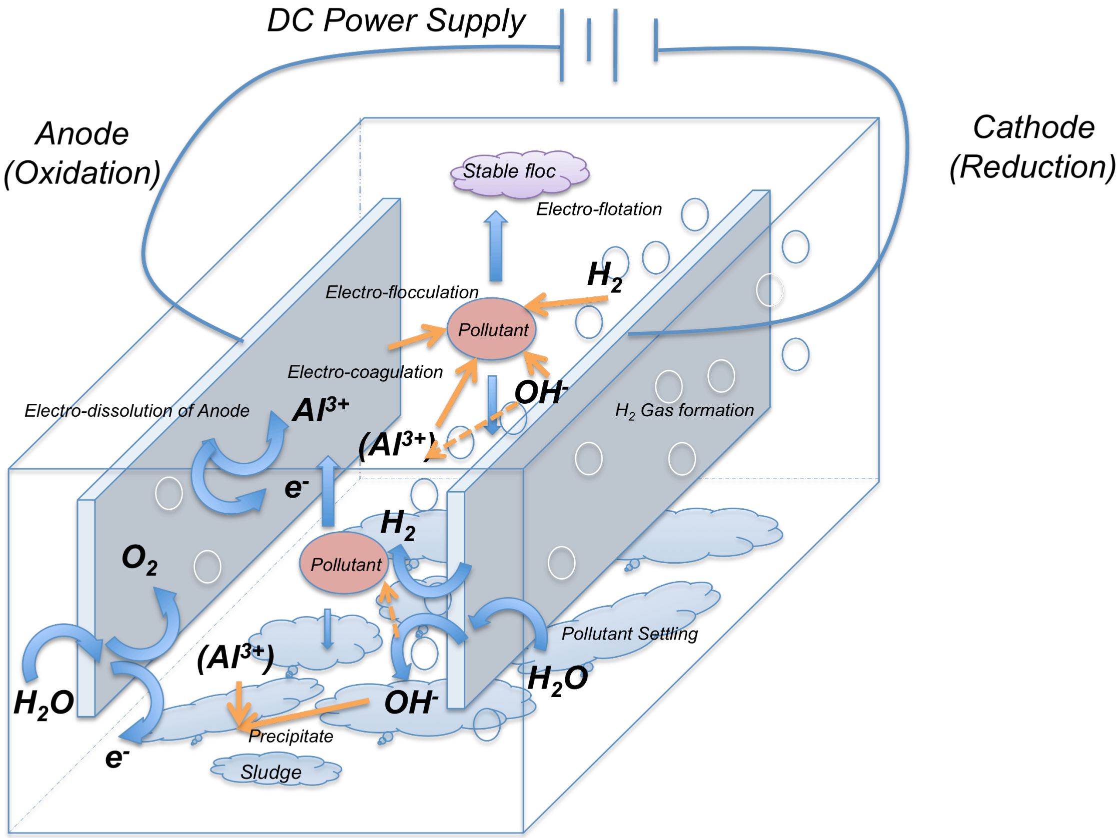


Figure 2-7 Interaction within EC process

The removal of pollutants has also been reported by cathodic reactions as well. Pollutants can be removed either by deposition to cathode surface or by flocculation due to formation of hydrogen gas bubbles (Chen 2004). The described mechanisms strongly depend on the pH and the concentration of metals released from the anode to the medium (Duan and Gregory 2003). Figure 2-7 illustrates the interactions taking place in an electrocoagulation process.

2.3.4. Factors Affecting EC Process

The current density (current (A) distributed over effective surface area (m^2) of an electrode) affects the amount of ions released from the electrodes to the solution; as the current density increases, the amount of ions increases as well. The electrochemical equivalent mass for aluminum is 335 mg/Ah and for iron is 1041 mg/Ah (Chen 2004). Although higher current density results in higher generation of ions however it might result in loss of energy for heating up the water (Chen 2004). Furthermore, current efficiency (CE) decreases when high current densities are applied. For aluminum electrodes the CE can reach up to 120 to 140% where as for iron it can reach 100%. Higher CE of aluminum can be attributed to the pitting of electrode surface due to the oxidation of chlorine anions as explained in Section 2.2.3. Current density is suggested to be 20-25 A/m^2 in order to have optimal operation for along period of time. However, selection of an accurate current density depends on pH, temperature and other parameters, which must also be taken into account (Kovatcheva and Parlapanski 1999).

The mechanisms of EC strongly depend on the chemical characteristics of the aqueous medium. Many researchers have studied the impact of conductivity and have demonstrated that conductivity is one of the most important parameters affecting the EC processes (Ilhan et al. 2008). Conductivity is defined by the concentration of salts (including NaCl) in the aqueous media. It was found that chlorine ions could reduce the negative effects of other anions such as HCO_3^- and SO_4^{2-}. These anions react with Mg and Ca in the solution and precipitate on the electrodes surface (creating an insulative layer on the electrodes), leading to higher potential between the electrode, a decrease in current efficiency and higher power consumption. It is suggested that 20% Cl^- ions, among the rest of components in water, should be present to reduce the passivation of electrodes (Chen 2004).

One of the most important parameters that have direct impact on EC mechanisms is pH. The pH value affects EC process from two different aspects: CE and solubility of metal hydroxides. It was found that aluminum electrodes have higher CE either in acidic or alkaline conditions rather than neutral conditions. On the other hand, neutral pH results in higher consumption of energy due to changes in conductivity. Therefore at higher conductivities, pH influence is insignificant. Furthermore, EC process can affect the pH of the wastewater. If the pH of present wastewater is acidic, evolution of hydrogen at cathode surface and the release of OH^- result in an increase in pH. Also, in acidic conditions, CO_2 is oversaturated in wastewater and due to the presence of hydrogen bubbles; they escape from the wastewater leading higher pH. On the other hand, in conditions where the pH of wastewater is high, Ca^{2+} and Mg^{2+} co-precipitate with $Al(OH)_3$ as hydroxides leading to a decrease in pH. Pollutants e.g. COD, oil and great removal has been investigated to be optimal in neutral pH for aluminum electrodes (Chen et al. 2000).

The impact of temperature on EC has not been widely investigated. Based on current literature, it was only found that increase in temperature up to 60 degrees would increase the CE and therefore minimize the power consumption (Chen 2004). The increase in CE was attributed to the destruction of aluminum oxide layer, which is formed on the anode surface. It was concluded that at higher temperatures, the flocs become denser due to the $Al(OH)_3$ gel shrinking and formation of more compact flocs, which have higher affinity to deposit on electrode's surface. In addition, higher temperature results in higher conductivities and therefore less energy consumption. Power supply for EC process is also another important parameter. Mostly direct current (DC) has been applied but in this case oxidation of anode and passivation of cathode might take place. It is recommended that in order to diminish the oxidation and passivation of aluminum electrodes, the direction of current should be changes every fifteen minutes (Chen 2004). In another study the on/off electrical modes were implemented to reduce these unfavorable phenomenon (Ibeid et al. 2010; Bani-Mehlem and Elektorowicz 2010). Moreover, Mao et al. (2008) found that alternating current prevents the fomartion of aluminum oxides (passivation) on the anode surface. The type of material used, as electrodes are very important since it generates the coagulants. Both aluminum and iron electrodes have been used for water and wastewater treatment. However, due to the high coagulation potential of Al^{3+}, Al electrodes have gained a great deal of attention in wastewater treatment. They can be used for both anode and cathode or in a combination with iron, aluminum as an anode and stainless steel as a cathode. The stainless steel cathode is recommended in case of high Mg and Ca ion concentrations in wastewater. Other important parameters that affect the EC process are particle size, retention time between electrodes, and electrode spacing (Kul'skii et al. 1978).

2.3.5. Advantages and Disadvantages

The advantages and disadvantages of electrocoagulation process have been illustrated in Table 2-3 and Table 2-4 (Chen 2004; Mollah et al. 2001).

Table 2-2 Advantages of EC technology

Advantages	a. The quality of treated wastewater obtained from EC process is excellent: minimum suspended solids, clear, odorless and edible
	b. Close to 100% removal of colloidal particles; due to the electrical field that is passing through the wastewater, colloidal particles are forced to move faster and therefore coagulation is enhanced
	c. Presence of minimum total dissolved solids (TDS); therefore, the cost of water recovery would be minimal
	d. Easy to operate, manage and control
	e. Minimum sludge production and good settling characteristics in case where appropriate current density is applied. The sludge produced by EC is mainly metallic oxide/hydroxide sludge which is readily dewaterable and settelable
	f. Chemical addition is minimized. Secondary pollutants are not generated while in chemical coagulation, the high concentrations of chemicals result in generation of the secondary pollution
	g. Flocs formed in EC process are much more dense and contain less bound water. In comparison to chemical coagulation, they are more compact, larger and stable in acidic conditions and readily separated from the wastewater
	h. In contrast to chemical coagulation, the bubble formation in EC process promotes the removal of some impurities by conveying them to the surface. Removal can be performed by skimming the surface of wastewater
	i. Solar energy can be used to create electrical energy for EC functioning
	j. Requires minimum and relatively simple maintenance

Table 2-3 Disadvantages of EC technology

Disadvantages	a. Its application is not beneficial where the cost of electricity is high
	b. Frequent replacement of electrodes; sacrificial anodes dissolute into wastewater due to corrosion of anode by electrochemical oxidation.
	c. Passivation of cathode and oxidation of anode; deposition of calcium carbonate and magnesium hydroxide on cathode surface decreases the electrical current efficiency and results in higher power consumption
	d. Requiring a high conductivity; if the wastewater does not contain substantial amount of salt ions (to increase the conductivity), higher electrical voltage is required to achieve the objectives
	e. Dissolution of coagulant hydroxides; pH changes might affect the generated hydroxides

2.3.6. Applications of EC

Electrocoagulation (EC) has been widely applied to remove a large range of pollutants from water and wastewater. Adhoum et al. (2004) investingated the EC potential (using aluminum electrodes) for the removal of heavy metals (e.g. Cu^{2+}, Zn^{2+} and Cr (VI)) in wastewater and found it to be highly effective. Optimum pH and current density was found to be 4-8 and 0.8-4.8 A/m^2 respectively while keeping the charge loading constant. Furtheremore, metal removal from acidic soil leachate was also studied using stainless steel electrodes and significant removal efficiency was obtained fro Pb, Cr and Cu (more than 99.8% removal). It was also found that the total cost of elecrocoagulation is five times lower than the conventional chemical coagulation (Meunier et al. 2006). The removal of chromium (VI) from synthetic wastewater by EC revealed that this technology was a cost effective technology and highly potential for the removal of heavy metals from wastewater. The time required to reduce the concnetration of heavy metals to less than admissible legal levels was only 20-40 minutes. Also, application of iron as anode had better results in removal of Cr in comparison to aluminum (Bazrafshan et al. 2008). Arsenic was also removed by electrocoagulation to less than 2 mg/L while the initial concnetration was 100 mg/L (Hansen et al. 2007). Removal of Zn, Cu, Ni, Ag in EC process was also studied while assessing many parameters that can affect the process. Initial concentration of 500 to 5000 mg/L of these metals did not have any impact on their removal rate. Higher current densities increased the rate of processes but reduced the efficiency (Heidmann and Calmano 2008).

Electrocoagulation has also been applied for the treatment of textile effulents. A level of 86% removal was obtained for COD (3 minutes opeartion time and at 600 mV electrical potential) while 100% color removal was achieved (Zaroual et al. 2006). Moreover, EC efficiency in organic pollutant removal from highly complex industrial wastewater yield 84% reduction in COD. The optimal conditions were found to be pH 8 and 45.45 A/m^2 current density. Color and turbidity were removed by percentage over 97% (Linares-Hernandez et al. 2007). Application of EC to potato chips manufacturing wasewater was investigated as well. Aluminum electrodes were found to have higher efficiency in removal of COD, turbidity and TSS in comparison to iron electrodes (Kobya et al. 2006).

Different EC operational parameters of EC was also studied to enhance phosphate removal. Disregard of the initial concentration of phosphate in wastewater, 100% removal of phosphate was achieved when aluminum electrodes were used. Increasing current density resulted in higher CE and removal rate however it increased the power consumption. In general, pH 7 was an optimal value for the removal of phosphate while other parameters were varing. It was concluded that aluminum electrodes are recommended in the aeras where phosphate removal is required (Irdemez et al. 2006).

In addition, hybrid processes, i.e. employing two or more treatments at the same time, have been recently investigated to enhance and improve the quality of wastewater. In this regard, Alshawabkeh et al. (2004) integrated the EC process into mixed liqour and appraised the effect of direct electric fields on physicochemical and biochemical properties of aerobic mixed sludge. Different charge loadings (0, 0.28, 0.57, and 1.14 V/cm) and direct currents (13-70 mA) were applied to activated sludge for a period of 50 hours. The values of pH and dissolved oxygen (DO) did not vary in different electrical fields, which indicated that EC does not have impact on them. Furthermore, applying voltage gradient lower than 0.28 V/cm did not have any impact on COD removal while the application of higher voltages than 1.14 V/cm had harmful effects and decreased the rate of COD removal. Therefore, the optimum electrical voltages were found to be in the range of 0.28 and 1.14 V/cm. In another batch study, the impact of EC on enhancement of nutrient removal from aerated culture was studied (Yu et al. 2006). Electricity requirement was less when iron electrodes were used and in terms of phosphorus removal, the electrolysis in aerobic conditions achieved higher removal than in anoxic conditions. It was concluded that phosphorus removal could be highly enhanced if intermittent electrocoagulation is combined with an intermittent aerated bioreactor. A sudden rise in the amount of produced sludge was observed when continuous electrolysis was applied to both aerobic and anoxic conditions (Yu et al. 2006). However, deep understanding of the impact of EC on reducing MBR fouling and enhancing its efficiency, as a hybrid, unit is missing in the literature. Hence, attention is directed to extension of knowledge concerning the processes and mechanisms, which take place in EC combined with MBR.

2.3.7. Electro-coagulation Applied to Membrane Processes

New approaches to improve the performance of wastewater treatment units are required. One of the modern approaches is usage of membranes due to higher quality of effluents, and other approach is to decrease the usage of chemicals for coagulation processes. Therefore, application of electrocoagulation to MBR, as one operation unit, permits to achieve the most successful results.

2.3.8. Submerged Membrane Electro-Bioreactor (SMEBR)

Direct implementation of electrocoagulation unit inside submerged membrane bioreactor has accomplished promising achievements towards the reduction of membrane fouling and increasing its efficiency (Bani-Mehlem and Elektorowicz 2010). This hybrid novel system is called submerged membrane electro bioreactor (SMBER) (Elektorowicz et al. 2009). In SMBER, the EC unit is incorporated inside the submerged membrane bioreactor allowing direct interactions between different processes. These processes consist of biological treatment, electrocoagulation processes and membrane filtration.

Aluminum electrode has gained better results; therefore, this metal has been applied as an anode material to release Al^{3+} for coagulation processes and stainless steel for the cathode material. These electrodes are submerged in the MBR system while surrounding the submerged membrane.

The SMEBR system has many advantages such as (Elektorowicz et al. 2009):

1. Small footprints
2. No addition of chemicals (no secondary pollutant generation)
3. Reduction in operating costs (less aeration requirement in comparison to conventional SMBR and no costs for chemicals)
4. High quality sludge (better dewatering and conditioning)
5. Introduction of a new sustainable design for wastewater treatment system

However, optimal functioning of SMBER requires further research from different aspects. As discussed in Section 2.1.2., the major issue that has restricted the application of membranes is fouling. Membrane fouling can be as a result of biofouling and inorganic fouling of membranes. The major inorganic foulant in aerobic MBRs was found to be calcium carbonate scaling (Jude 2004). On the other hand, calcium was shown to have beneficial effects on membrane filterability from the biofouling point of view according to DCB theory. Arabi and Nakhla (2008) discovered that 250 mg Ca^{2+}/L in influent wastewater resulted in higher filterability of membrane due to divalent cations bridging with negatively charges functional groups and reduction in SMP whereas 750 mg Ca^{2+}/L clogged the membrane due to formation of calcium carbonate precipitates which deposited on membrane surface. Furtheremore, presence of calcium salts affects the electrical conductivity of the medium used which, as dicussed in Section 2.2.4., is one of the most important factors influencing the EC process. Therefore, investigations are required to undertand the impact of different direct electrical fields and conductivities on actiavted sludge characteristics, in the zone between anode and cathode in EC process. Evaluation of the impact of calcium either on sludge properties or on electrocoagulation process through direct application of DC field to activated sludge is missing throughout the literature. It is assumed that increasing the conductivity, by addition of calcium salt, can reduce the electrical charge loading and enhance EC pollutant removal efficiency. In addition, it might be able to improve the sludge characteristics through bridging with negatively charged collidal particles and enhance bioflocculation, which later results in improvement of membrane filterability. Therefore, the main objective of this research is to evaluate the activated sludge properties under different DC electrical fields and calcium concentrations. From the literature it was found that MLSS is also one of the factors that has significant impact on sludge characteristics and membrane fouling. Therefore, the impact of MLSS was also studied for different variations of electrical fields and conductivities.

Chapter 3 Methodology

3.1. Introduction

In order to achieve the objectives of this research outlined in Chapter 2, a series of bench scale laboratory tests were performed. The detailed approach for performing these tests in order to obtain the required data was set based on a literature review and previous experience generated by Dr. Elektorowicz's research team. The experiments were implemented in a manner to reveal the following information: a) impact of different DC electrical fields on activated sludge properties, b) impact of different calcium concentrations on activated sludge properties, c) impact of different calcium concentrations on electrocoagulation process, d) impact of activated sludge composition on the deposition on the electrodes' surface. Figure 3-1 is a schematic diagram indicating the approaches developed and followed throughout this laboratory study: I. Preparation and set up, II. Laboratory experiments III. Analyses. In order to investigate the impact of the MLSS concentration, all laboratory experiments were carried out for both low and high concentration ranges of MLSS where:

Low Range MLSS (abbreviated LR MLSS): 5 000-7 000 mg/L

High Range MLSS (abbreviated HR MLSS): 10 000-12 000 mg/L

The above-mentioned ranges are provided in the literature on membrane bioreactors.

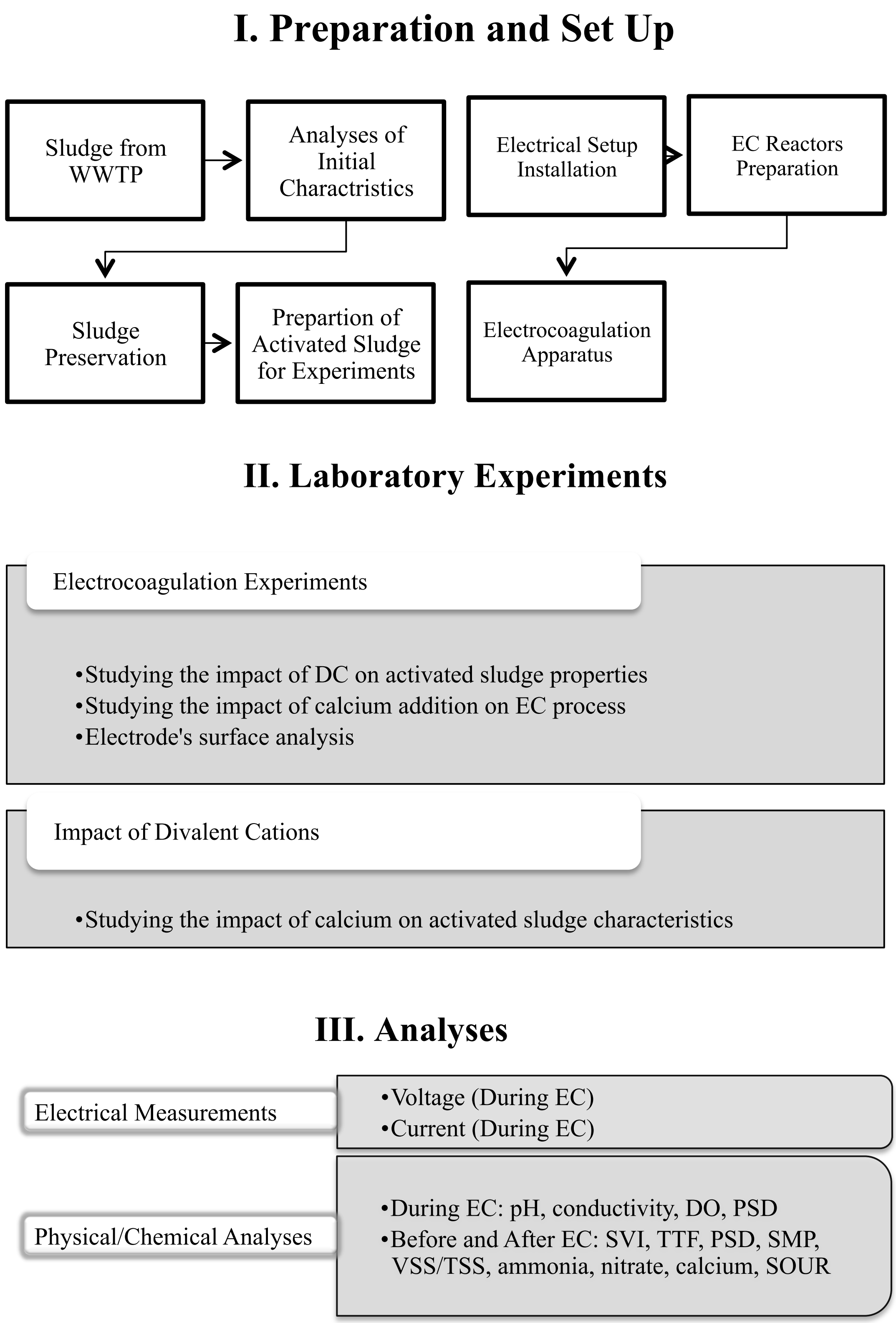


Figure 3-1 Schematic diagram of the approaches followed throughout this study

3.2. Experimental Work

A series of experiments were grouped into three categories, those studying the impact of electrocoagulation process on electrodes and activated sludge, with and without the addition of calcium, and those studying the impact of divalent cations on activated sludge in the context of calcium bridging phenomena:

- The impact of electrocoagulation was divided into two subcategories, which permitted to generated data on:
    i. The impact of electrical field exposure to activated sludge properties
    ii. The impact of calcium concentration on electrocoagulation processes and activated sludge properties
- The impact of sludge composition on organics and inorganics depositions on electrode surface during the electrocoagulation process
- Impact of divalent cations such as calcium on divalent cation bridging in activated sludge

3.2.1. Experimental Reactors for Electrocoagulation Process

In order to investigate the above aims, several experimental runs were performed. The design of electrodes and operation conditions used in this research were dictated by the patented design of Submerged Membrane Electro-bioreactor - SMEBR (Elektorowicz et al. 2009). Bench scale electrocoagulation tests were performed in a series of 1.5 L containers, equipped at the bottom with three cubic aeration porous stones for keeping the DO level concentrations constant (6-8 mg/L) and mixing sludge purposes. All reactors were monitored during the EC process to ensure the aerobic condition within the cells. The operation time was chosen to be 48 hours to ensure sufficient biological treatment and coagulation processes. Samples were taken from the reactors before the run, after 8 hours, after 24 hours and after 48 hours of operation to control and monitor the variations within the system. The activated sludge (Section 3.4.1.) was not fed during the operations.

Each bench bioreactor was employing a flat aluminum perforated (40% opening) as the anode and stainless steel mesh as the cathode. The stainless steel mesh was fixed with a stainless steel frame to minimize its movement during the experiment. Both electrodes were attached to a plexiglass frame in order to keep them in a vertical position at the constant distance of 5 cm. In addition, above this frame each electrode had a 1 cm extension providing a sufficient space for DC power connections (Figure 3-2).

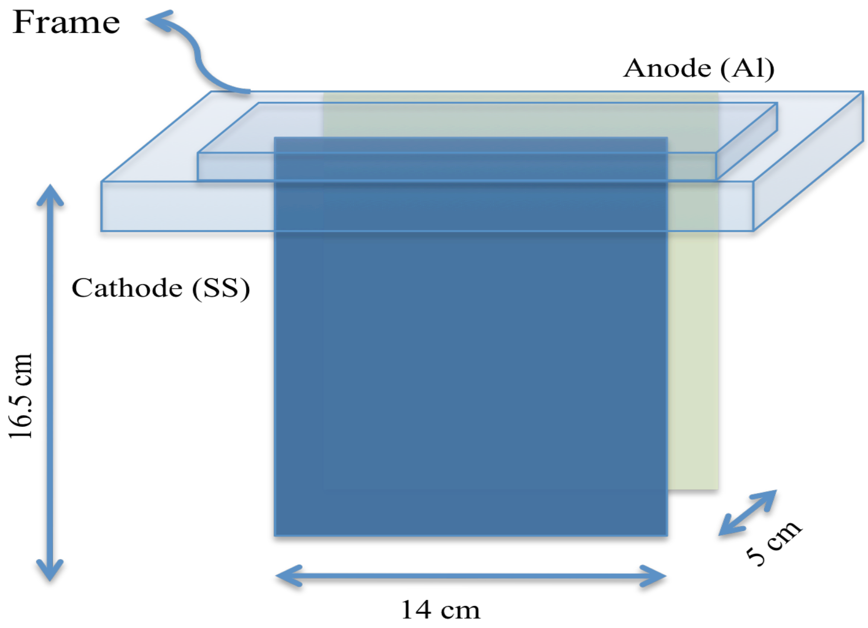


Figure 3-2 Configuration of electrodes immersed in EC reactor

DC power supply (TES 6230) and all electrodes were connected through a distribution panel. In case of having different operation times for electrocoagulation process, a switch-timer was connected to the circuit (between the distributor and the cathode) in order to control the sludge exposure time to DC. Based on previous research (Ibeid et al. 2010), in all experiments the current density was kept constant to the value of 20-25 A/m^2. Current density was calculated as follow:

Current density (A/m^2) = Electrical current (A) / Effective surface area of electrode (m^2)

Table 3-1 is a summary of the characteristics of the electrocoagulation reactors with their dimensions.

Table 3-1 Characteristics of EC reactor

Electrodes		**Reactors**		**Power Supply**	
Material (anode and cathode)	Aluminum (Al) and Stainless Steel (SS)	**Material**	Plastic	**Current density (A/m^2)**	20-25
Shape	Rectangular plate	**Reactor mode**	Batch mode	**Voltage (V)**	Variable
Size (cm)	14×16.5	**Dimension (cm)**	17×18.5×8		
Number	2	**Volume (L)**	1.9		
Plate arrangement	Parallel	**Used wastewater volume**	1.5		
Effective electrode surface area (cm^2)	107	**Electrode gap (cm)**	5		
		Stirring mechanism and aeration system	Cubic air stones		

The air stones implemented to supply aerobic conditions were connected to an air valve, which supplied the air in the reactors.

i. Impact of EC on Activated Sludge Properties

The conditions applied to the experimental runs for investigating the variations in activated sludge properties, while being exposed to electrical field, are provided in Table 3-2. In these experimental runs, four different electrical modes and two concentration ranges of MLSS were considered. A control reactor without electrical field (electrocoagulation) was run in parallel to other electro-bioreactors for comparison purposes.

Table 3-2 Electro-bioreactor operational conditions

MLSS (mg/L)	**Electrical modes (minutes)**	**Abbreviations used for electrical modes**	**Abbreviations used for CONTROL reactors (No EC)**	**Current density (A/m^2)**	**Total number of experiments**	**Operation time (hour)**
5000-7000	Continuous On	Continuous [a]	**C1**	20-25	10	48
	5 minutes On/ 5 minutes Off	5 ON: 5 OFF [b]				
10000-12000	5 minutes On/ 10 minutes Off	5 ON: 10 OFF	**C2**			
	5 minutes On/ 15 minutes Off	5 ON: 15 OFF				

[a] Continuous application of DC without any interruption during the 48 hours

[b] Intermittent application of DC for 5 minutes and disconnection for 5 minutes during the 48 hours of operation

In each run, four reactors at different electrical modes and one control were operating simultaneously, therefore a total of 10 experiments were performed. Figure 3-3 depicts the sketch for the experimental set up applied to these experiments. The picture of the set up is presented in Appendix II.

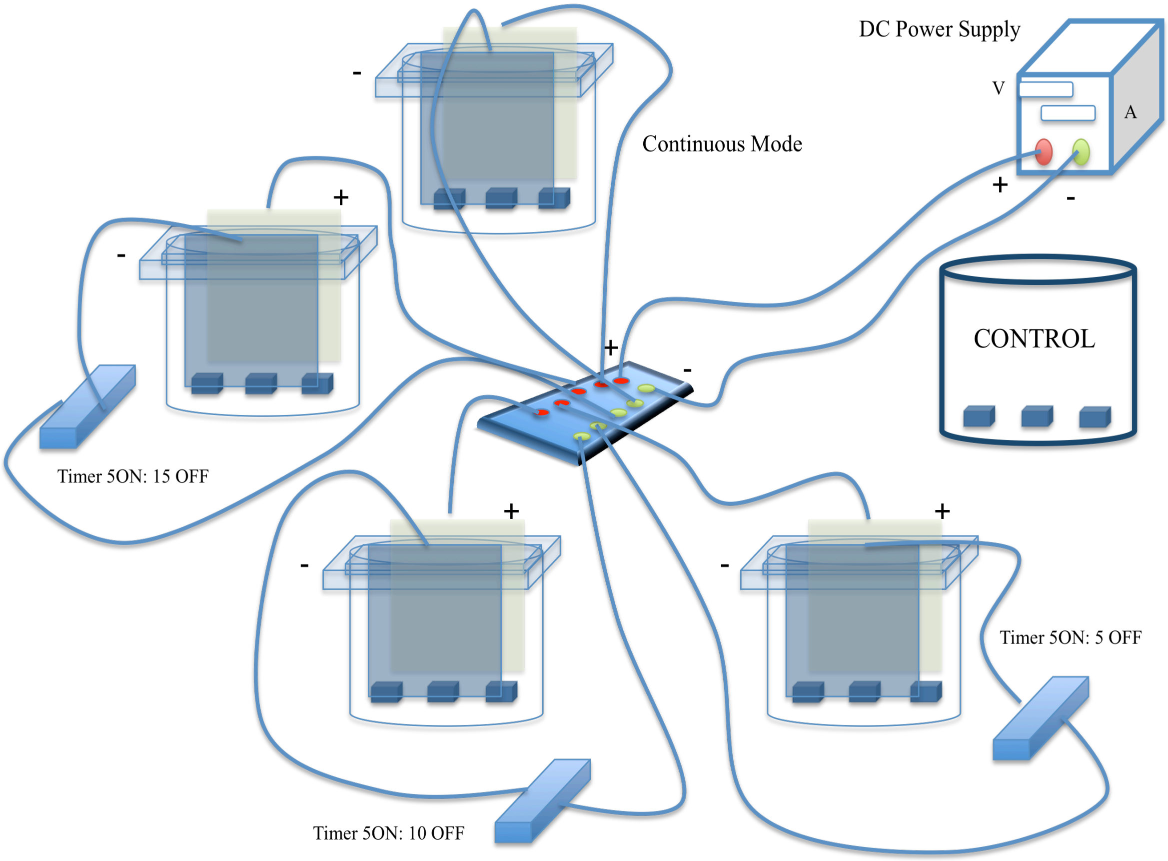


Figure 3-3 Electrical connections applied to electro-bioreactors for investigating the impact of EC on AS properties

Since the components of the electrical circuit were connected in parallel, the same voltage (V) was applied to each reactor. On the other hand, the current showing on the DC power supply was the sum of the currents of all the four reactors (considering one reactor did not have EC process). The corresponding current density (20-25 A/m^2 or 2.5 mA/cm^2) for each reactor during the experiment was calculated as follow:

$$I = A \times 2.5 \times 4 \qquad \text{(Eq. 12)}$$

Where,

I = Current showing on power supply, mA

A = Effective electrode surface area (cm^2)

Since the effective electrode surface area was 106.29 cm^2, the current applied to one reactor was 0.267 A and the current for four reactors was 1.07 A. In order to monitor the voltage and current during the EC process for each reactor, all connections except for one reactor were disconnected so that the current for that specific reactor could be read. In case of a drop in the current value, due to the increase in electrical resistance, the voltage was increased to obtain the same constant value for current density.

ii. Impact of Calcium Addition on EC process

As discussed in Section 2.1.4., since calcium is a divalent cation, it has the potential to bind with negatively charges particles (SMP), thus, enhance the bioflocculation phenomenon in the activated sludge. On the other hand, calcium salt increases the conductivity in EC process resulting in lower power consumption i.e. lower voltage is required to obtain the same current. Therefore, calcium chloride was chosen for this experiment to study the impact of calcium addition from two aspects simultaneously: bioflocculation and electrocoagulation. All runs were performed for two concentration ranges of MLSS to study the impact of MLSS as well. For this purpose, prior to the commencement of EC process different concentrations of $CaCl_2$ salt were added directly to the reactors. Table 3-3 reveals the operational parameters used in this experiment. In each run, four reactors were running simultaneously with different electrical modes. Run C3-4 was used as the control for run A3 and A4 and run C5-6 was used as the control for run A5 and A6 (no addition of calcium). Therefore, a total of 24 experiments were performed to investigate the impact of calcium addition on EC performance and activated sludge properties. The typical concentration of calcium in municipal wastewater is reported to be between 20 and 120 mg/L. 250 and 750 mg Ca^{2+}/L was chosen for this experiment to better understand the role of calcium on both electrocoagulation and bioflocculation phenomena.

Table 3-3 Operational parameters for studying the impact of conductivity on activated sludge

Ca^{2+} (mg/L)	MLSS (mg/L)	Electrical modes (minutes)	Abbreviations used for electrical modes	Corresponding conductivity (µS/cm)	Current density (A/m^2)	Total number of experiments	Operation time (hour)
0	5000-7000	Continuous On 5 minutes On/ 5 minutes Off 5 minutes On/ 10 minutes Off 5 minutes On/ 15 minutes Off	Continuous 5 ON: 5 OFF 5 ON: 10 OFF 5 ON: 15 OFF	1191	20-25	24	48
250				2436			
750				4010			
0	10000-12000			977			
250				2240			
750				4870			

[a] Control reactor (C3-4) for run A3 and A4

[b] Control reactor (C5-6) for run A5 and A6

The electrical set up used in this experiment was the same as the set up used for investigating the impact of EC on activated sludge properties except for the control reactor. In this experiment, at all times, the control reactor had electrocoagulation process but no calcium was added to the reactor. Removal of soluble microbial products (SMP) and particle size were the chosen parameters to assess the bioflocculation and coagulation phenomena.

3.2.2. Depositions on Electrodes' Surface

The depositions of organic and inorganic sludge components on the electrodes were investigated to assess their affinity to electrodes while being exposed to electrical field. Since organic matters mostly bear a negative charge, it was expected that their affinity was higher to the anode; however, cations (including calcium used in this experiment) having positive charges were expected to have higher affinity to the cathode. To investigate the fractioning of these substances on electrodes, at the termination of each experiment, organics and inorganics were desorbed from the electrode surface and analyzed.

When the bench scale operations were terminated after 48 hours, at first, while the aeration was still blowing, samples were taken from the space between the electrodes for further analysis. After sampling, the electrodes were taken out from the reactors and disassembled from the supporting frame. Each electrode (anode and cathode) was vertically cut in half, assuming uniform distribution of sorbed substances throughout the electrode surface. One half of each electrode was used for organic material analysis and the other half was used for inorganic. In order to desorb organic material from the electrode surface, half of each electrode was soaked in 50 ml alkaline solution (solution pH was set to 11 by the addition of sodium hydroxide, NaOH) for five minutes. Meantime, the surface of the electrodes was also manually wiped to ensure that all sorbed substances are detached. After desorption, the solutions were filtered through 0.45 μm filter paper to obtain the soluble organics and measurement of soluble COD were carried out as a representative of soluble microbial products (SMP) (Meng et al. 2006). Desorption of inorganic matters attached to the electrodes' surface were performed by soaking the other half of each electrode in 50 ml 4% HNO_3 for 5 minutes while all attached substances were also manually wiped from electrode surface. The solutions obtained were filtered through 0.45 μm filter paper and analyze for the calcium concentration. In order to consider the other half of the cut electrode, for both organic and inorganic materials, the concentration values obtained after analysis were multiplied by two.

3.2.3. Impact of Divalent Cations on Activated Sludge Properties

Divalent cations are widely known to improve the microbial flocculation by formation of bridges with extracellular polymeric substances. This flocculation promotes activated sludge settling characteristics and also helps the formation of biological flocs in the bioreactors (Song et al. 2008). Therefore, a series of experiments were performed to study the impact of calcium on the sludge characteristics in batch reactors.

Since the typical calcium concentration in municipal wastewater is between 20-120 mg/L (Arabi and Nakhla 2008), two calcium concentrations were chosen (250 and 750 mg/L) to better understand the role of calcium on the characteristics of activated sludge at low and reach calcium wastewater. These concentrations were directly added to the activated sludge. As for the control reactor, one reactor was operated in parallel to other bioreactors without any addition of calcium. This impact was studied for two MLSS concentration ranges (LR and HR MLSS). Bench scale 1.5-liter reactors, equipped with aeration apparatus, were filled with activated sludge and the corresponding calcium concentration. These reactors were aerated for 48 hours to ensure sufficient time for biological reactions.

After this operation time, samples were taken out from the zone between the electrodes and analyzed for soluble COD and calcium concentration. Soluble COD (sCOD) represents the soluble microbial products (SMP) in activated sludge therefore reduction in sCOD corresponds to a decrease in SMP, which could be as a result of calcium cations bridging with positively charges extracellular polymeric substances. A total of six experiments were performed: three experiments for LR MLSS and three experiments for HR MLSS. It is noteworthy to state that in this stage of research electrical field (DC) was not applied to the reactors; therefore, the interactions within activated sludge were only studied under aerobic conditions. The operational parameters in this stage are shown in Table 3-4 representing a total of six experiments from B1 to B6.

Table 3-4 Operational parameters for studying the impact of calcium addition on activated sludge properties

Ca^{2+} addition (mg/L)	MLSS (mg/L)	Total number of experiments	Operation time (hour)
0	5000-7000	6	48
250			
750			
0	10000-12000		
250			
750			

3.3. Sampling and Sample Preservation

3.3.1. Sampling in EC Reactors

After 48 hours of operation, right after disconnecting the DC power supply and while the aeration was on and electrodes were in place, a required volume of activated sludge was sampled from the space between the electrodes by immersing a sampling vial in the activated sludge. To ensure that the obtained data from analysis are a representation of a completely mixed reactor, three sequential samples were taken from different depths of the reactor (top, middle and bottom). A total of five 50 mL samples were collected for analyses. One liter of the remaining activated sludge was withdrawn to a graduated cylinder for SVI analysis. Obtained samples were right away analyzed for TTF, particle size distribution, MLSS, MLVSS and total solids. In order to analyze the components of supernatant, samples were first centrifuged for 20 minutes at 4000 rpm and then filtered through Whatman No.40 filter papers. The filtered samples were preserved in 4 °C refrigerator until analyses were performed.

3.3.2. Sample Preparation and Sampling for the Impact of Divalent Cation (Calcium) Bridging on Electrocoagulation Process

For each experiment, 1.5-liter reactor was filled with activated sludge and prepared in order to achieve the final concentration of Ca^{2+} of approximately 0, 250 and 750 mg/L in addition to the calcium that was naturally present in the activated sludge. Calcium was added to the reactors by preparing a stock solution of $CaCl_2$; for each sample, a certain volume of 50 mg $CaCl_2$ was added to the activated sludge in order to achieve an approximate concentration of the desired Ca^{2+}. After filling the reactors with the activated sludge and connecting them to the aeration system, they were left for 48 hours. After this period, samples of activated sludge were taken from the bioreactors while being aerated continuously for mixing purposes. The samples were prepared as described in Section 3.3.1 and preserved in refrigerator for further analyses. One liter of the remaining activated sludge was used for SVI measurement.

3.3.3. Preparation of MLSS for LR and HR Concentrations

Mixed liquor suspended solids (MLSS) concentrations were prepared as follow: considering the fact that the MLSS concentration of activated sludge brought from the WWTP was between 5000 and 7000 mg/L; therefore, in experiments with low range (LR MLSS) concentrations, the AS samples were directly used. However, in experiments with high range (HR MLSS), decanted sludge was used in order to achieve the target MLSS concentration.

3.4. Materials and Sample Analyses

The analyses performed in this study were divided into three categories: i) parameters that were analyzed before and after the experiments, ii) parameters that were analyzed during the experiments, and iii) parameters analyzed for electrodes' surface.

Chemical and physical analyses performed before and after the experiments:

- pH, conductivity, SOUR, temperature, current, voltage, PO_4^{3+}, NH_3-N, NO_3^-, alkalinity, MLSS (TSS), MLVSS, TS, PSD, TTF, total metal concentrations (Ca, Mg, K, Al) and SMP as sCOD.

Parameters analyzed during the experiments:

- Current, voltage, pH, conductivity, temperature and PSD

Parameters analyzed for electrodes' surface after the experiments:

- Metal (Ca) and SMP (sCOD)

Please refer to Glossary for the list of abbreviations used in the text.

3.4.1. Activated Sludge

The activated sludge (AS) used in this research was obtained from the St. Hyacinthe wastewater treatment plant, Quebec (Canada), which treats domestic wastewater by using activated sludge process. The activated sludge taken as grabbed samples from the return activated sludge line. This sludge was brought in 20 L plastic containers from the plant to the laboratory every three weeks and was stored in refrigerator at 4 °C until experiments were performed. The initial characteristics of this activated sludge are given in Table 3-5.

3.4.2. Particle Size Distribution Analysis

During the experiments (after 8, 24 and 48 hours) 5 ml-sample of AS was taken and analyzed for particle sizes in order to obtain the variation in floc sizes by time. The particle size distribution (PSD) analysis was performed with a small amount of well-mixed activated sludge sample inserted into the Horiba, Partica LA-950 V2 Laser Scattering Particle Size Distribution Analyzer and obtaining the mean value for floc sizes using its software.

Table 3-5 Initial characteristics of activated sludge brought from St. Hyacinth WWTP

Parameter	Value [a]	Standard Deviation
pH	7.6	±0.4
Conductivity (µS/cm)	1043	±226.3
MLSS (mg/L)	5637	±662.7
MLVSS (mg/L)	5193	
Total Dissolved Solids (mg/L)	812	
VSS/TSS (%)	88	
Particle Size Distribution (µm)	55.6	±11.1
Time To Filter (Seconds)	48	±15.5
Sludge Volume Index (mL/gr)	126	±29.9
NH_3-N (mg/L)	77.7	±33.9
PO_4-P (mg/L)	44.4	±23
NO_3^- (mg/L)	14.6	±5.8
sCOD (mg/L)	298	±39.7
Ca^{2+} (mg/L)	33.7	±0.5
Alkalinity (mg/L)	326	±50.9
K^+ (mg/L)	87.8	±6.3
Mg^{2+} (mg/L)	14.8	±5.2
Temperature (°C)	19.0	
Dissolved Oxygen (mg/L)	7.6	±1.2
Cl^-	36.7	±8.1

[a] Average of six measurements

3.4.3. Analysis of Activated Sludge Characteristics

The following parameters were measured based on Standard Methods (APHA 1998): MLSS (2540 D), MLVSS (2540 E) and TS (2540 B), SVI (2710 D), TTF (2710 H), alkalinity (2320 B) and specific oxygen uptake rate (2710 B). SVI was measured using one liter graduated cylinder, where sludge was left behind to settle for 45 minutes. Time to filtration (TTF) was measured using 20 ml of AS sample, Whatman No. 40 filter paper and a stopwatch for counting the time required for filtration of 10 ml of the sample.

3.4.4. Analysis of Liquid Phase (Supernatant) and Electrode Solutions

The following components of supernatant were analyzed using HACH instrument (Hach-DR 2800). The methods used are as follow: NH_3-N: Method 10031, PO_4-P: Method 8178.

Nitrate (NO_3^-) was measured using the corresponding ion meter (probe) for nitrate measurements and Accumet Research AR 25 Dual Channel pH/Ion meter (Fisher Scientific).

As stated by Meng et al. (2006), the soluble COD can be recognized as SMP (soluble microbial products). In order to analyze this parameter, samples were first filtered through 0.45 μm filter papers (PALL Life Science GN-6 0.45 μm, 47 mm) to separate all the colloidal particles from the soluble substances. Then, by using Hach HR COD TNT-822 vials, soluble COD was measured. A similar procedure for organic fraction analysis was performed for the basic solution obtained from the electrode's surface. Hach KTO HQ30d Portable Meter and the corresponding probes were used for measuring pH, conductivity, temperature and SOUR. In this regard, methods 8156, 8160 and 10360 were applied for pH, conductivity and SOUR measurements respectively.

3.4.5. Metal Analysis

Analysis to determine the metal content in the activated sludge supernatant was performed according to the Standards Methods (3030 B) (APHA 1998) and the following procedure:

All samples obtained from the bioreactors were first centrifuged at 4000 rpm for 20 minutes and filtered through 0.45 µm membrane filter papers (PALL Life Science GN-6 0.45 µm, 47 mm) to acquire dissolved metals and were then acidified using concentrated nitric acid (HNO_3, analytical grade) to $pH<2$. The filtrate was then analyzed for the metal contents using an Atomic Absorption Spectrometer (Perkin Elmer, Analyst 100). The metals analyzed were Ca, Mg, K. Concentration of metals was then calculated as follows:

$$\text{Metal concentration (mg/L)} = A\times(B/C), \qquad \text{(Eq. 13)}$$

where:

A = Concentration of metal in filtrate solution (mg/L)

B = Final volume of filtrate (mL)

C = Sample size (mL)

Solutions obtained from the electrode's surface were analyzed in the same manner. Since the initial concentration of these solutions only represented half of each electrode, the values obtained as the metal concentration from electrode were multiplied by two. (refer to Apendix I)

3.4.6. Assessment of Aluminum Concentration

The concentration of aluminum in the samples obtained from reactors was calculated based on the amount of aluminum ion released into the solution by electrolytic oxidation of the anode material. This amount was calculated using anode weight loss. After the electrodes were immersed in the acid and base solution for electrode's surface analysis, they were subsequently washed with acid and water and completely dried. The following formula was used to calculate the concentration of aluminum in the bulk solution:

$$\text{Concentration of aluminum (mg/L)} = (D - H) / L \qquad \text{(Eq. 14)}$$

where,

D = Initial weight of aluminum electrode (mg)

H = Weight of aluminum electrode after the experiment (mg)

L = Volume of activated sludge used (1.5 L)

Chapter 4 Results and Discussions

4.1. Impact of Different Electrical Modes (EC) on Activated Sludge Properties

The results of a series of experiments, described in Chapter 3, are presented here from various aspects. Direct application of different electrical modes to activated sludge and its impact on activated sludge properties were investigated.

4.1.1. Impact on Sludge Volume Index (SVI)

The SVI index has been used in order to assess the settling ability of the particles in activated sludge. Figure 4-1 demonstrates the changes of SVI through different electrical modes in EC process for two MLSS concentration ranges (LR: 5000-7000 and HR: 10 000-12 000 mg/L).

Comparison between the initial value of SVI with the rest of data in Figure 4-1a indicates that continuous electrical mode had the highest impact (58%) on SVI reduction The 5ON:5OFF mode reached 45% reduction in SVI and there was no significant difference between 5ON:10OFF and 5ON:15OFF modes in SVI reduction (26% and 21% respectively). Since no significant change was observed for the control reactor (C1), it can be concluded that aeration itself does not have impact on SVI. It can be said that the SVI reduction is associated with both: the exposure time of the anode to dissolution and activated sludge to electrical field. Higher concentration of aluminum in the system has resulted in lower SVI value, and thus, better sludge conditioning. Since the initial SVI value was higher than 100 mL/g, it can be concluded that electrocoagulation has the potential to decrease this value to less than 100 mL/g, which represents sludge with high settleability potential.

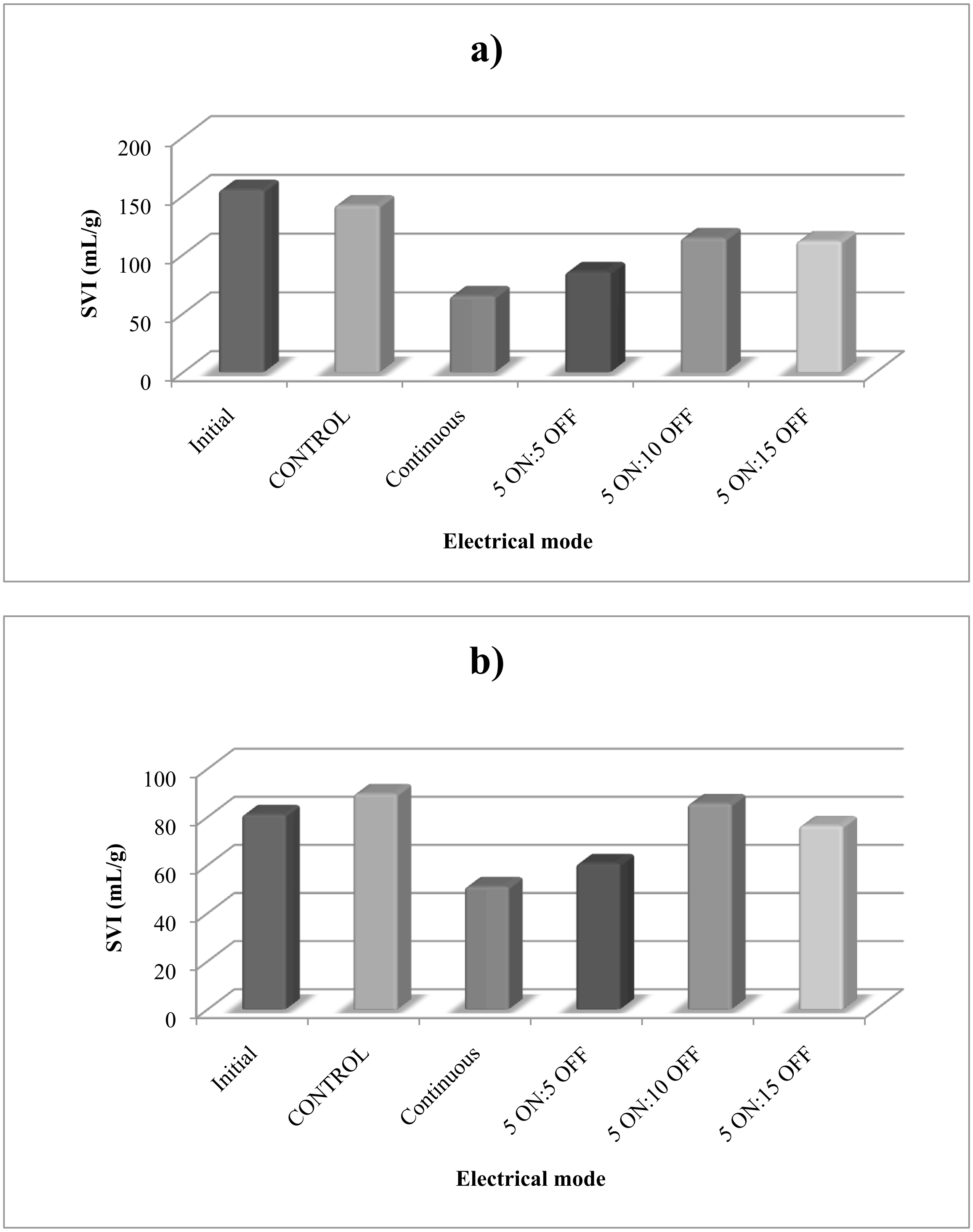


Figure 4-1 SVI Variations at LR and HR MLSS for different electrical modes (mL/g)

Furthermore, the impact of different electrical modes was also studied on HR MLSS (10000-12 000 mg/L). Figure 4-1b indicates the changes in SVI through different electrical modes for high range of the MLSS concentrations. Similar to low range MLSS, the continuous electrocoagulation process had the highest impact on the reduction of SVI (37%). The control reactor (C2) had a negative impact which resulted in higher SVI value. On the other hand, 5ON:10OFF and 5ON:15OFF modes had no significant impact on SVI reduction (5% reduction) whereas 5ON:5OFF reached 25% reduction in SVI.

It was concluded that continuous and 5ON:5OFF electrical modes have an apparent impact on SVI parameter for all ranges of MLSS concentrations. There was no significant difference between 5ON:10OFF and 5ON:15OFF modes especially at the HR MLSS concentrations. A longer exposure time to electrical field might result in denser flocs that could settle faster. In addition, the effect of EC was more considerable when applied to LR MLSS than to HR MLSS. This might be due to the ratio between the dissolved Al and the available surface of organic particles i.e. the amount of aluminum generated has not been enough to change the floc properties. The error percentage for this analysis was ± 15%.

4.1.2. Impact on Mixed Liquor Suspended Solids

Due to the fact that electrocoagulation process generates aluminum ions, it is believed that these ions react with the OH^- present in the bulk solution and form amorphous $Al(OH)_{3(s)}$, which eventually precipitates (Mouedhen et al. 2006). As a result, it is expected that MLSS concentration increases during EC process.

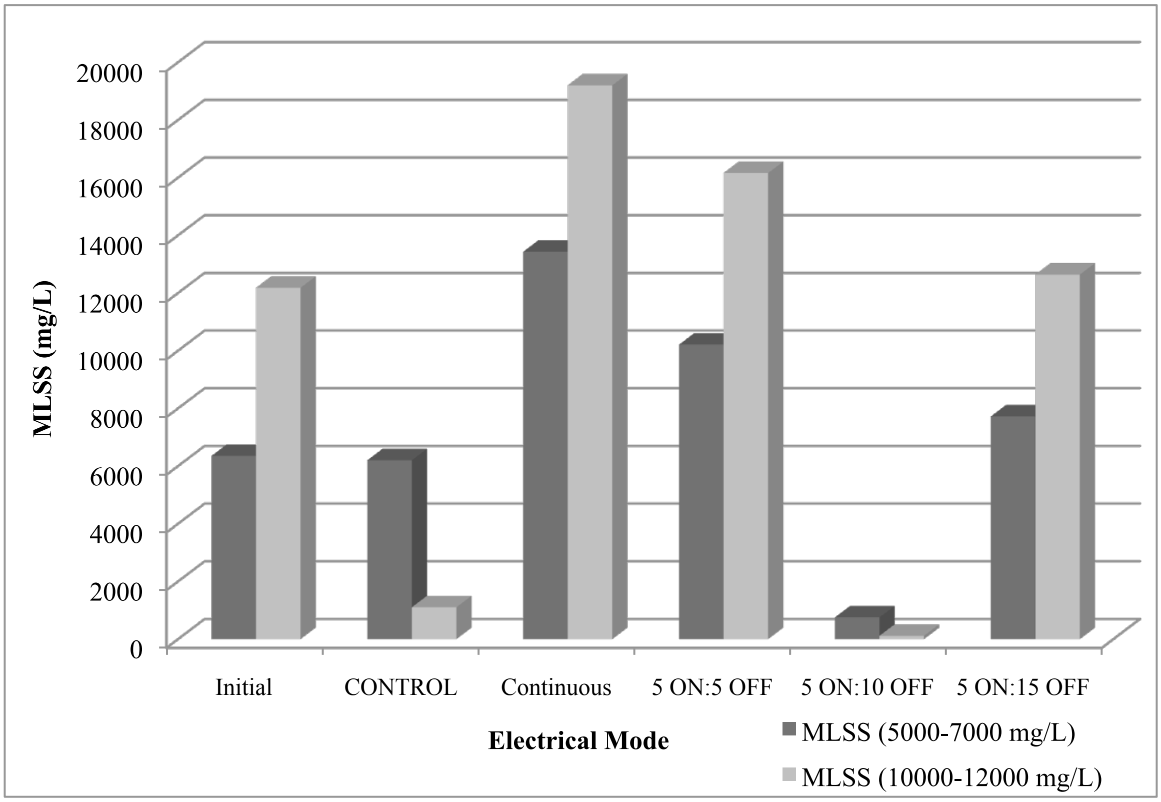


Figure 4-2 Variations of MLSS due to exposure of activated sludge to different electrical modes

As presented in Figure 4-2, the highest MLSS concentration (111% more than the initial value), at LR MLSS condition, was seen where continuous electrical mode was applied leading to high amount of aluminum release and $Al(OH)_{3(s)}$ formation. The increase in MLSS reduces as the exposure time to electricity decreases. As expected, no difference between the initial MLSS and the control cell C1 (see also Chapter 3, Section 3.1.1.) was found. The same trend was observed in HR MLSS conditions, where the continuous mode provoked an increase in MLSS concentration (57%). The percentage error in Figure 4-2 was ±15%. In this regard, Figure 4-3 shows the amount of aluminum released in the reactors after the operation time (refer to Section 3.3.6.).

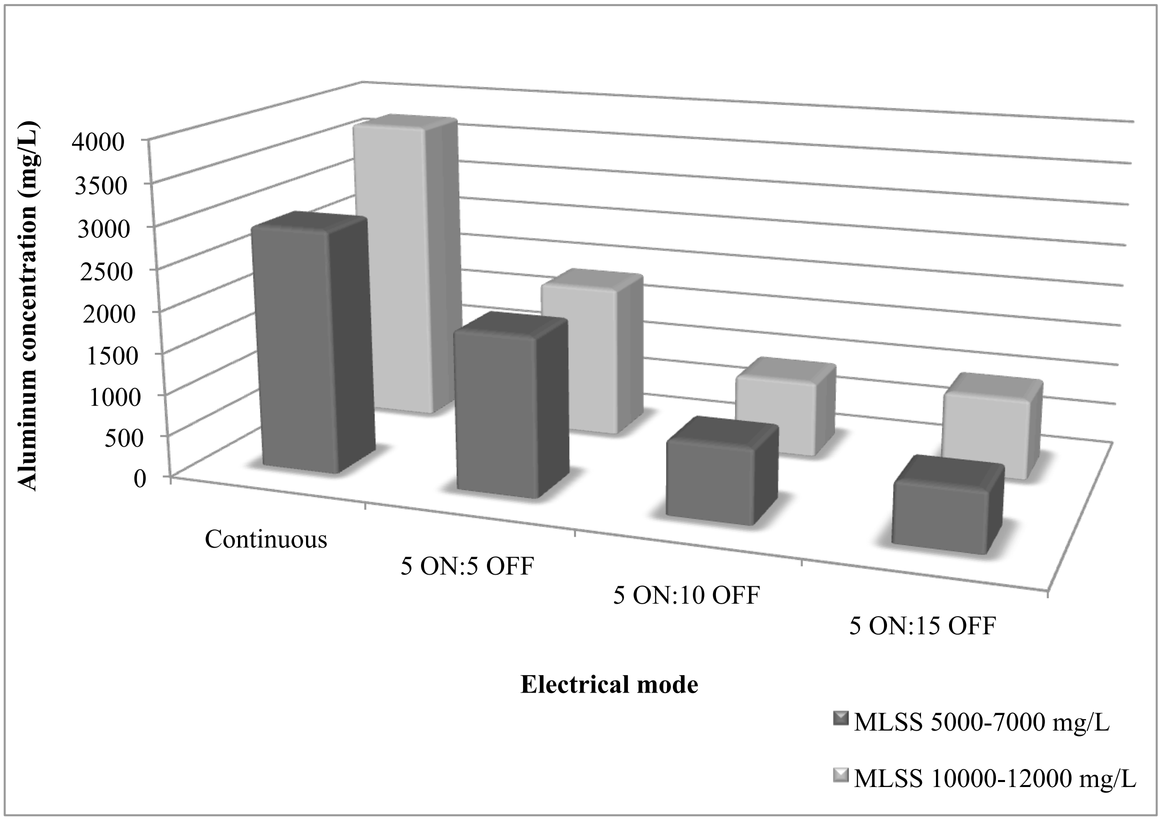


Figure 4-3 Aluminum ion released due to different electrical modes

Figure 4-3 shows similar production of aluminum ions for both ranges of MLSS concentration in all electrical modes. The only exception is the continuous electrical mode which generated 2950 and 3732 mg/L of Al in LR MLSS and HR MLSS, respectively. In other words 26% more aluminum was released to HR MLSS than to LR MLSS for continuous electrical mode.

4.1.3. Impact on VSS/TSS Ratio

In order to better understand the changes within the system, VSS/TSS ratio was used to analyze the formation of precipitates after coagulation process has taken place in the reactors. Figure 4-4 indicates the changes in this ratio initially and after 48 hours of operation for different electrical modes for both LR and HR MLSS.

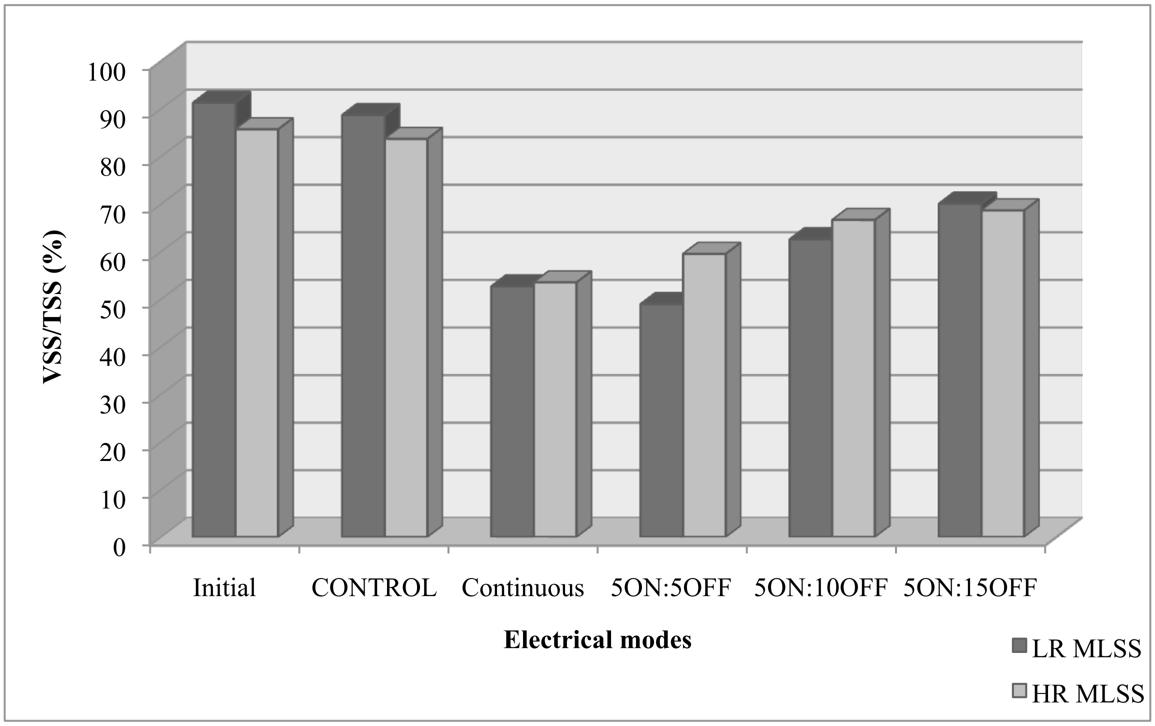


Figure 4-4 Variation in VSS/TSS ratio at LR and HR MLSS and different electrical modes

Figure 4-4 shows that VSS/TSS ratio has dropped to 53% in comparison to the initial value (around 88%) for continuous electrical mode in all MLSS concentrations. This behavior might be as a result of the aluminum hydroxide precipitates' formation within the bioreactor during coagulation process. As expected, there is an increasing trend in this ratio as activated sludge exposure time to electricity decreases since less coagulant is generated throughout the system, therefore, less solid particles are formed. There was no change between the initial values and the control cells (C1 and C2) since no coagulant was added. Consequently, Figure 4-4 clearly demonstrates the effect of electrocoagulation process on MLSS vs. different exposure modes of activated sludge to DC.

4.1.4. Impact on Activated Sludge Particle Sizes

In MBR, floc particle sizes are usually between 10 to 40 µm with the mean size value of 25 µm (Bae and Tak 2005). Addition of coagulant in the form of Al^{3+} is expected to enhance the formation of the floc and floc sizes. Furthermore, application of electrical field is expected to affect the properties of flocs. Figure 4-5 depicts the reduction in floc sizes at LR MLSS and HR MLSS during the EC process for different electrical modes. In this figure, the negative values represents an increase in particle sizes. The error percentage of this analysis was ±10%.

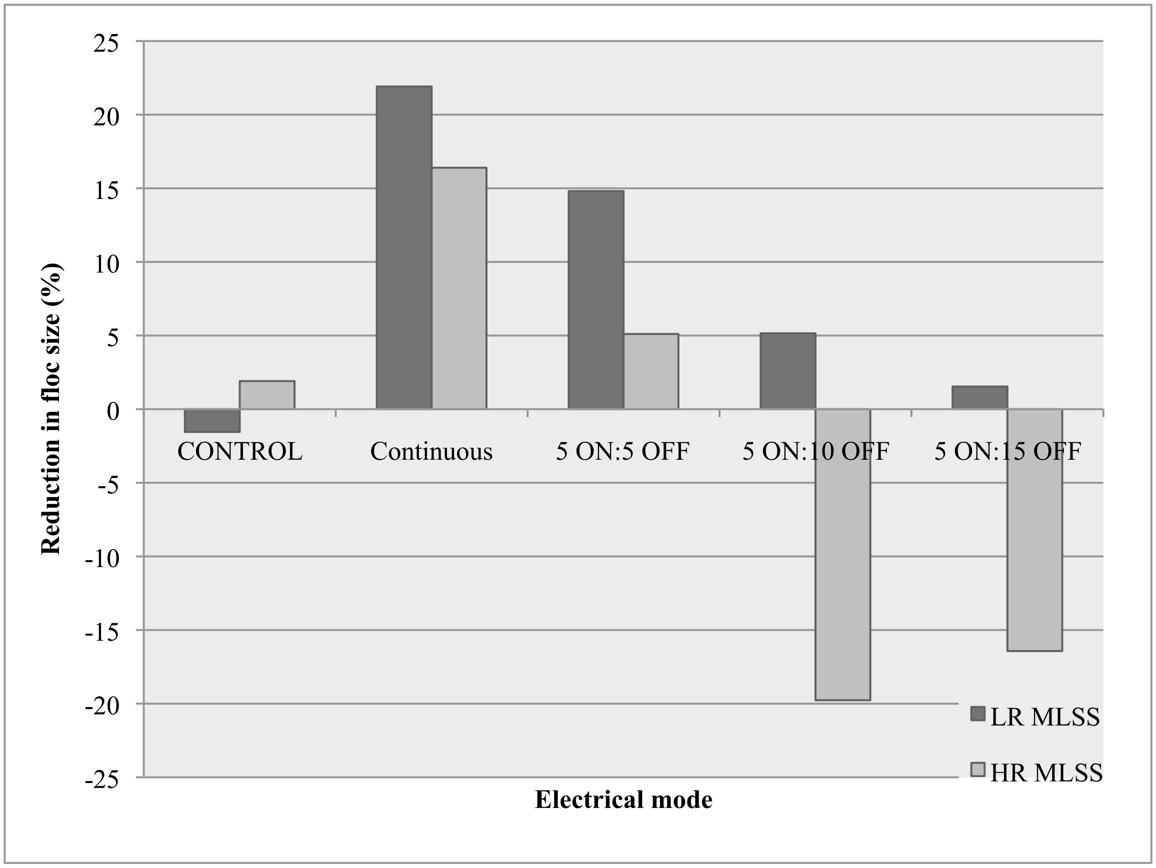


Figure 4-5 Trend in floc size variation for different electrical modes

As it can be seen from the figure, and after 48 hours of operation, that the particle size has become smaller in all electrical modes with the highest reduction in continuous electrical mode. In LR MLSS, there is trend between the time of exposure to electrical field and particle sizes. It can be observed that the longer exposure time of activated sludge to electrical field has yield smaller floc sizes. On the other hand, in case of HR MLSS, final particle sizes are larger than the initial value when 5ON:10OFF and 5ON:15OFF modes are applied.

Therefore, it can be concluded that in HR MLSS, longer operation time (more than 48 hours) is required to obtain smaller particle size than the initial size. Furthermore, in LR MLSS flocs become smaller in comparison with HR MLSS. Smaller particle size might be attributed to the removal of bound water to the flocs due to electrokinetic phenomena such as electroosmosis. Electroosmosis in electrokinetic systems is defined as the removal of water from colloidal particles under applied electrical field (Ibeid et al. 2010). In order to better understand the above-mentioned behavior, time to filtration (TTF) of samples taken after the EC process was studied. Figure 4-6 and Figure 4-8 indicates the changes in TTF for different electrical modes for LR and HR MLSS respectively. The percentage of error for this analysis was ± 5%.

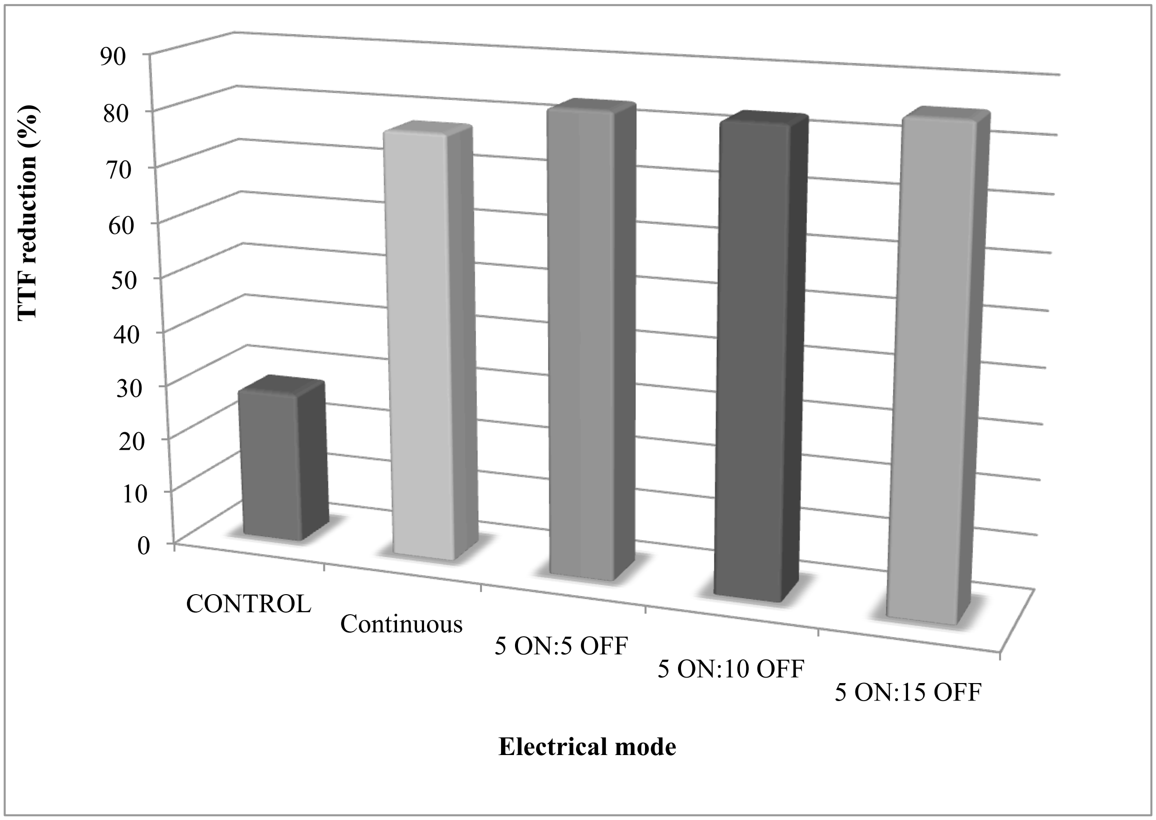


Figure 4-6 Impact of electrical field on time to filtration (TTF) reduction (LR MLSS)

This figure shows that the highest reduction in TTF was obtained in 5ON:15OFF, 5ON:10OFF and 5ON:5OFF modes reaching values between 85% and 83%. The continuous mode had a slight lower reduction in TTF (78%). These results indicate that continuous exposure of activated sludge to electrical field has rather lower impact on TTF parameter than an intermittent exposure. Therefore, it can be concluded that 5ON:5OFF mode has higher impact in terms of particle size, TTF and reduction in energy consumption since it not only reduces the time required for filtration but also forms flocs having higher density leading to better settleability of sludge. In this regard, the particle size variation was also studied during the period of 48-hour EC operation.

The results are provided in Figure 4-7 and Figure 4-9 for LR and HR MLSS respectively. The percentage of error for this analysis was ± 8%.

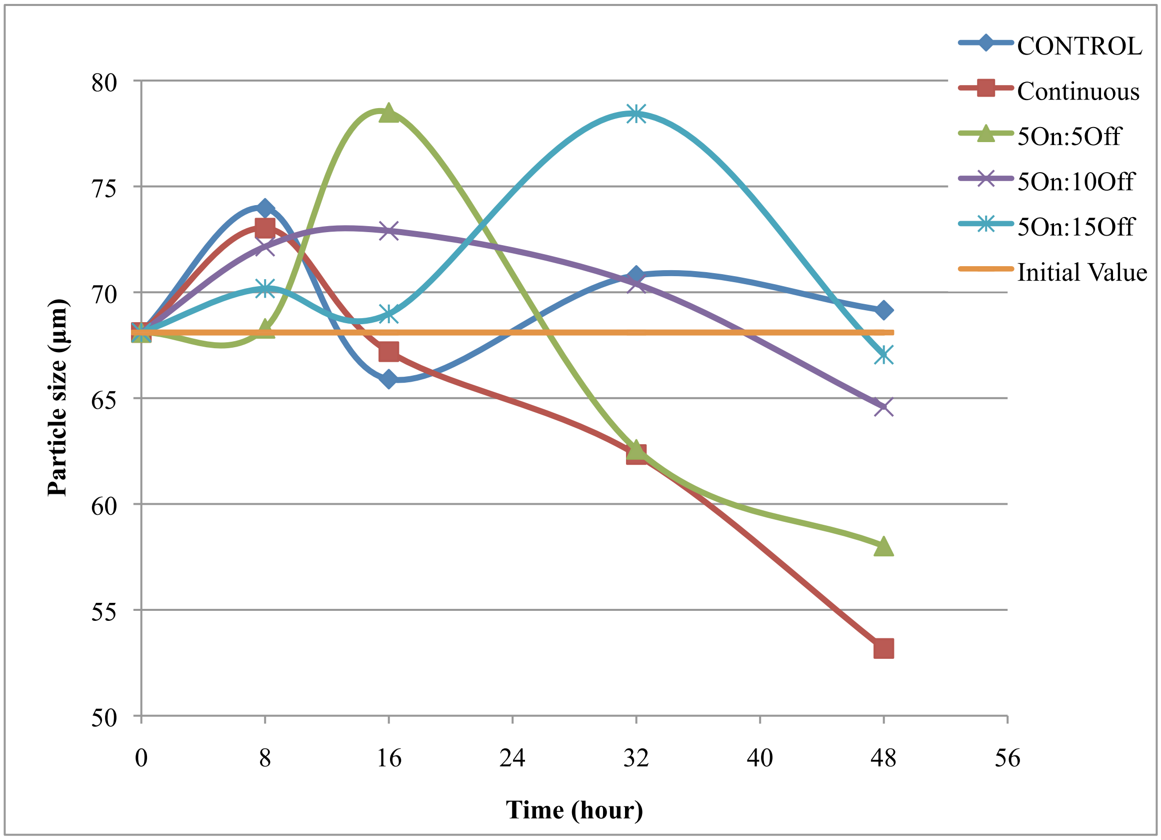


Figure 4-7 Floc size variation in different electrical modes during 48 hours of operation (LR MLSS)

This figure indicates that after 8 hours of operation, in continuous electrical mode, particle size has reached a maximum value and then has started to become smaller. The same trend was observed for other electrical modes with the difference in the time required to reach the maximum particle size. It can be said that as the exposure time period to electrical field decreases, more time is required to reach the maximum floc size. In this experiment, after 32 hours of operation, floc sizes were becoming smaller for all electrical modes. This might be due to the removal of bound water from the flocs by electroosmosis phenomenon. It can be assumed that longer exposure time to electricity enhances the electroosmosis phenomenon and more water is removed from colloidal particles (Ibeid et al. 2010). In addition, smaller particle size might be beneficial for membrane bioreactors, since it was found that the small sludge particles can provide a favorable environment for enhancement of mass transfer, thus enabling the system to show a higher organic removal rate and more adaptability to changes in the influent quality and quantity (Huang et al. 2001).

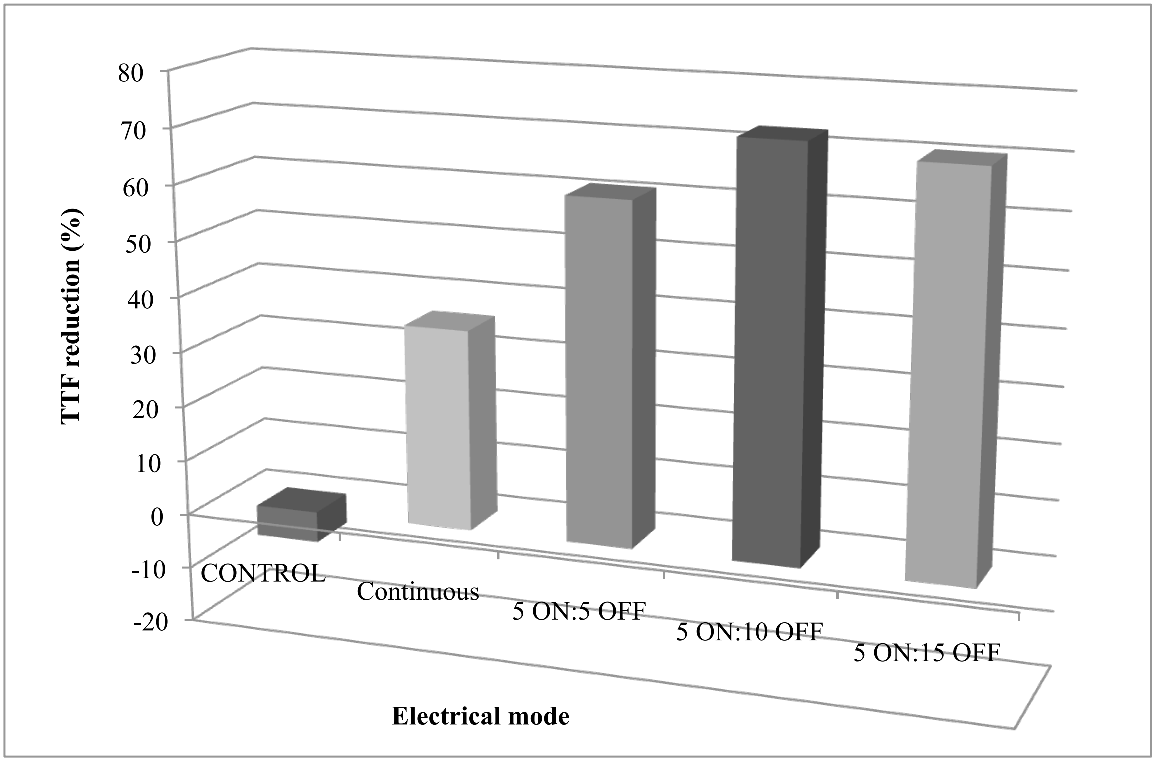


Figure 4-8 Variation in TTF reduction with different electrical modes for HR MLSS

The same analyses were performed for HR MLSS in terms of TTF and particle size. Figure 4-8 shows that 5ON:10OFF and 5ON:15OFF modes had the highest impact (72%) in reduction of TTF, whereas continuous mode had the lowest impact (36%). The same trend was observed in LR MLSS however the impact of electrical field on HR MLSS was less explicit than that of LR MLSS. The maximum particle size values (Figure 4-9) were reached after 8 and 24 hours in the case of continuous and 5ON:5OFF modes respectively, whereas 5ON:10OFF and 5ON:15OFF modes reached a maximum value after 24 hours and then stabilized (i.e. did not become smaller). It can be concluded that in HR MLSS conditions, shorter exposure time to electrical field requires longer operation time to reach smaller particle sizes.

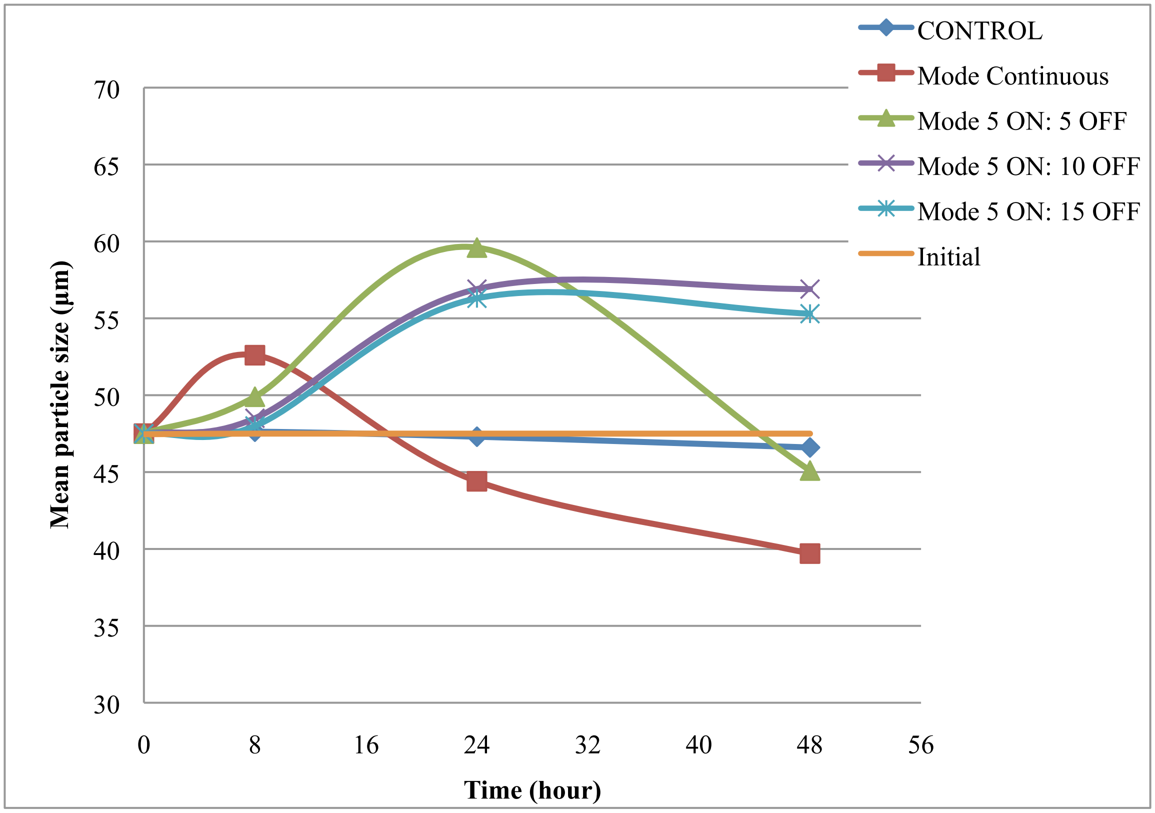


Figure 4-9 Variation of floc size during 48 hours of operation in HR MLSS

4.1.5. Impact of Electrical Field on Sludge Bioactivity

In order to study the impact of direct electrical current on microorganisms and activated sludge, specific oxygen uptake rate (SOUR) parameter was measured for all the electrical modes. This parameter can indicate whether microorganisms have been affected by electrical field or not and if electrocoagulation has any negative effect on their bioactivity.

Figure 4-10 indicates that applied electricity had the same impact in all electrical modes except for 5ON:15OFF mode. As a result, SOUR dropped from 3.4 to 1.6 mg O_2/g VSS/hour and to 1.3 mg O_2/g VSS/hour for continuous and 5ON:15OFF mode respectively.

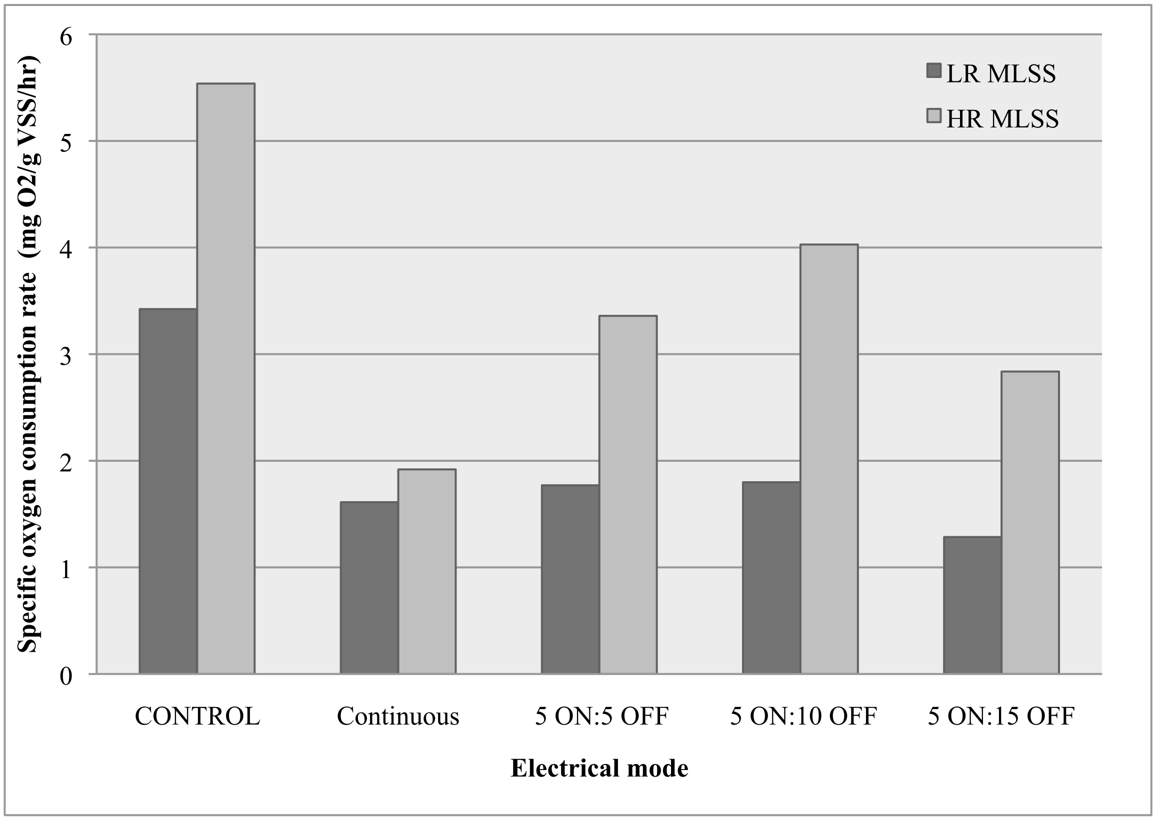


Figure 4-10 Specific oxygen uptake rate (SOUR) variation for LR and HR MLSS

The same results were observed at HR MLSS for continuous mode but with a higher impact. In continuous mode, SOUR dropped from 5.5 to 1.9 mg O_2/g VSS/hour, which indicates that the impact of electrical field on bioactivity of microorganisms is more evident at higher sludge concentrations. In both MLSS ranges, as less exposure time to electricity was applied, microorganism's activity increased except in 5ON:15OFF mode where the SOUR dropped from 3.4 and 5.5 to 1.3 and 2.8 mg O_2/g VSS/hour for LR and HR MLSS respectively. It can be concluded that the electrical mode 5ON:10OFF, has the lowest negative impact on microorganisms bioactivity. However, it can be speculated that the drop in dissolved oxygen concentration was not only related to microorganisms' activity but also other processes could consume the present oxygen.

4.1.6. Impact of Electrical Field on Supernatant Characteristics

To observe the effect of electrical modes on biological treatment, parameters such as SMP (measured as sCOD), PO_4^{3-}, NH_3-N and NO_3^- were measured. Figures 4-11 to 4-14 indicate the changes in SMP, PO_4^{3-}, NH_4^+ and NO_3^- for different electrical modes and for two ranges of MLSS respectively. In all figures the negative values represent the generation of the corresponding parameter.

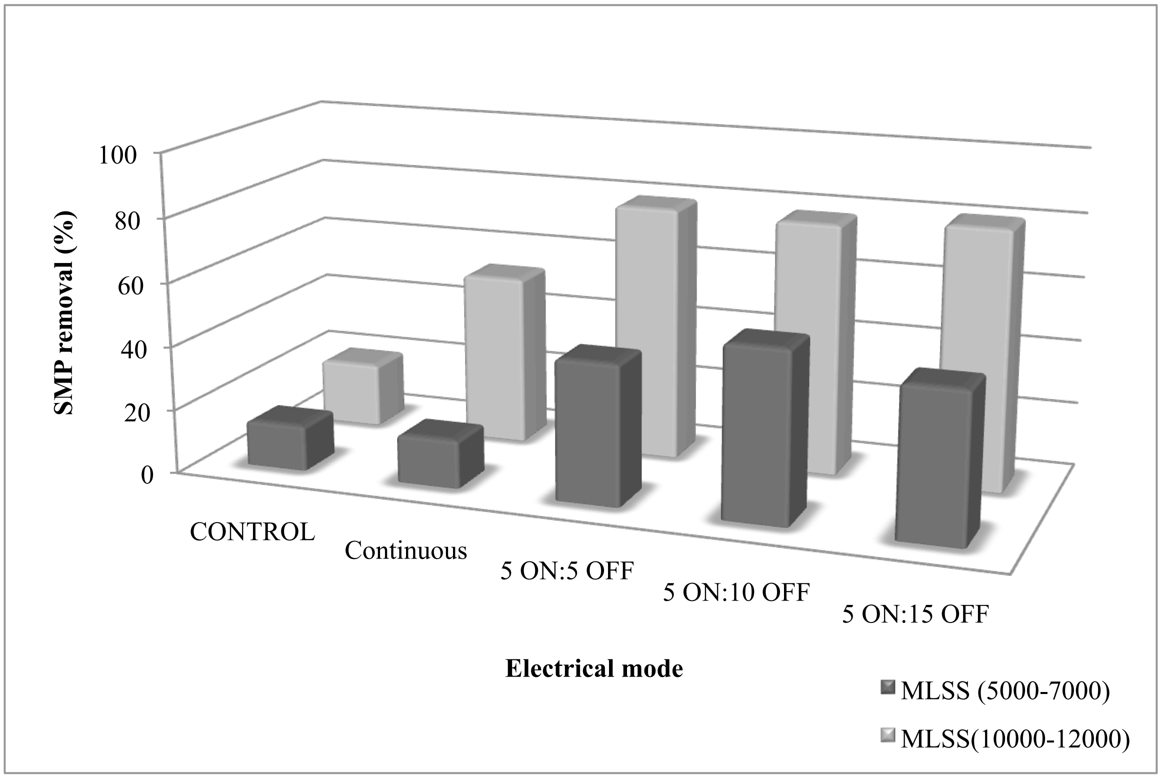


Figure 4-11 Removal efficiency of soluble microbial products for LR and HR MLSS at different electrical modes

At LR MLSS, the highest SMP reduction (53%) was obtained when 5ON:10OFF mode was applied, whereas at HR MLSS there was no significant difference between operational modes and the removal efficiency reached 80% (Figure 4-11). At both MLSS ranges, the continuous modes had the lowest SMP removal. Subsequently, it can be concluded that 5ON:10OFF and 5ON:15OFF might be the best modes applied to LR MLSS and HR MLSS respectively in terms of SMP removal. Also, it is observed that electrocoagulation process has a high potential for the removal of SMP from wastewater. The percentage of error for this analysis was ±10%.

Figure 4-12 depicts the removal of phosphate in different conditions. It was observed that the optimum removal efficiency in LR MLSS was obtained when continuous electrical mode was applied (78%). In addition, as the exposure time to electricity was decreased, phosphate removal efficiency decreased insignificantly. Therefore, it is noteworthy to point that all electrical modes had similar impact on phosphate removal. On other hand, for HR MLSS, at 5ON:5OFF mode the removal of phosphorous reached the highest removal efficiency. However, for all electrical modes the observed trend was the same as in LR MLSS; i.e. as the exposure time to DC was decreased, less phosphate was removed. At HR MLSS, continuous mode had the same impact as LR MLSS. Therefore, continuous exposure and 5ON:5OFF were the best modes in the phosphate removal for LR and HR MLSS respectively among other modes. The percentage of error for this analysis was ± 12%.

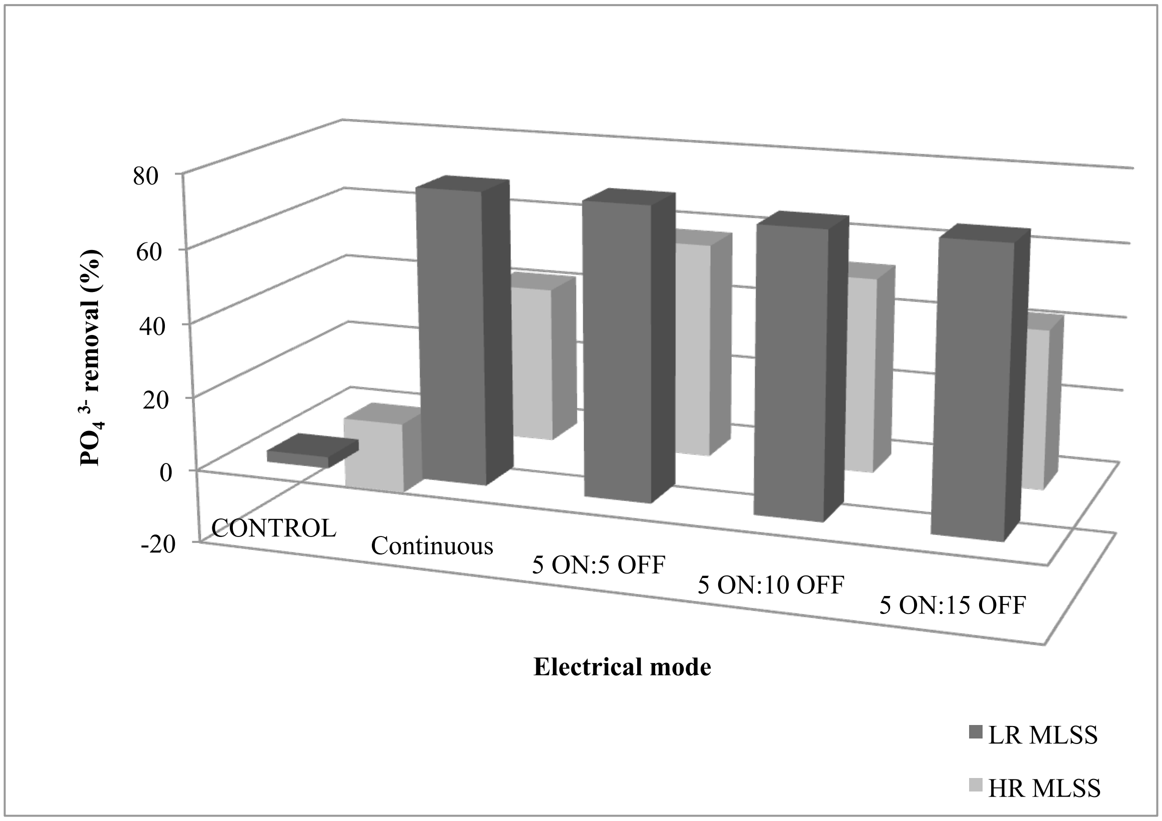


Figure 4-12 Phosphate removal with respect to MLSS ranges and different electrical modes

Figure 4-13 shows the efficiency removal of ammonia (as NH_3-N in supernatant) in different conditions. The highest removal of ammonia for LR and HR MLSS ranging from 56% to 50% respectively was obtained for 5ON:15OFF mode. Since there was an aerobic condition in the reactor and no feeding was applied, the control reactors (C1 and C2) showed a slight increase in ammonia concentration. Applying DC field continuously resulted in extremely high ammonia production, which could be the result of microorganisms' death and cell lysis. For both MLSS ranges, less exposure time to electrical field has resulted in better removal of ammonia. The percentage of error for this analysis was ± 14%.

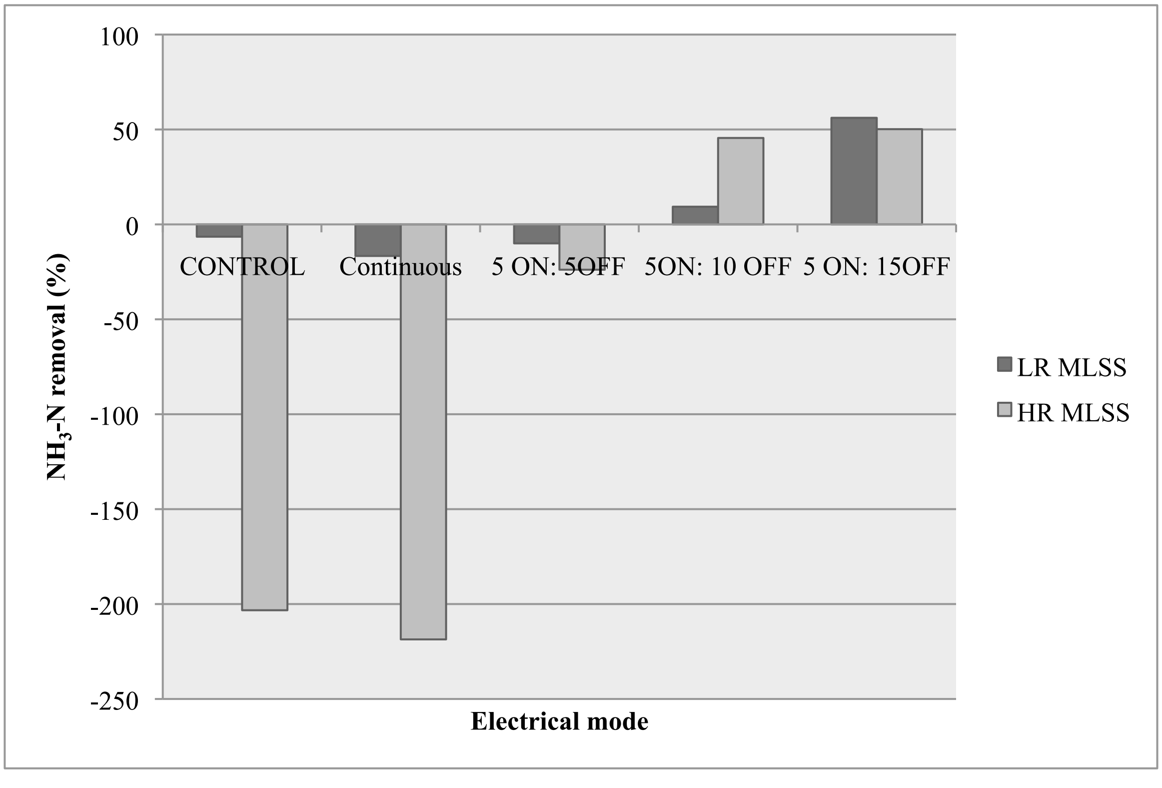


Figure 4-13 Removal of NH_3-N at LR and HR MLSS at different electrical modes

As shown in Figure 4-14, the highest nitrate concentration in the supernatant occurred in the reactor (C1) whereas the highest reduction in nitrate took place in continuous electrical mode (21 and 46% for LR and HR MLSS respectively). The generation of nitrate in the control reactor at LR MLSS (C1) was two times less than HR MLSS (C2). The same figure indicates a trend for the behavior of nitrate throughout the reactors: as exposure time to DC decreases, more nitrates are generated. Variations in the concentration of nitrate are higher at HR MLSS than at LR MLSS e.g. at 5ON:5OFF electrical mode, HR MLSS yielded 34% removal in nitrate concentration whereas LR MLSS obtained 39% increase in nitrate concentration. Therefore, it can be concluded that electrocoagulation is capable in removing nitrate from activated sludge, however, a longer exposure time to DC is required to obtain better results. The percentage of error for this analysis was ± 11%.

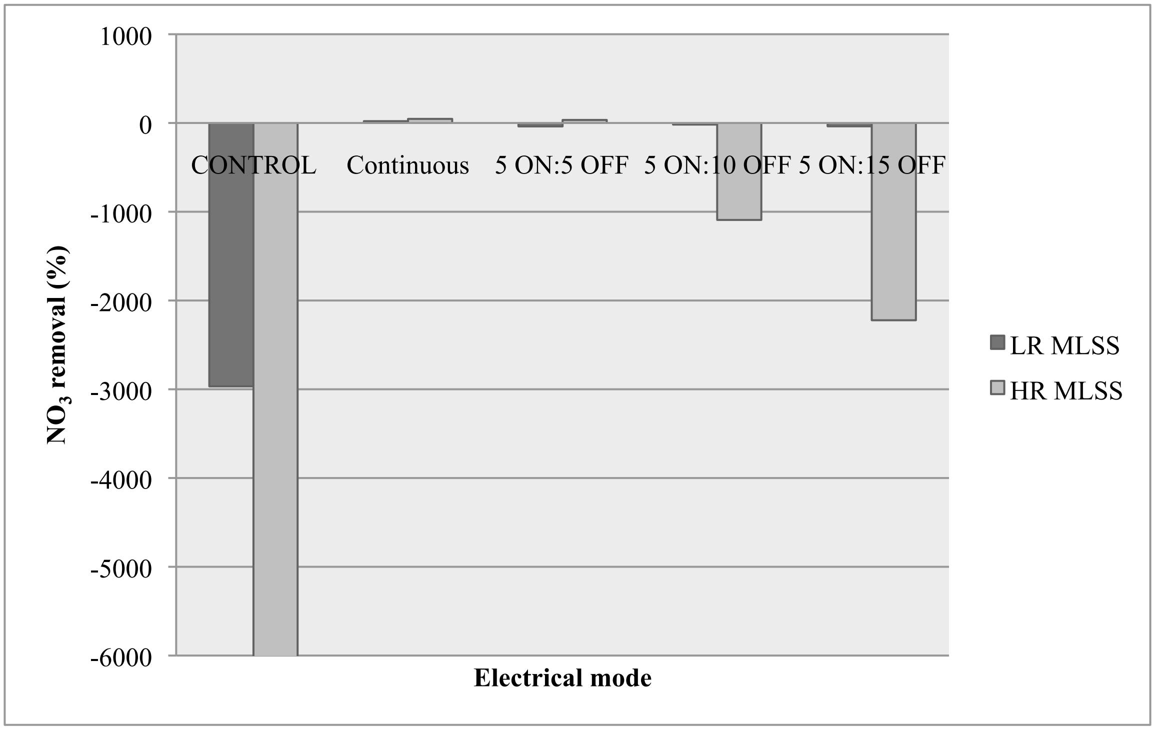


Figure 4-14 Nitrate removal in LR and HR MLSS at different electrical modes

On the other hand, DC might impede the function of nitrifying bacteria by decreasing nitrate generation as the exposure time to DC expands.

4.1.7. Impact of Different Electrical Modes on Wastewater Conductivity

Conductivity is one of the important parameters measured in electrocoagulation process. Conductivity affects the current efficiency, electrokinetic cell voltage (if a constant CD is applied) and consumption of electrical energy. Figure 4-15 illustrates the changes of conductivity in LR MLSS during 48 hours of operation time. During the first 8 hours, conductivity increased from the initial value, 1200 μS/cm to around 1300 μS/cm in all reactors. After 8 hours, conductivity in the control reactor (C1) continued to increase, however, this parameter started to decrease in the reactors with electrocoagulation process and reached a constant value with time. The final value of conductivity was 1644 μS/cm in the control reactor (C1), while in continuous, 5 ON:5 OFF, 5 ON:10 OFF and 5 ON:15 OFF modes it reached 1177, 1181, 1198 and 1182 μS/cm respectively.

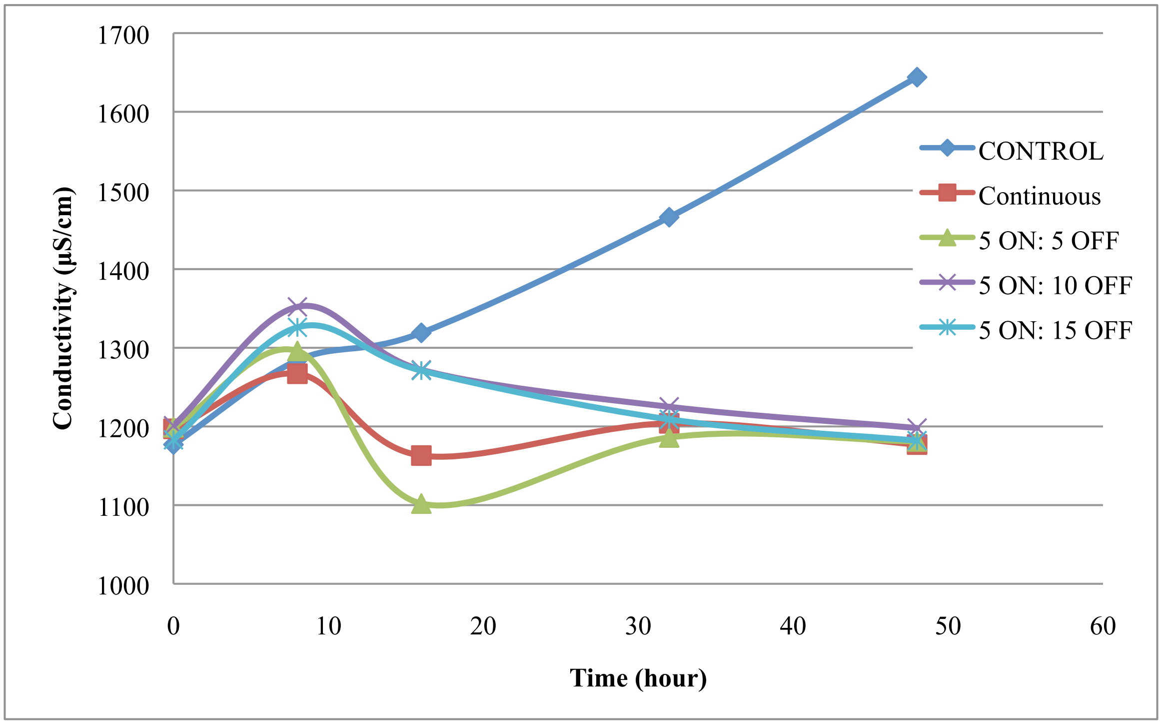


Figure 4-15 Conductivity variation versus time at LR MLSS

Since bioreactors were not supplied with food, the behavior in the control reactor (C1) might be attributed to the death of microorganisms. Conductivity might have increased due to the presence of higher ion concentrations. In the case of reactors with electrical field, same explanation can be used for the first 8 hours. After 8 hours of operation, the observed drop in conductivity can be attributed to the removal of ions from the reactor due to electrical processes (electrocoagulation, electrophoresis and electromigration) and precipitation due to the coagulation process. Reaching a constant value at the end of the operation time can be the result of a balance between the death of microorganisms (increase in conductivity) and electrokinetic/precipitation processes (reduction in conductivity).

Furthermore, the variations in conductivity with time were also studied at HR MLSS (Figure 4-16). The control reactor (C2) shows the same trend as in LR MLSS (initial value was 860-900 µS/cm and after 48 hours of operation it reached 1716 µS/cm), whereas the reactors with electrical field at HR MLSS do not show the same trend.

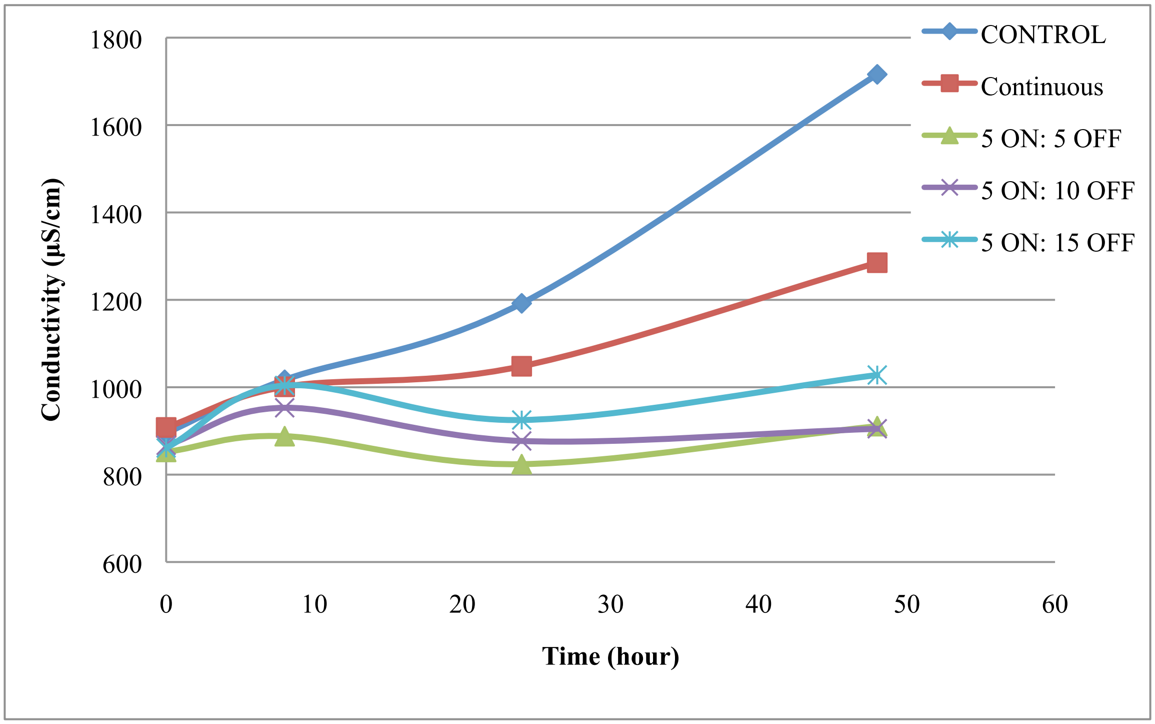


Figure 4-16 Variation in Conductivity versus Time at HR MLSS

At HR MLSS, after 8 hours of operation there was an increase in conductivity in all reactors. Between 8 hours and 24 hours, excluding continuous mode, the other three modes faced a slight drop in their conductivity, which can be attributed to the coagulation/precipitation processes. In continuous mode, conductivity increased until it reached the value of 1285 µS/cm. The 5ON:5OFF mode had the minimum variation in conductivity (final value of 911µS/cm). In the latter electrical mode it can be assumed that the rate of microorganisms' death was almost the same as the rate of coagulation/precipitation processes. 5ON:10OFF and 5ON:15OFF mode reached 905 and 1028 µS/cm after 48 hours of operation which might indicate that more ions were generated in comparison to 5ON:5OFF mode.

4.1.8. Variation in Voltage Gradient in Different Electrical Modes

In order to better understand the electrocoagulation process, electrolysis voltage was monitored throughout the experiments (Figure 4-17).

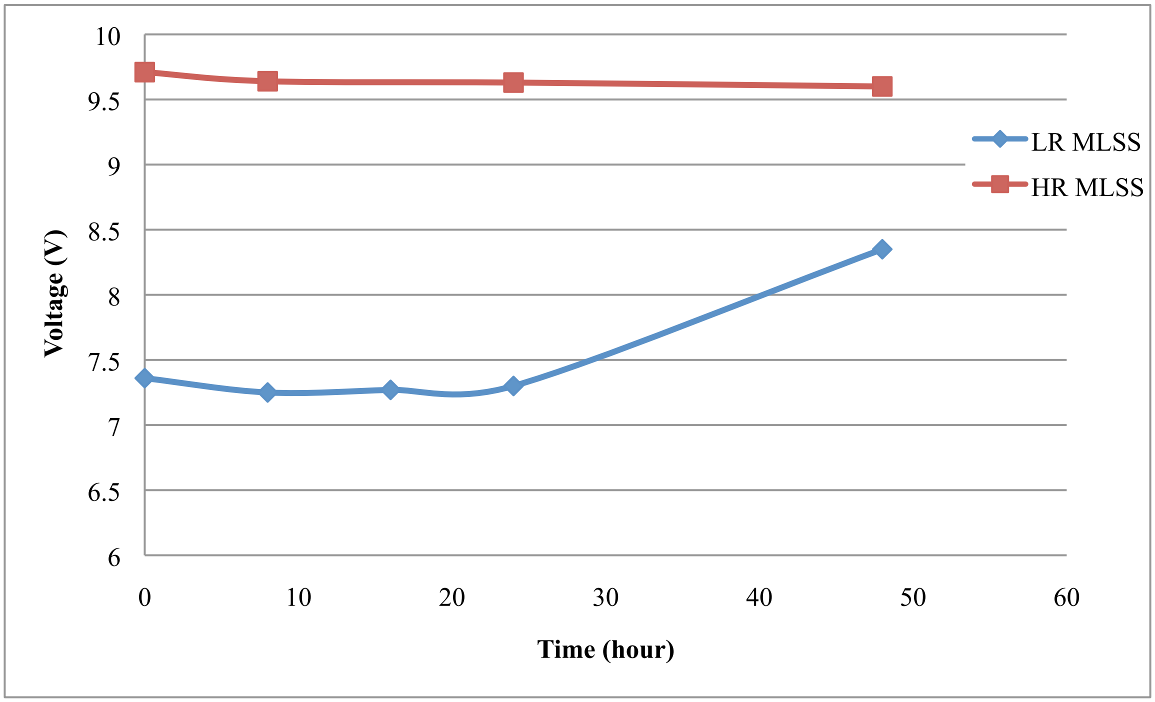


Figure 4-17 Variation of electrolysis voltage with time

At LR MLSS, the first 24 hours of experiment did not show any significant changes in voltage where as between 24 and 48 hours, the voltage increased from 7.3 V (1.46 V/cm) to 8.35 V (1.67 V/cm) indicating higher resistance in the reactors. On the other hand, at HR MLSS, voltage slightly decreased from 9.71 V (1.94 V/cm) to 9.6 V (1.92 V/cm). These results are in agreement with the results obtained from Figure 4-15 and 4-16 due to the relationship between conductivity and applied voltage. Furthermore, comparison between the required applied potential (V) for LR and HR MLSS indicates that higher voltage is required for HR MLSS.

4.1.9. Variations in pH for Different Electrical Modes During 48 Hours of Operation

It has been established that pH has an important role in electrochemical process performance. Since the described system is a biological system, changes in pH not only affect the electrochemical processes but it can affect the microorganism's functions. In order for microorganisms to be able to perform biological treatment, the pH should be maintained in the range of 6-9. For this purpose, pH was monitored during the electrocoagulation process for all electrical modes to ensure that biological degradation is not impeded by pH.

As it was expected, in the reactors with electrical field in LR MLSS (Fig. 4-18), pH increased over time, which illustrates that cathodic activity is more dominant (Kurt et al. 2006). With the initial value of pH being 8, comparison between different electrical modes indicates that continuous mode reached the highest final pH (pH= 8.52). Furthermore, fluctuations in pH value were less when intermittent DC was applied e.g. 5ON:15OFF mode reached the same pH as the initial value. On the other hand, in the control reactor (C1), pH started to decrease with time until it reached pH= 6.63.

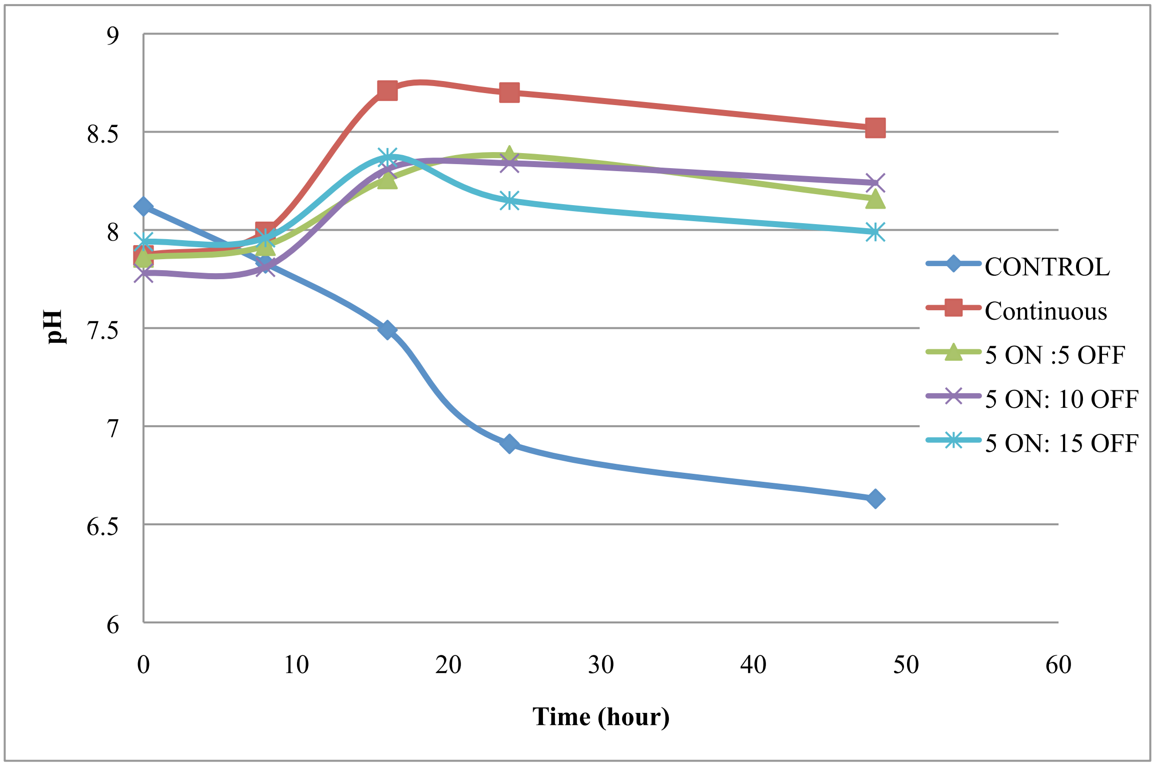


Figure 4-18 pH variation during the experiment at LR MLSS

Variation in pH values for HR MLSS is shown in Figure 4-19. The initial pH was 7.3 and continuous electrical mode reached pH 8.4 after 48 hours of operation, which can be explained similar to the case of LR MLSS. The pH in the control reactor (C2) dropped from the initial value to pH 6.87. It can be seen that the trend in pH changes is similar for LR and HR MLSS and in both ranges the pH values did not exceed 9 and did not go lower than 6. It can be concluded that variation in pH does not impede the biological treatment. Furthermore, since the values of pH, obtained from the reactors with electrical field were higher than the control reactor, it can be assumed that the dominant electrical activity in these reactors is the cathodic activity.

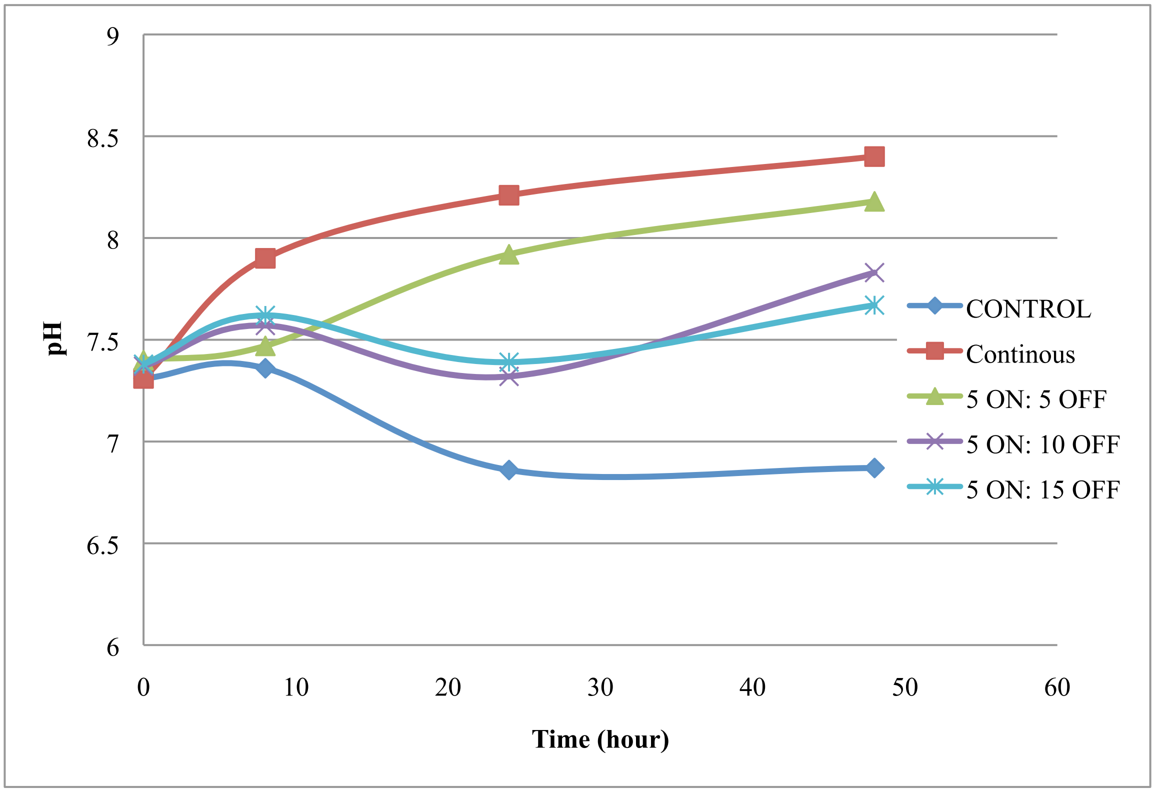


Figure 4-19 pH variation during the experiment at HR MLSS

4.2. Impact of Calcium on Activated Sludge Characteristics

Divalent cations are widely known to improve the microbial flocculation due to formation of bridges with extracellular polymeric substances. This flocculation promotes activated sludge settling characteristics and also helps the formation of biological flocs in the reactors. Calcium, which is the most common divalent cation present in the environment, has an important role in the formation of bioflocs (Song et al. 2008). Therefore, experiments were performed to study the impact of calcium on activated sludge characteristics in batch reactors. Although the typical calcium concentration in municipal wastewater is between 20-120 mg/L (Arabi and Nakhla, 2008), two calcium concentrations such as 250 and 750 mg/L as well as comparative runs without calcium addition were chosen in this study to better understand the role of calcium in the activated sludge when DC was applied. This study was also performed for two different sludge concentrations, LR and HR MLSS.

4.2.1. Impact on Sludge Volume Index (SVI)

Sludge Volume Index has been used to evaluate the impact of divalent cation addition on settling characteristics of activated sludge. Figure 4-20 depicts the variation in SVI for three different calcium concentrations and for two ranges of MLSS.

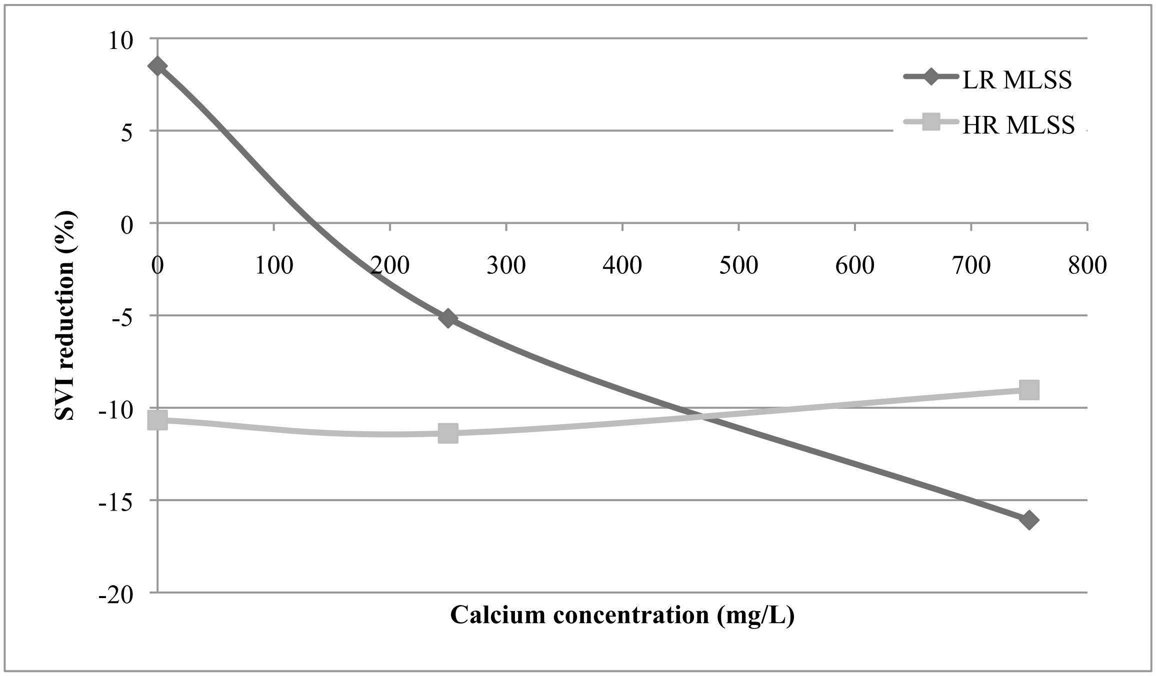


Figure 4-20 Variation in reduction of SVI with different calcium concentrations for LR and HR MLSS

At LR MLSS, addition of 250 and 750 mg Ca^{2+}/L of resulted in 13 and 24% increase in SVI in comparison to the control reactor (no addition of calcium). It can be understood that as the concentration of calcium in the reactors increased, the sludge volume index became larger. This indicates that addition of calcium is not beneficial to this index and might deteriorate the settleability of sludge. This behavior is in contradiction with the work of Sobeck and Higgins (2002) who stated that addition of calcium would improve the SVI value and higher calcium concentration would yield better SVI. This contradiction might be due to the fact that their reactor was a continuous flow reactor. Sobeck and Higgins (2002) believed that short duration batch reactors would not be able to precisely represent the behavior of cations in activated sludge and sufficient time is required to allow the system to reach steady state condition. Moreover, at HR MLSS, the addition of 250 mg Ca^{2+}/L did not have any impact on SVI in comparison to the reactor without the addition of any calcium (89 mL/g). Also, the addition of 750 mg Ca^{2+}/L did not have a significant effect on SVI and it only decreased it by 2%. The percentage of error for this analysis was ± 15%.

4.2.2. Impact on Time to Filtration (TTF)

Time to filtration parameter can be used to assess the rate of water release from sludge. The impact of different calcium concentration on TTF value was investigated for two MLSS ranges. Figure 4-21 depicts the impact of calcium concentration on TTF reduction, with respect to its initial value, at different sludge concentrations. The percentage of error for this analysis was ± 5%. At LR MLSS, no addition of calcium yielded 28% reduction in TTF. However, when calcium concentration was increased to 250 mg/L and 750 mg/L, the reduction in TTF reached 65%. After 48 hours of operation, the reactor without addition of calcium had TTF of 42 seconds while addition of calcium yield TTF of 13 seconds for 250 and 750 mg Ca^{2+}/L. It can be concluded that addition of calcium can improve the ability of sludge to release water. In addition, increasing the calcium concentration above 250 mg/L does have any impact on improvement of TTF value.

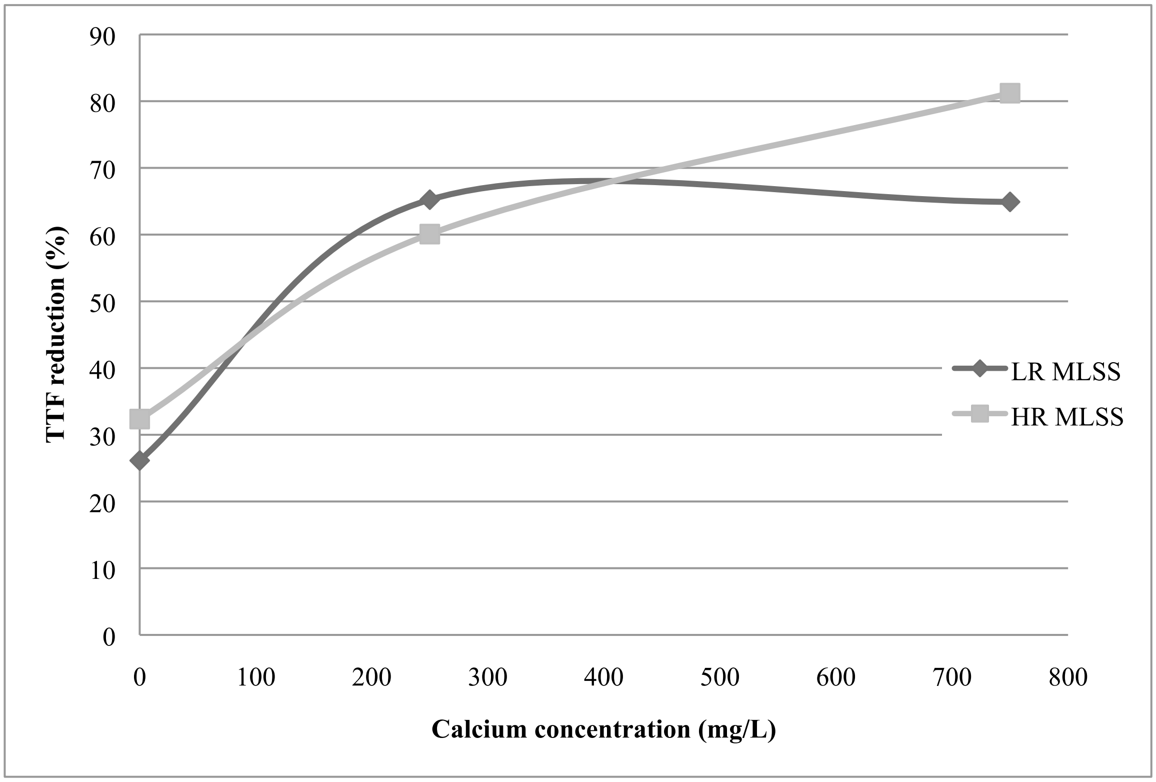


Figure 4-21 Variation in TTF reduction for different calcium concentrations at LR and HR MLSS

Furthermore, at HR MLSS, the same trend as LR MLSS was observed. However, at HR MLSS, when the concentration of calcium was increased to 250 and 750 mg/L, the reduction in TTF reached 60 and 81% respectively. Reactor without addition of calcium obtained 32% reduction in TTF. Therefore it can be concluded that at higher sludge concentration, higher calcium concentration lead to higher reduction in TTF whereas at low sludge concentrations, calcium additions higher than 250 mg/L did not have any impact on improving the time to filtration parameter.

4.2.3. Impact on Particle Size Distribution

Arabi and Nakhla (2008) indicated that due to the gelling and bridging of SMPs molecules with the calcium ions present in the reactors, larger flocs would be formed. In this regard, the mean floc sizes were measured and the increase in particle size after 48 hours of operation has been demonstrated in Figure 4-22 for three different calcium concentrations. The negative values represent the decrease in floc sizes.

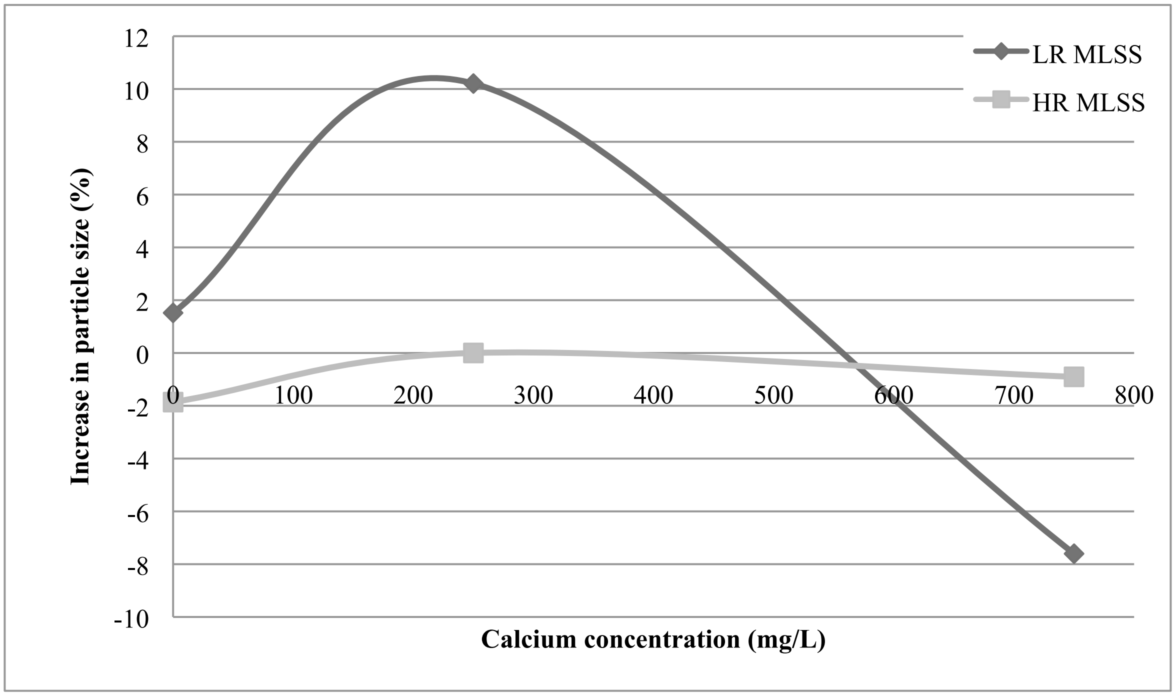


Figure 4-22 Increase in particle size with increase in calcium concentration for LR and HR MLSS

It can be observed that at LR MLSS, the addition of 250 mg Ca^{2+}/L resulted in 10% increase in mean particle sizes while no addition of calcium had only 1.5% increase in particle sizes. The initial mean particle size was 65.5 µm, which increased to 74 µm for 250 mg Ca^{2+}/L. Moreover, the addition of 750 mg Ca^{2+}/L had an opposite impact on particle size and resulted in 18% reduction in the mean floc sizes in comparison to 250 mg Ca^{2+}/L. These behaviors can be explained as follows; addition of 250 mg Ca^{2+}/L might have resulted in divalent cation bridging with soluble EPS, which resulted in larger floc sizes. On the other hand, addition of 750 mg Ca^{2+}/L might have resulted in formation of inorganic precipitates such as calcium carbonate in the reactor. Therefore, since calcareous flocs are more dense and smaller than the microbial flocs, the mean particle size for 750 mg Ca^{2+}/L is smaller 250 mg/L addition of calcium (Arabi and Nakhla 2008).

At HR MLSS, the addition of 250 mg Ca^{2+}/L did not have any impact on the floc sizes and the mean particle size remained at the level of 47.1 μm. On the other hand, increasing the calcium concentration to 750 mg/L resulted in 1% reduction in floc sizes. Smaller particle size in higher calcium concentration might be due to formation of inorganic precipitates. However, it can be assumed that addition of calcium to HR MLSS did not have any impact on activated sludge particle sizes. It can be concluded that the impact of calcium on sludge mean particle size at HR MLSS is much lower than its impact on LR MLSS. The percentage of error for this analysis was 8%.

4.2.4. Impact on SMP Removal

Soluble EPS (SMP) were analyzed as soluble COD in the supernatant after 48 hours of EC operation for two different calcium concentrations and one control without the addition of any calcium. Figure 4-23 illustrates the variation of SMP removal for different calcium and sludge concentrations.

At LR MLSS, the addition of 250 mg Ca^{2+}/L into the bioreactor reduced the supernatant SMP concentration by 50%, whereas the SMP removal efficiency in the reactor without addition of calcium (control) was 17%. However, increasing the concentration of calcium to 750 mg/L resulted in 37% removal in SMP. In other words, 250 mg Ca^{2+}/L and 750 mg Ca^{2+}/L resulted in SMP reduction by 33% and 20% respectively in comparison to the control reactor. Therefore, the calcium addition had a significant impact on removal of SMP due to the possible bridging of divalent cations with negatively charged soluble

EPS. It can be concluded that at LR MLSS, increasing the concentration of calcium ion up to 250 mg Ca^{2+}/L is beneficial to SMP removal but higher calcium concentrations might lead to less SMP removal efficiency.

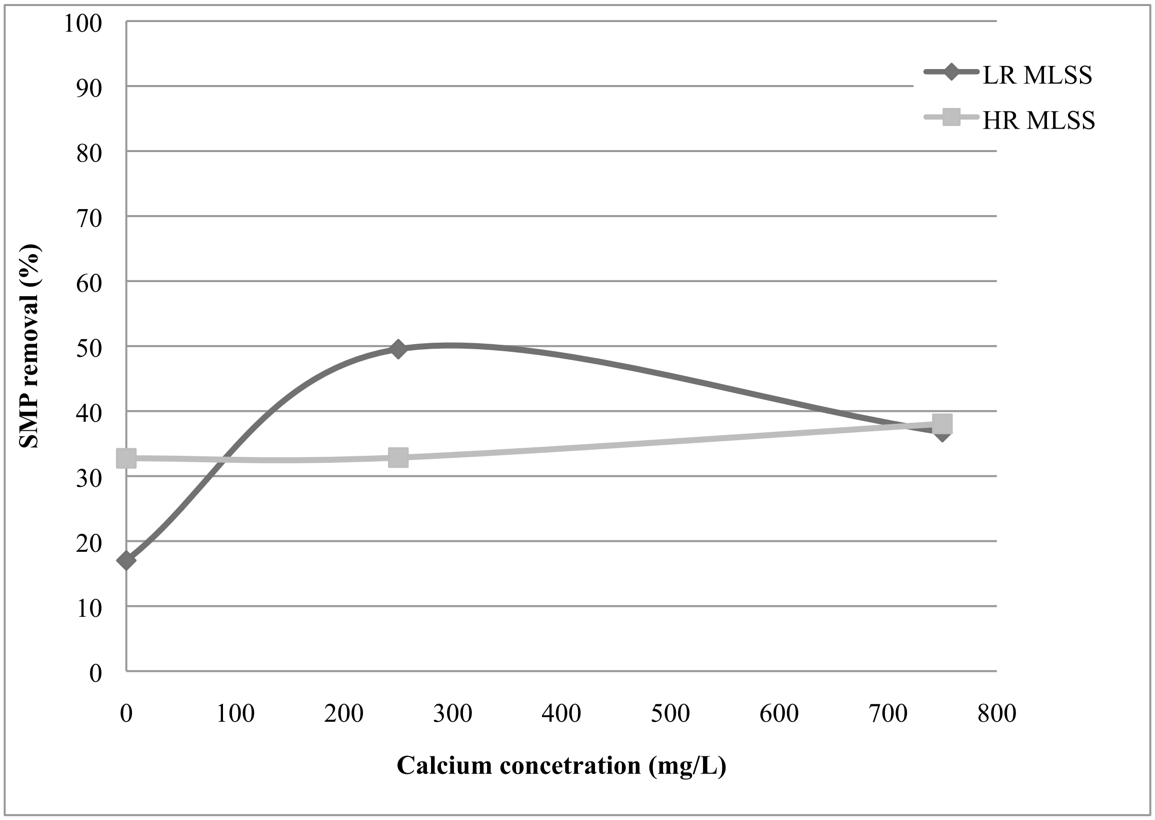


Figure 4-23 Changes in removal of SMP for three calcium concentrations at LR and HR MLSS

At HR MLSS, the calcium addition had a slight effect on SMP removal efficiency and at 750 mg Ca^{2+}/L only 5% removal was observed. In this experiment no significant impact was observed in removal of SMPs by increasing the calcium concentration in the reactors. The percentage of error for this analysis was ± 10%.

4.2.5. Impact on Phosphate Removal

The presence of calcium might have impact on phosphate removal due to the formation of inorganic precipitates of calcium phosphate. Therefore, the phosphate removal was investigated for two different calcium concentrations and one control reactor (Figure 4-24).

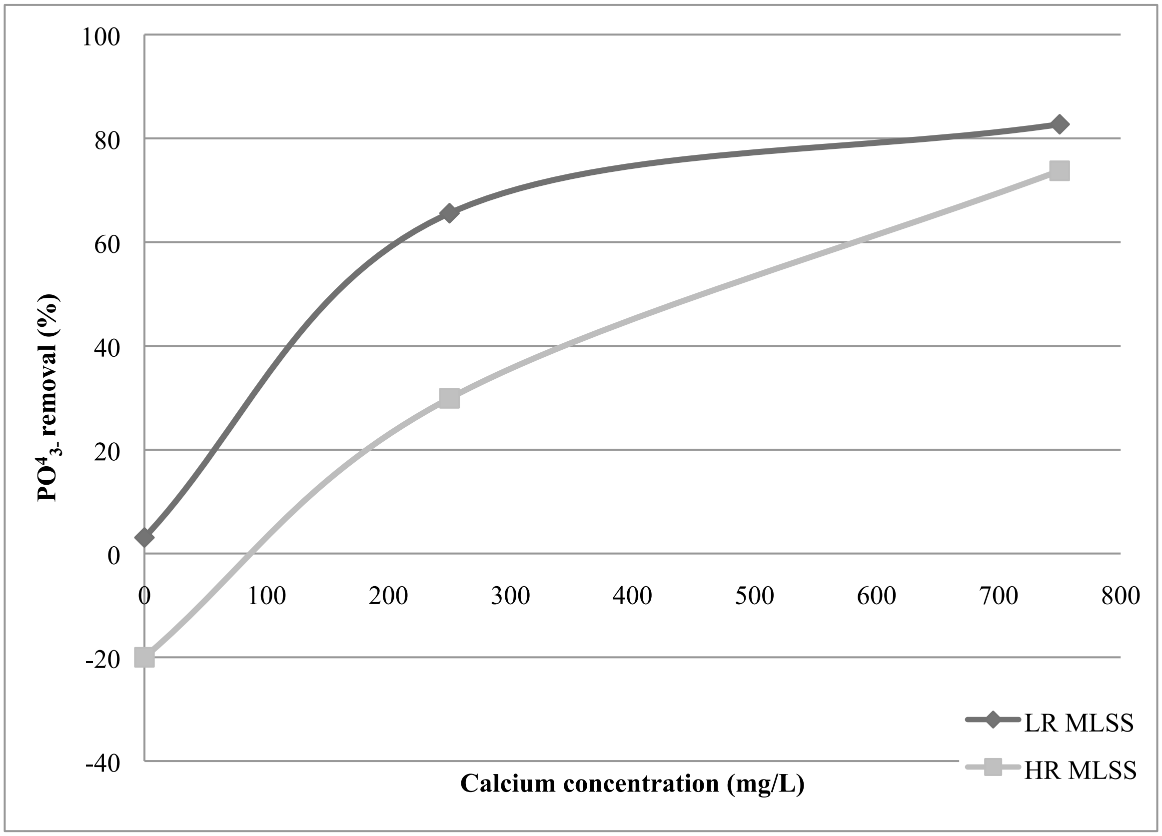


Figure 4-24 Phosphate removal for different calcium concentrations at LR and HR MLSS

The results show that at both LR and HR MLSS, as the concentration of calcium increases, the removal efficiency of phosphate also increases. At HR MLSS, the control reactor showed 20% increase in phosphate concentration in comparison to the initial value, which might be due to death of microorganisms and release of phosphate. On the other hand, when 250 mg Ca^{2+}/L was added to the reactors, 66% and 30% removal of phosphates were observed for LR and HR MLSS respectively. Furthermore, the addition of 750 mg Ca^{2+}/L yielded 83% and 74% reduction in phosphate in LR and HR MLSS respectively.

Therefore, no significant relationship was observed between MLSS and the impact of calcium addition on removal of phosphates. Furthermore, at LR MLSS same amount of calcium is able to remove more phosphate from wastewater in comparison to HR MLSS. The percentage of error for this analysis was ± 12%.

4.2.6. Variation in Calcium Concentration

Variation in the supernatant calcium concentration after the experiments has been shown in Figure 4-25 for different ranges of MLSS. At LR MLSS, addition of 250 mg Ca^{2+}/L resulted in 51% higher removal of calcium from the supernatant. This behavior can be attributed to bridging of a fraction of calcium added to the wastewater with soluble microbial products through divalent cation bridging theory; addition of 250 mg Ca^{2+}/L resulted in 33% higher SMP removal and 10% increase in particle size. It could be assumed that added calcium had the potential to enhance bioflocculation and therefore reduce the amount of SMP present in the wastewater. In the course of higher initial calcium concentration (750 mg/L), 29% reduction of Ca^{2+} concentration was achieved in comparison to reactors without addition of calcium. In the same conditions, calcium did not have any significant impact on SMP removal efficiency while particle size was decreased by 10%. This behavior might be as results of calcium precipitate formation (e.g. calcium carbonate or calcium phosphate) due to the high concentrations of calcium in the activated sludge, which has also resulted in smaller particles. Therefore, it can be concluded that at LR MLSS, addition of 250 mg Ca^{2+}/L might enhance the bioflocculation and removal of SMP from wastewater.

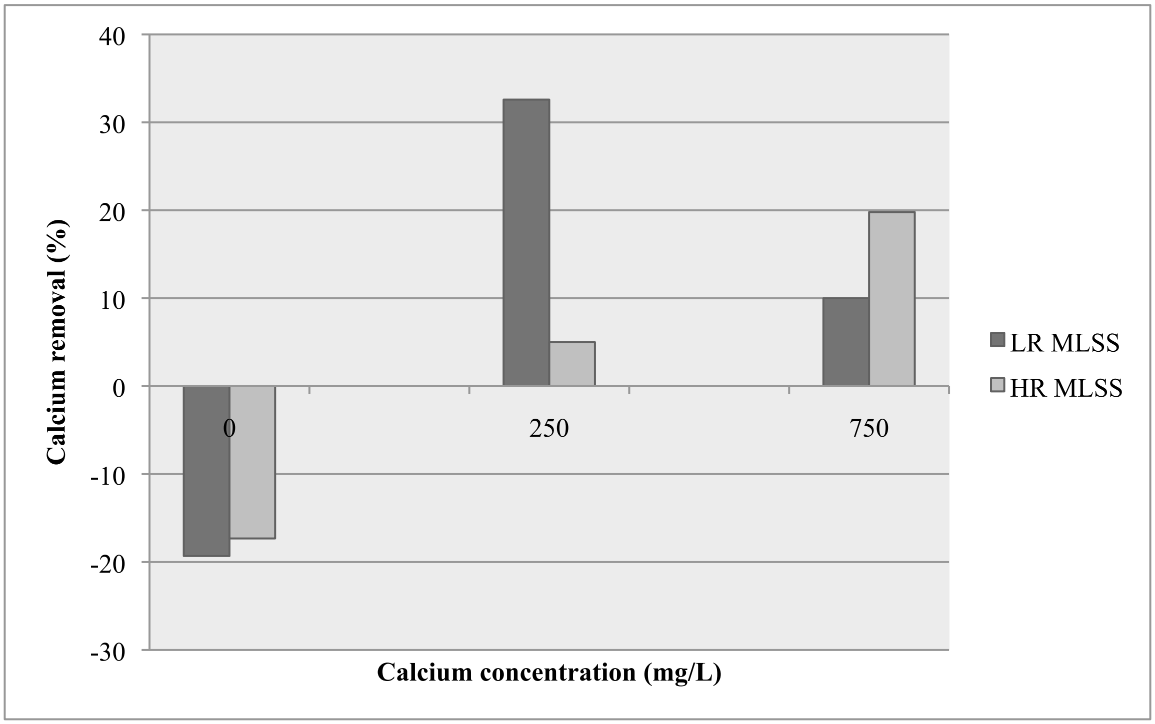


Figure 4-25 Variation in calcium concentration after 48 hours

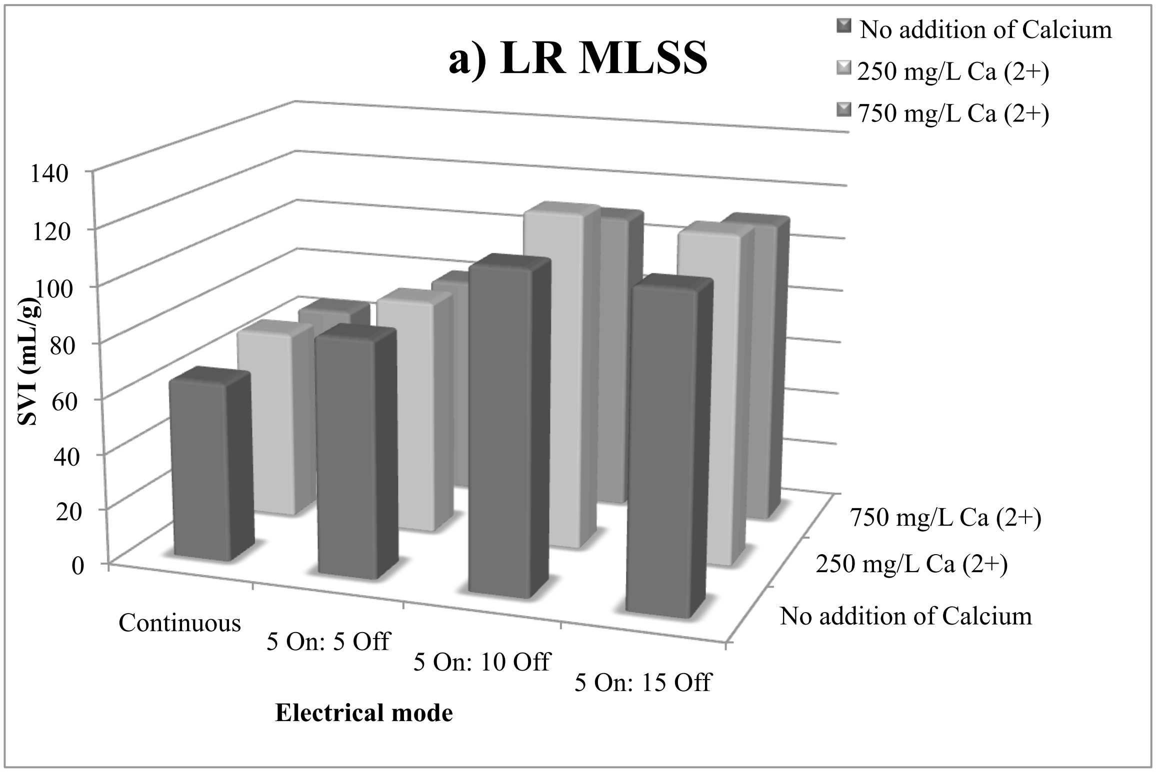
However, at HR MLSS, initial calcium concentration of 250 mg Ca^{2+}/L resulted in 22% higher removal efficiency where as 750 mg Ca^{2+}/L resulted in 37% higher calcium removal. Furthermore, it was found that at HR MLSS, addition of calcium did not have any significant impact on the particle size and removal of SMP from wastewater. Therefore at HR MLSS, higher initial calcium concentration might form precipitates with phosphates and carbonates present in the activated sludge. In addition, Results of reduction in TTF and phosphate removal efficiency confirm this behavior.

4.3. Impact of Calcium Addition on Electrocoagulation Process

The introduction of calcium not only affects the properties of activated sludge but also increases the conductivity of it. Therefore, addition of calcium to EC process can have different impact on different phenomena, which are taking place during the electrocoagulation process. The conductivity affects the voltage (applied potential) in the cell, current efficiency and electrical energy consumption. Higher ionic strength causes a reduction in the cell voltage, at the same current density, due to less ohmic losses. In other words, higher conductivities diminish the necessary voltage required to attain a certain current density; therefore, the consumed electrical energy would be reduced. In this research, the initial conductivity of samples obtained from wastewater treatment plant was between 900 and 1200 μS/cm. When 250 and 750 mg Ca^{2+}/L were added, the sample conductivity increased from the approximate value of 900-1200 to 2250-2450 and 4000-4900 μS/cm respectively. In this section the impact of calcium addition to EC process on different sludge parameters has been shown.

4.3.1. Impact on Sludge Volume Index (SVI)

Figure 4-26 shows the effect of calcium addition on SVI for LR MLSS and HR MLSS during EC process. At LR MLSS (Figure 4-26a), results indicated that higher electrolyte concentrations did not have a significant impact on SVI value regardless of the electrical mode applied. For instance, in continuous electrical mode the SVI improved by 4%, however, the addition of 750 mg $Ca^{2+/}$L preserved the same value of SVI as no calcium was added. The percentage of error for this analysis was ± 15%. As Figure 4-26b indicates, addition of 250 mg Ca^{2+} /L did not affect the SVI considerably, whereas addition of 750 mg Ca^{2+}/L had adverse impact on SVI. For instance, in 5ON:15OFF electrical mode SVI increased by 16% in comparison to the control cell where no calcium chloride was added. In overall, it can be concluded that higher calcium concentrations and conductivity are not expected to affect the SVI at either LR or HR MLSS and further research is required to investigate this behavior.



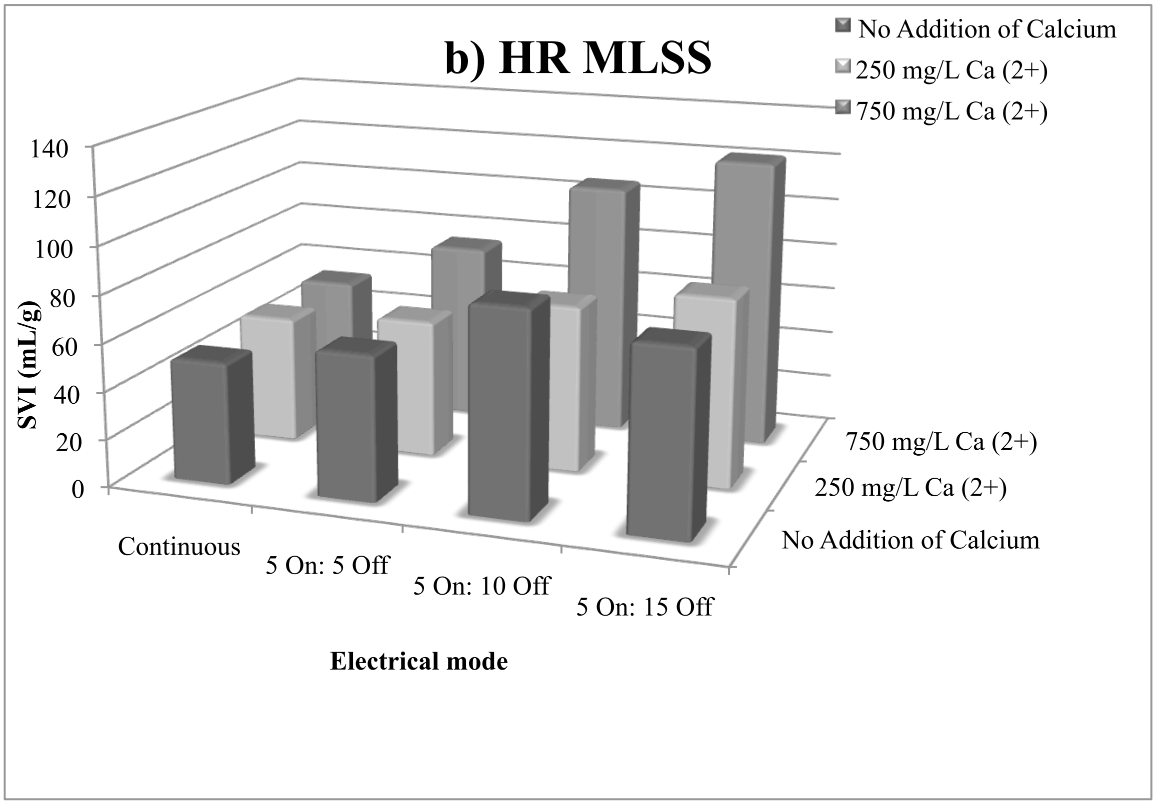


Figure 4-26 Impact of calcium on SVI at different electrical modes for LR MLSS

4.3.2. Impact on Mixed Liquor Suspended Solids

Mixed liquor suspended solids were studied to investigate the impact of calcium addition on mixed liquor suspended solids. Conductivity was increased by addition of calcium chloride that not only affects the generation of Al^{3+} at the anode, but also at high concentrations, it can increase the possibility of formation of calcium carbonates. Figures 4-27a and b illustrate the variation in MLSS for both LR and HR MLSS. Both figures indicate that higher calcium concentrations lead to higher MLSS concentration. For instance, at LR MLSS, 46% and 82% increase in suspended solids were observed when conductivity was increased by addition of 250 and 750 mg Ca^{2+}/L respectively in comparison to the control reactor where no calcium was added. The continuous mode had the highest generation of suspended solids in comparison to other electrical modes. The MLSS variation for concentrated sludge was much less in comparison to low sludge concentration. Furthermore, 5ON:10OFF and 5ON:15OFF electrical modes, at HR MLSS, did not get affected by higher calcium concentrations. Impact of calcium on MLSS can be attributed to the formation of aluminum hydroxide and carbonate calcium, which later can be removed by settling or filtration. The percentage of error for this analysis was ± 10%.

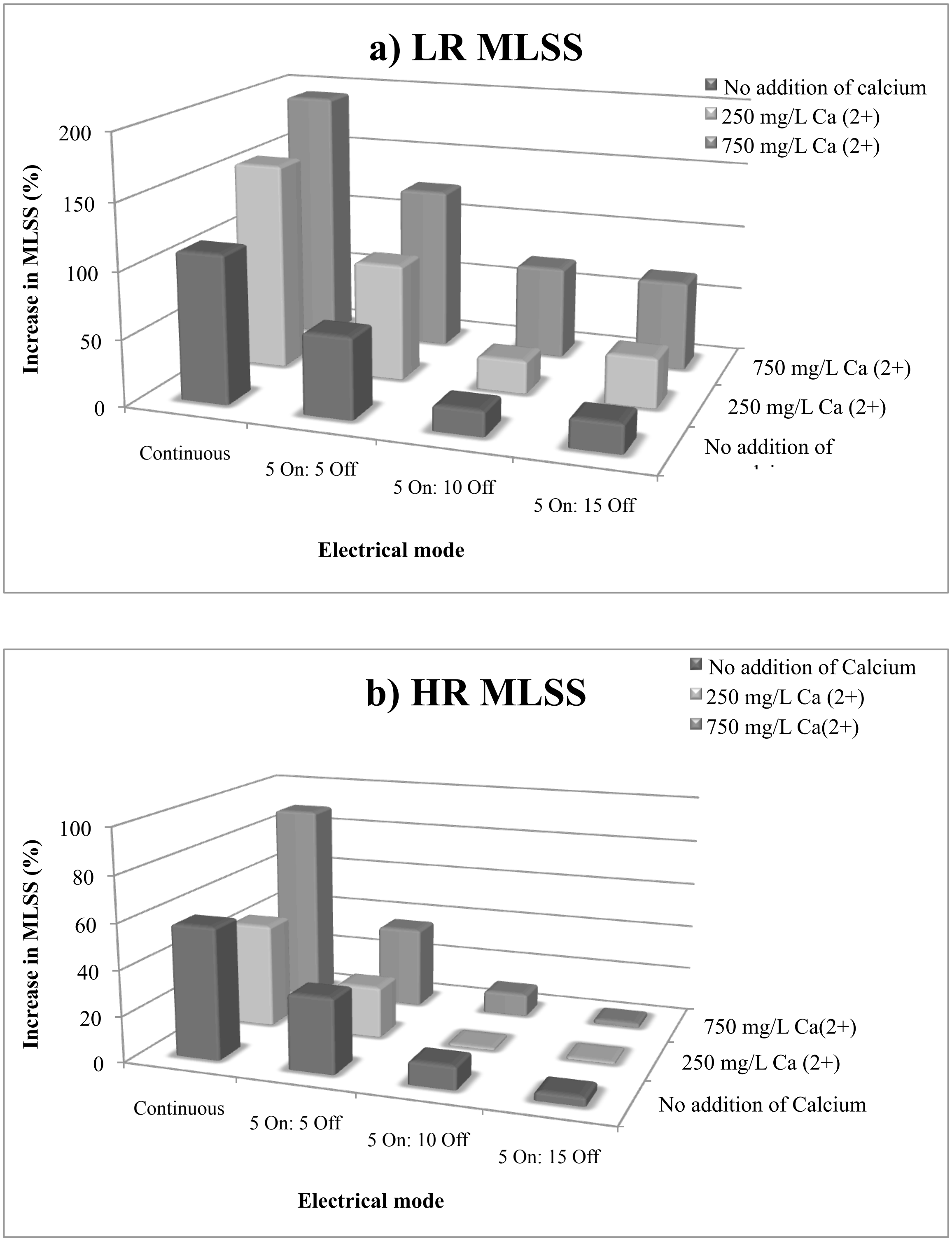


Figure 4-27 Variation in the MLSS concentration for different calcium concentrations and electrical exposure modes (LR and HR MLSS)

In order to better understand the impact of calcium addition on EC process, the amount of aluminum released to the systems were also analyzed (Chapter 2, Section 3.3.6.).

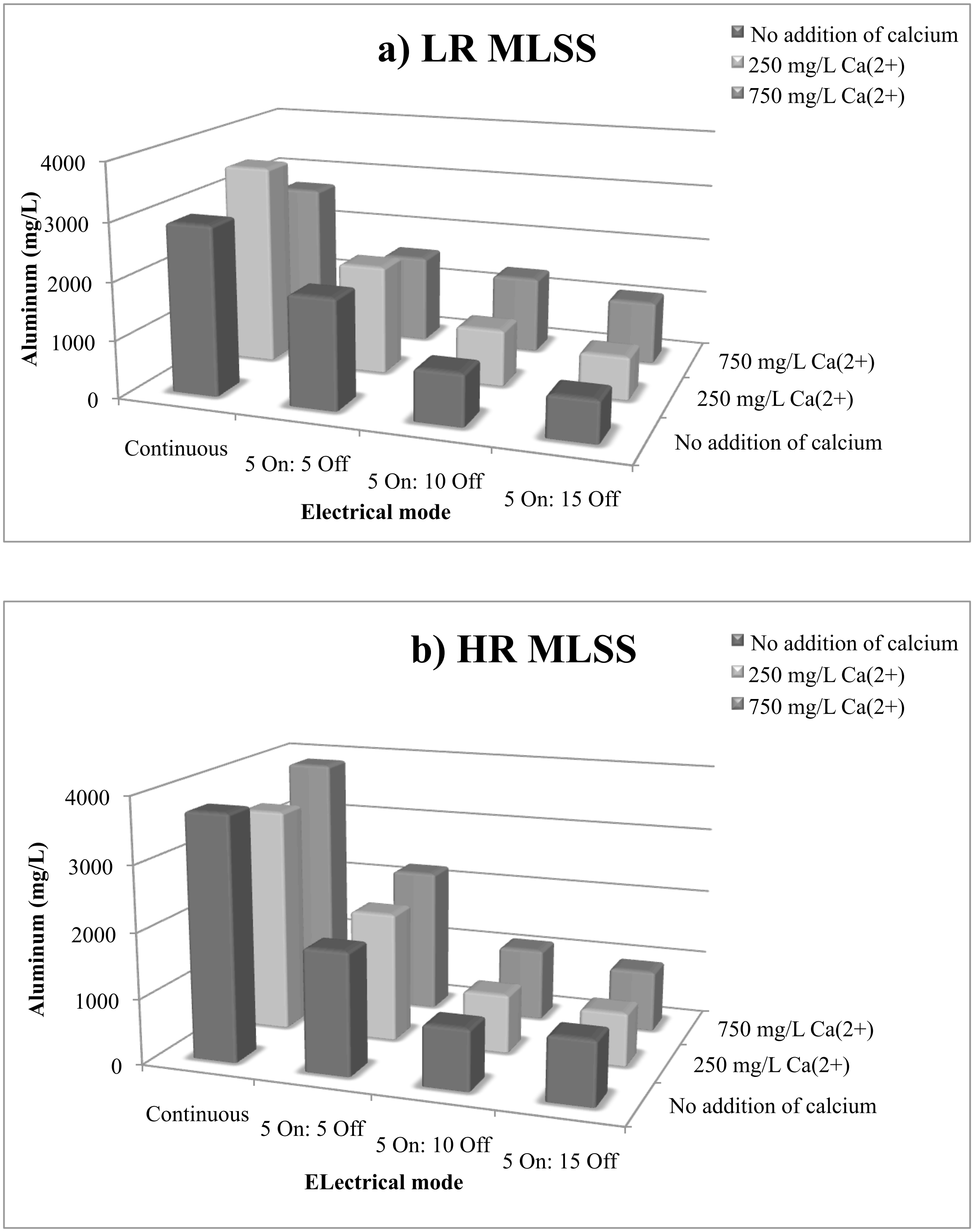


Figure 4-28 Impact of calcium addition on the amount of aluminum released in different electrical mode a) LR MLSS b) HR MLSS

Figure 4-28 depicts the amount of aluminum released to the bulk solution by electrocoagulation process in different electrical modes. Higher calcium concentrations did not have a considerable impact on the electrolytic dissolution of the anode. For instance, at HR MLSS (Figure 4-28b) and 5ON:5OFF electrical mode, 250 mg Ca^{2+}/L resulted in 6% higher aluminum production while 750 mg Ca^{2+}/L achieved 19%. Increasing the calcium concentration, resulted in ±20% variation in aluminum production, which compared to the amount released to the reactors, in different electrical modes, can be neglected. Therefore, it can be concluded that electrochemical dissolution of anode is independent from the conductivity of the electrolyte when calcium is added and it might only be affected by current density. Since current density was kept constant in all the experiments, the amount of aluminum produced was almost the same at each electrical mode with different conductivity.

4.3.3. Impact on Activated Sludge Particle Sizes

Figure 4-29 shows the variations in mean activated sludge particle size vs. calcium concentration for different electrical modes. The negative values represent the increase in floc sizes. The highest mean particle size was obtained when 5ON:5OFF mode and 250 mg Ca^{2+}/L were applied. At LR MLSS, this mode and conductivity resulted in 34% larger floc size and at HR MLSS resulted in 26% larger floc size. Mean particle sizes for the higher conductivity (750 mg Ca^{2+}/L) resulted in smaller particle size in comparison to lower conductivity (250 mg Ca^{2+}/L). At 250 mg Ca^{2+}/L comparison between different electrical modes indicated that 5ON:5OFF had the highest impact on floc size whereas 5ON:15OFF mode had the least effect. When 750 mg Ca^{2+}/L is added to the reactors, due to high calcium concentrations, generation of calcium carbonate precipitation is probable.

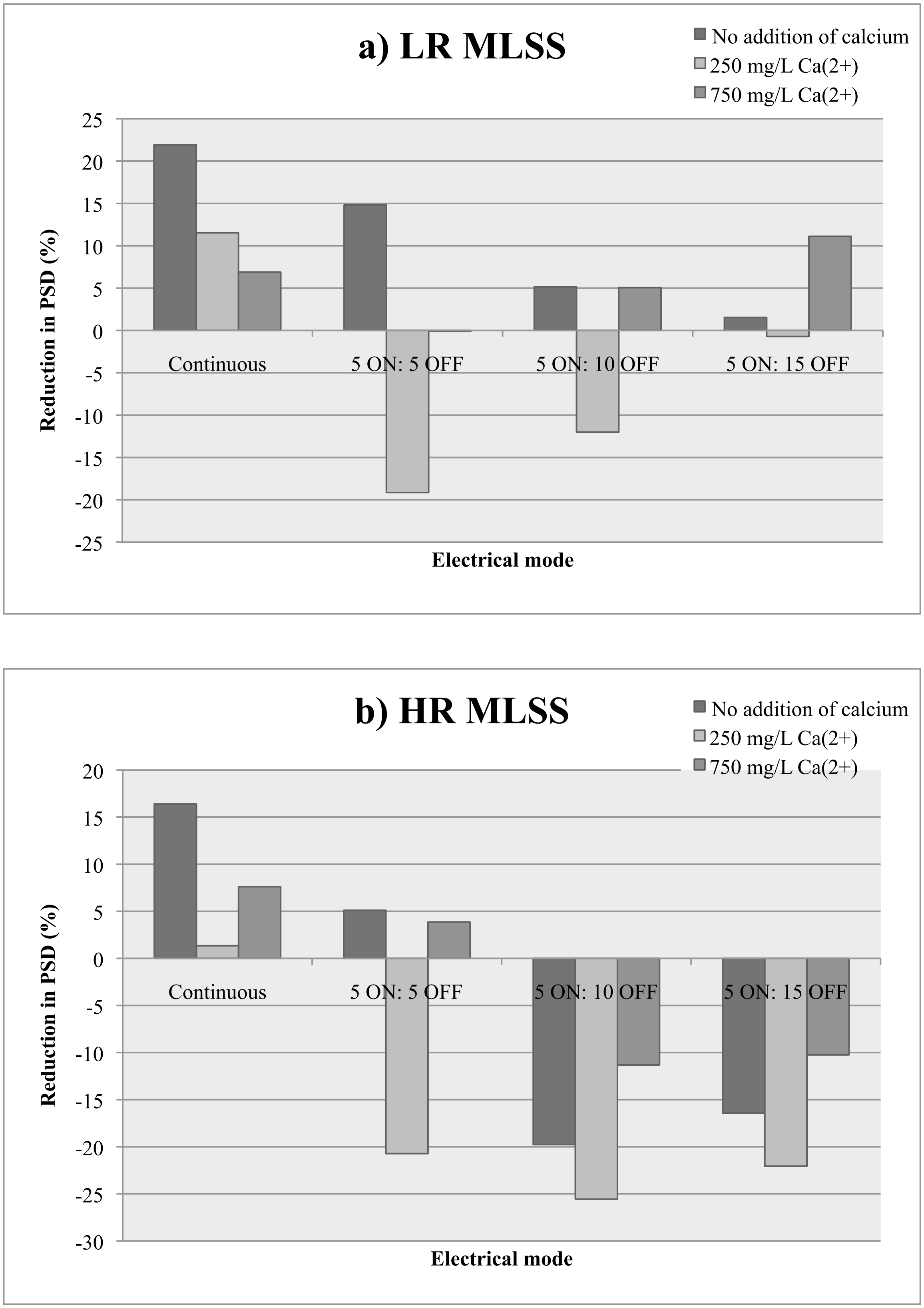


Figure 4-29 Impact of calcium addition on mean particle size at a) LR MLS b) HR MLSS

For this reason, the reduction in floc sizes when increasing the concentration of calcium might be due to inorganic precipitates such as calcareous flocs that are dense and their size is smaller than the microbial flocs. Among different electrical modes, 5ON:5OFF electrical mode obtained the larger floc size in comparison to the control value which might be as result of better coagulation/flocculation and bioflocculation process. Therefore, addition of 250 mg Ca^{2+}/L obtained higher floc sizes, which represents the impact of calcium addition on EC process. The percentage of error for this analysis was ± 8%.

4.3.4. Impact of on Time to Filtration (TTF)

Like SVI, time to filtration (TTF) has also been used as a filterability index to predict the dewaterability of sludge. Figure 4-30 shows the variation in TTF for different electrical modes as the calcium concentration increases. Figure 4-30a indicates that in continuous mode, addition of 750 mg Ca^{2+}/L resulted in 42% reduction in TTF in comparison to the control whereas addition of 250 mg Ca^{2+}/L resulted in 27% reduction. At 5ON:5OFF mode, addition of 250 mg Ca^{2+}/L resulted in 42% reduction in TTF. As the exposure time to electrical field decreased, the difference between control and the reactors with higher conductivity decreased. As a result, at 5ON:15OFF mode, 250 and 750 mg Ca^{2+}/L resulted in 8 and 21% reduction in TTF respectively. This results also indicated that where no calcium was added to the reactors, 5ON:15OFF mode had the highest impact on reducing the TTF. However, where conductivity increases, application of 250 mg Ca^{2+}/L at 5ON:5OFF and 750 mg Ca^{2+}/L at continuous mode, have the highest effect on reduction in TTF. The trend shows that the impact of conductivity was more obvious when more exposure time to electricity was applied.

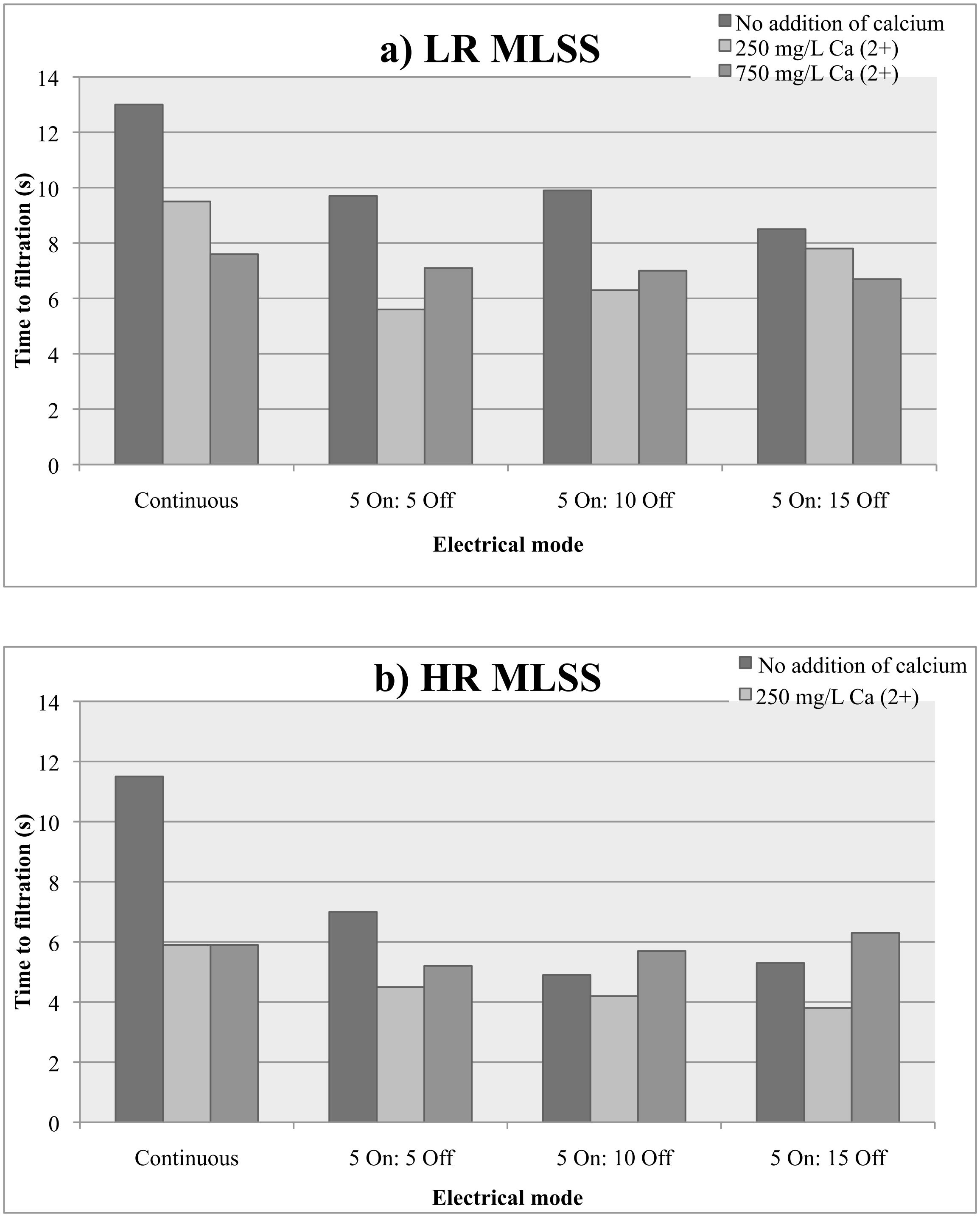
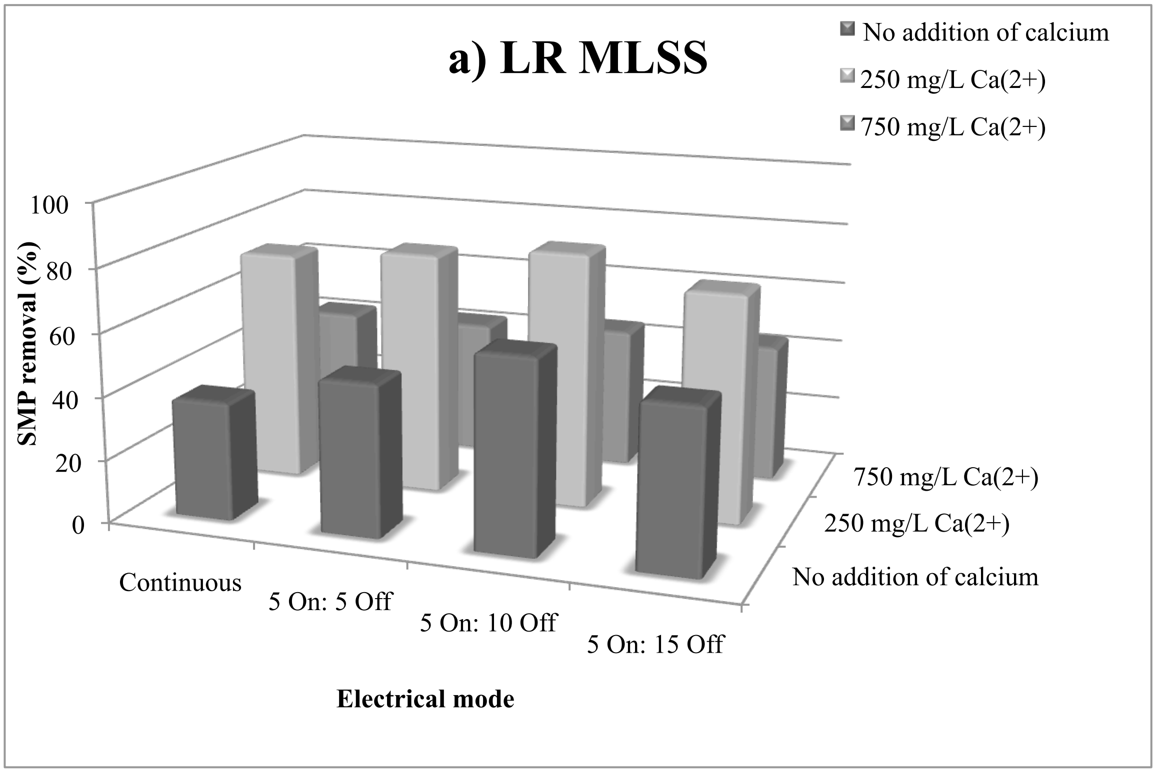


Figure 4-30 Impact of calcium addition on activated sludge time to filtration (TTF) a) LR MLSS b) HR MLSS

Furthermore, no significant difference in reduction of TTF between application 250 or 750 mg Ca^{2+}/L was observed. It could be concluded that conductivities obtained by addition of calcium concentration higher than 250 mg/L does not have a considerable impact on the reduction of TTF at LR MLSS. At HR MLSS (Figure 4-30b) and continuous mode 49% reduction in TTF was obtained for both 250 and 750 mg Ca^{2+}/L - that was the highest impact of addition of calcium on TTF observed in this study. At 5ON:5OFF mode, at the concentration of 250 mg Ca^{2+}/L and 750 mg Ca^{2+}/L resulted in 36% and 26% reduction in TTF respectively. A general trend states that the addition of salt at the concentration higher than 250 mg/L does not have a significant impact on reduction in TTF. Moreover, effects of calcium addition on the variation of TTF are not significant when the exposure time to electricity is reduced. The percentage of error for this analysis was ± 5%.

4.3.5. Impact on Supernatant Characteristics

Soluble microbial product removal efficiency was studied under different electrical modes when different conductivity was applied to the reactors. Figure 4-31a illustrates that for continuous mode, when 250 mg Ca^{2+}/L was added to the reactors, the SMP removal efficiency increased by 37% in comparison to the control reactor. However, addition of 750 mg Ca^{2+}/L increased the removal efficiency by 5%. Furthermore at 250 mg Ca^{2+}/L, as the exposure time to electricity decreased, the SMP removal efficiency decreased until it reached 72%, which is still 21% higher than the control value. When 750 mg Ca^{2+}/L was added the SMP removal efficiencies achieved were lower than the control reactors where no calcium was added. Therefore, addition of 750 mg Ca^{2+}/L had adverse effect on the removal efficiency of SMP whereas addition of 250 mg Ca^{2+}/L had significant impact. Furthermore, for both calcium concentrations, continuous mode had the highest impact on the SMP removal.



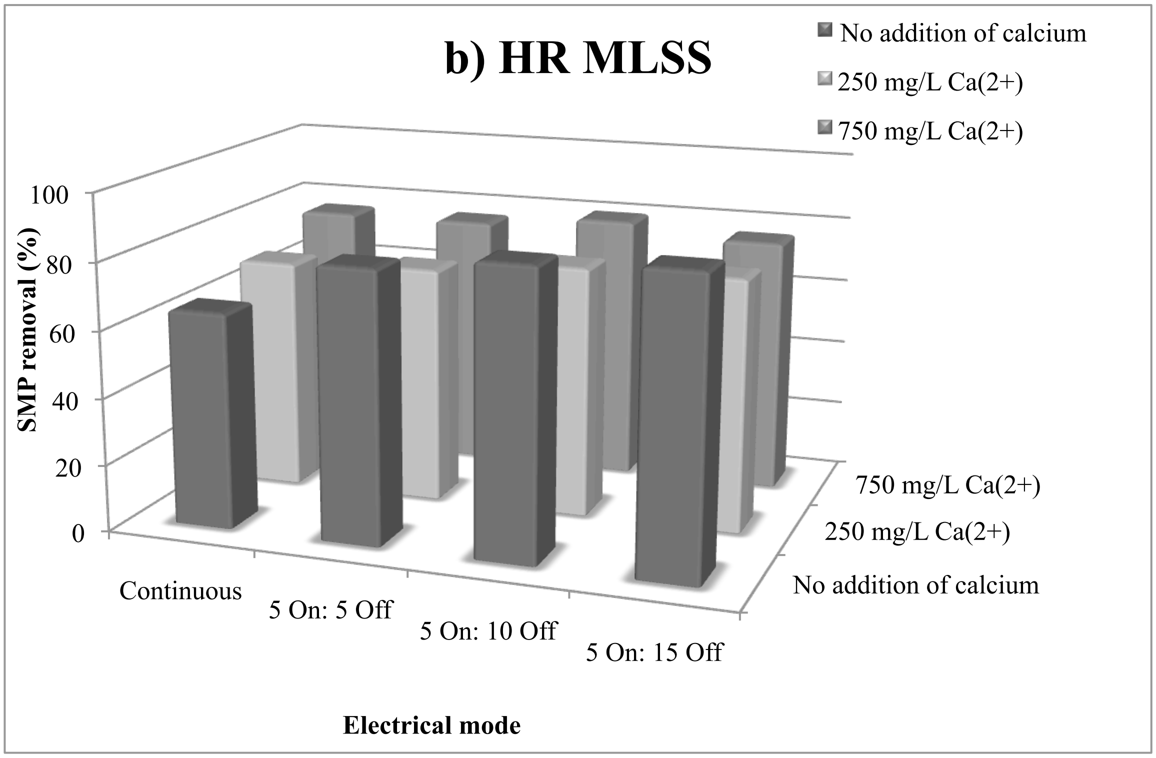
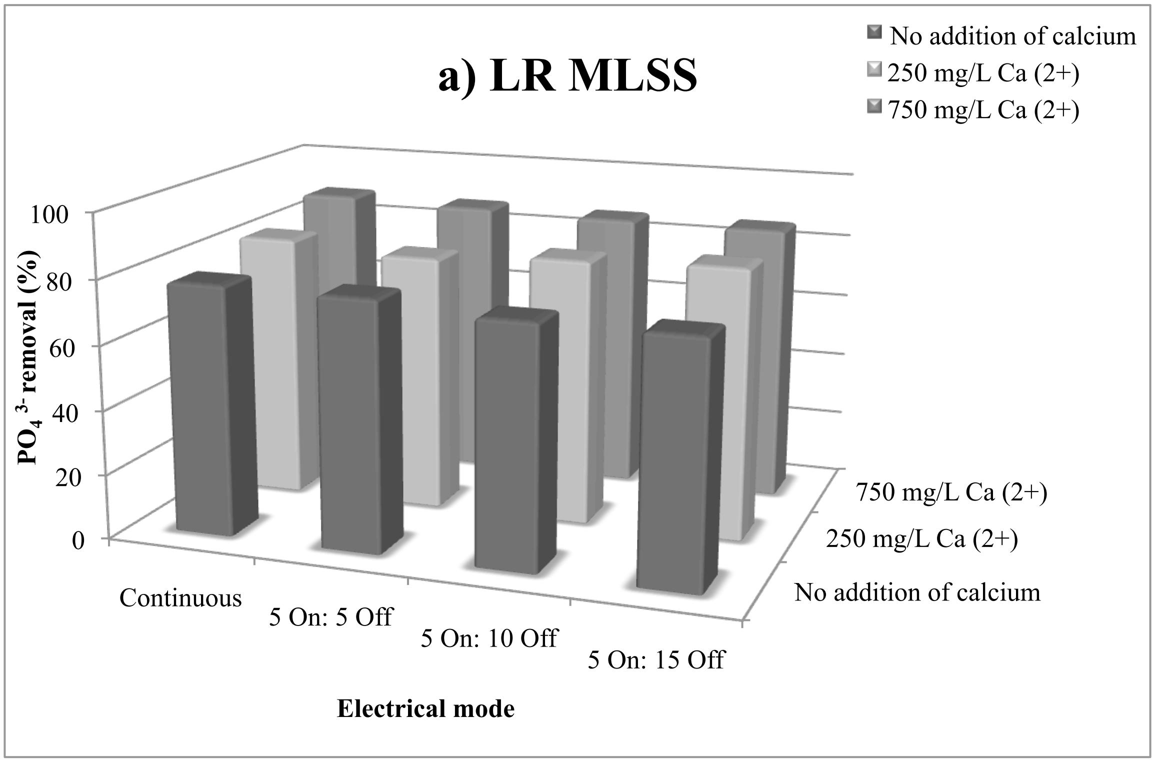


Figure 4-31 Impact of calcium addition on SMP removal in different electrical modes a) LR MLSS b) HR MLSS

Figure 4-31b shows the variation in removal efficiency of SMP for HR MLSS. It can be seen that increasing the conductivity by addition of calcium did not have a significant impact on the improvement of SMP removal efficiency. Only at continuous mode, an increase in the conductivity resulted in 5% to 12% higher removal efficiency in comparison to the control. The percentage of error for this analysis was ± 10%.

Figure 4-32 depicts the removal efficiency of phosphate in different electrical modes when conductivity was increasing. At LR MLSS, for continuous electrical mode, the addition of 250 and 750 mg Ca^{2+}/L resulted in 5% and 11% higher phosphate removal respectively in comparison to the control reactor with no addition of calcium. Results obtained from increasing the conductivity by addition of 250 mg Ca^{2+}/L, had insignificant impact on PO_4^{3-} removal efficiency with the highest impact of 9% higher in comparison to the control reactor for 5ON:15OFF mode. Furthermore, the addition of 750 mg Ca^{2+}/L had a slightly higher impact on PO_4^{3-} removal efficiency, which reached 11 to 12% higher percentage in comparison to the control for the same electrical mode. No major difference was observed between different electrical modes as conductivity increased. Higher calcium concentration obtained a slightly higher phosphate removal.

On the other hand, Figure 4-32b shows that at HR MLSS, an increase the conductivity results in improvement of PO_4^{3-} removal. In continuous mode, the addition of 250 mg/L and 750 mg Ca^{2+}/L resulted in 17 and 44% higher phosphate removal respectively. The addition of 250 mg Ca^{2+}/L in 5ON:5OFF mode did not have any effect whereas the removal efficiency increased by 29% when the conductivity was increased by addition of 750 mg Ca^{2+}/L. It is observed that less exposure time to electricity has resulted in higher phosphate removal.



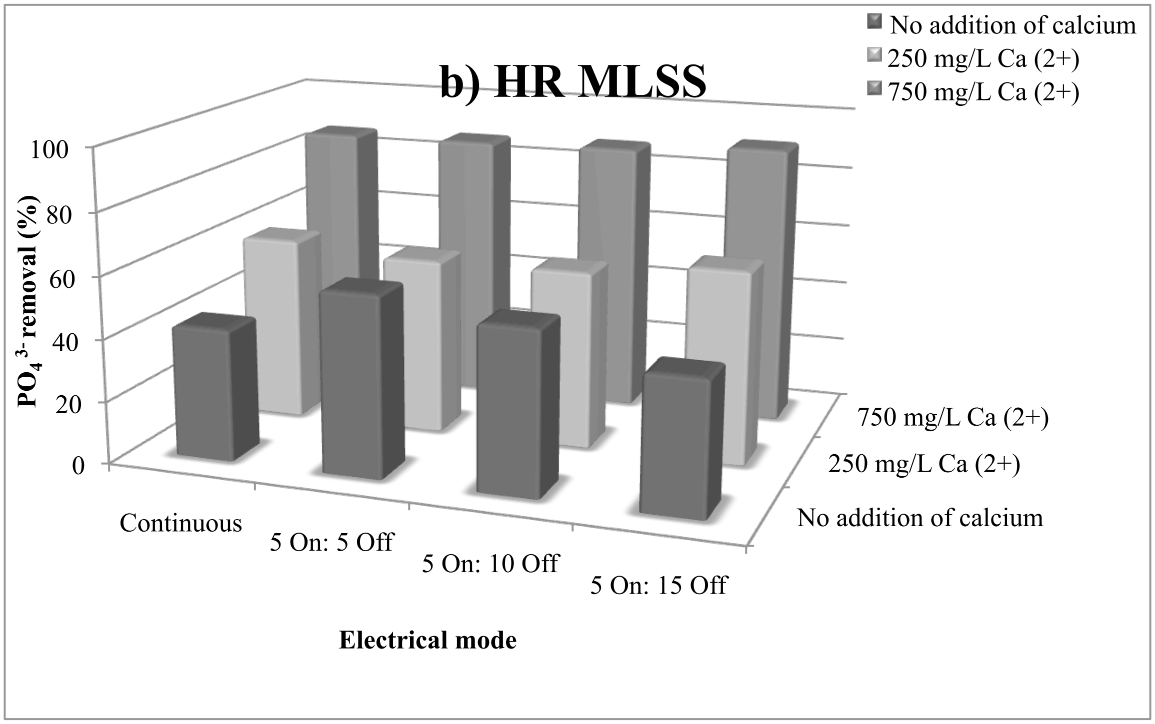


Figure 4-32 Impact of calcium addition on phosphate removal for different electrical modes a) LR MLSS b) HR MLSS

Furthermore, higher calcium concentration has resulted in much higher phosphate removal. This behavior might be as a result of calcium phosphate formation due to high concentration of calcium in the system. In general, in both MLSS ranges, higher conductivity had higher impact on phosphate removal especially at HR MLSS. The electrical mode of 5ON:15OFF reached the highest phosphate removal from the wastewater. When operating at HR MLSS, the increase in calcium concentration would result in more efficient phosphate removal. When no calcium is added, due to low conductivity of the electrolyte, coagulation process might be less efficient. However, when calcium is added to the reactors, not only the electrochemical processes is improved but also phosphate is removed by due to formation of calcium phosphates. The percentage of error for this analysis was ± 12%.

4.3.6. Impact on Applied Potential (Voltage)

Addition of salts to the electrolyte results in higher conductivity, therefore, it is expected that, at constant current density, voltage would be reduced as the conductivity increases. Figure 4-33 depicts the evolution of voltage in all reactors containing electrical field during 48 hours of operation for different conductivities. Results in Figure 3-33a shows that reactors with no addition of calcium experienced an increase in applied potential between 24 and 48 hours of operation whereas the applied potential in the reactors with addition of calcium did not change significantly during the 48 hours of operation. The increase in reactors without calcium addition might be as a result of coagulation process and removal of ions from the bulk solution where as in reactors with addition of calcium, due to high concentration of salt, conductivity did not change. Addition of 250 and 750 mg Ca^{2+}/L decreased the applied potential from 1.47 to 1 V/cm and 0.7 V/cm respectively.

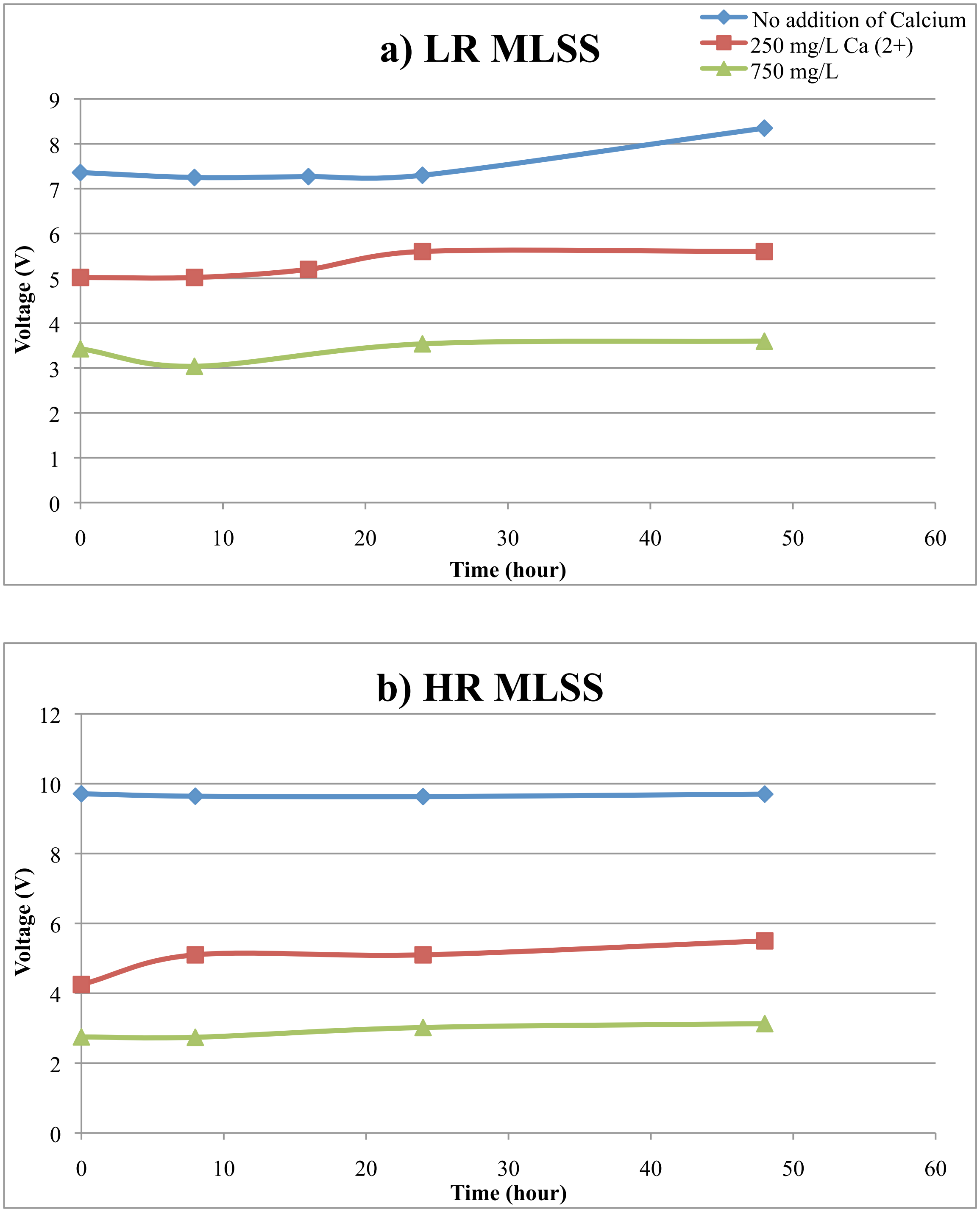


Figure 4-33 Evolution of voltage in all reactors all electrical vs. time a) LR MLSS b) HR MLSS

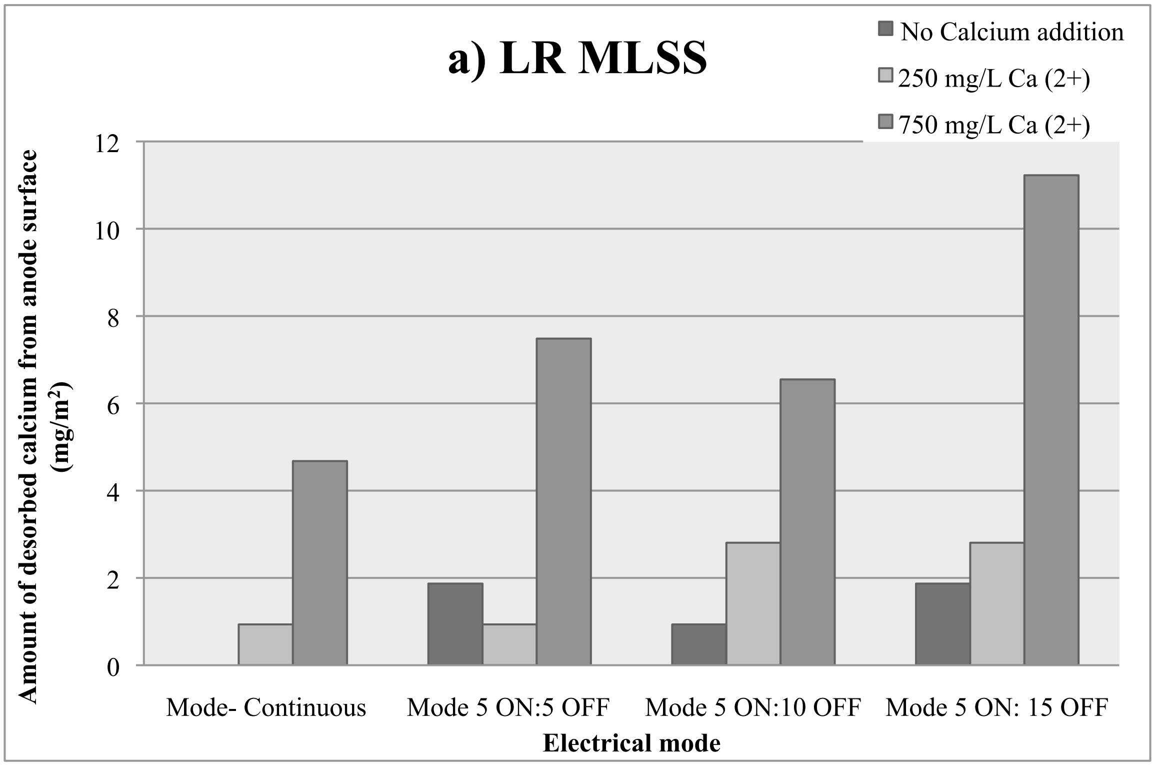
At HR MLSS (Figure 4-33b), there was no considerable change in applied potential with time for all reactors containing electrical field. Addition of 250 and 750 mg Ca^{2+}/L decreased the applied potential from 1.94 to 0.85 V/cm and 0.55 V/cm respectively.

4.4. Analysis of Electrode's Surface

Analyses of the attached materials to the surface of the electrodes (anode and cathode) were performed by extracting the inorganic fraction, using HNO_3, and organic fraction, using base solution (NaOH). All the figures in this section are on the basis of a unit electrode surface area.

4.4.1. Inorganic Fraction

Figure 4-34 is an indication of the amount of desorbed calcium concentration from anode surface for LR and HR MLSS. Figure 4-34a indicates the amount of calcium that is adsorbed to anode surface at LR MLSS. It can be observed that when calcium ion was not added to the reactors, the amount of calcium adsorbed to anode was almost the same for all electrical modes, which is an insignificant amount. Furthermore, when calcium concentration was increased to 250 mg/L, as the exposure time to electricity was decreased; more calcium was adsorbed to the anode surface. For instance, in continuous mode, after 48 hours of operation, 0.9 milligram calcium per each square meter of electrode surface (mg/m^2) was adsorbed whereas in 5ON:15OFF electrical mode, 2.8 mg/m^2 calcium was attached to the anode surface. Same behavior was observed when calcium concentration was increased to 750 mg/L. Comparison between 250 and 750 mg/L addition of calcium for one electrical mode shows that higher amount of calcium was adsorbed to anode surface when calcium concentration was increased to 750 mg/L.



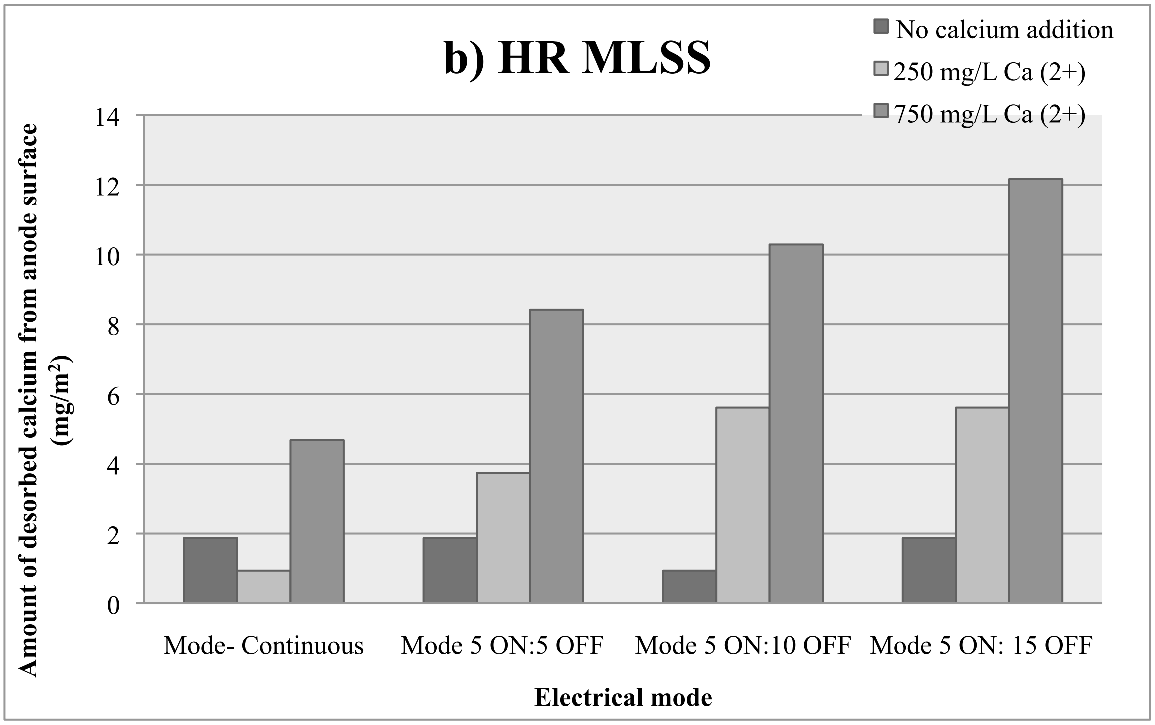


Figure 4-34 Amount of calcium desorbed from anode surface a) LR MSS b) HR MLSS

Figure 4-34b indicates the amount of calcium, which was adsorbed to anode surface when HR MLSS was applied; the same behavior of calcium ion was observed as LR MLSS.

Figure 4-35 is an indication of the amount of desorbed calcium from cathode surface for LR and HR MLSS. Calcium in the form of cations is expected to be much more present on the surface of cathode since it has a negative charge than that of the anode surface. At LR MLSS (Figure 4-35a), the amount of calcium that was adsorbed to the cathode surface when calcium was not added was insignificant in comparison to higher concentrations of calcium. As it can be observed, in continuous mode, when 250 mg Ca^{2+}/L was added to the reactors, 29467 mg Ca^{2+}/m^2 was adsorbed to cathode surface, whereas the addition of 750 mg Ca^{2+}/L resulted in 33957 mg Ca^{2+}/m^2. In other words, increasing the calcium concentration up to three times only resulted in 13% more adsorption of calcium on the cathode surface. Moreover, when 5ON:5OFF electrical mode was applied, a sudden drop in the amount of calcium was observed for both calcium concentrations reaching 18616 and 24883 mg/m^2 for 250 and 750 mg Ca^{2+}/L respectively. Furthermore, as the exposure time to DC decreased the amount of calcium adsorbed to the cathode surface was almost the same for these electrical modes. The trend observed at HR MLSS (Figure 4-35b) was the same as LR MLSS. However at HR MLSS, the amount of calcium adsorbed to the surface of cathode was higher in comparison to LR MLSS.

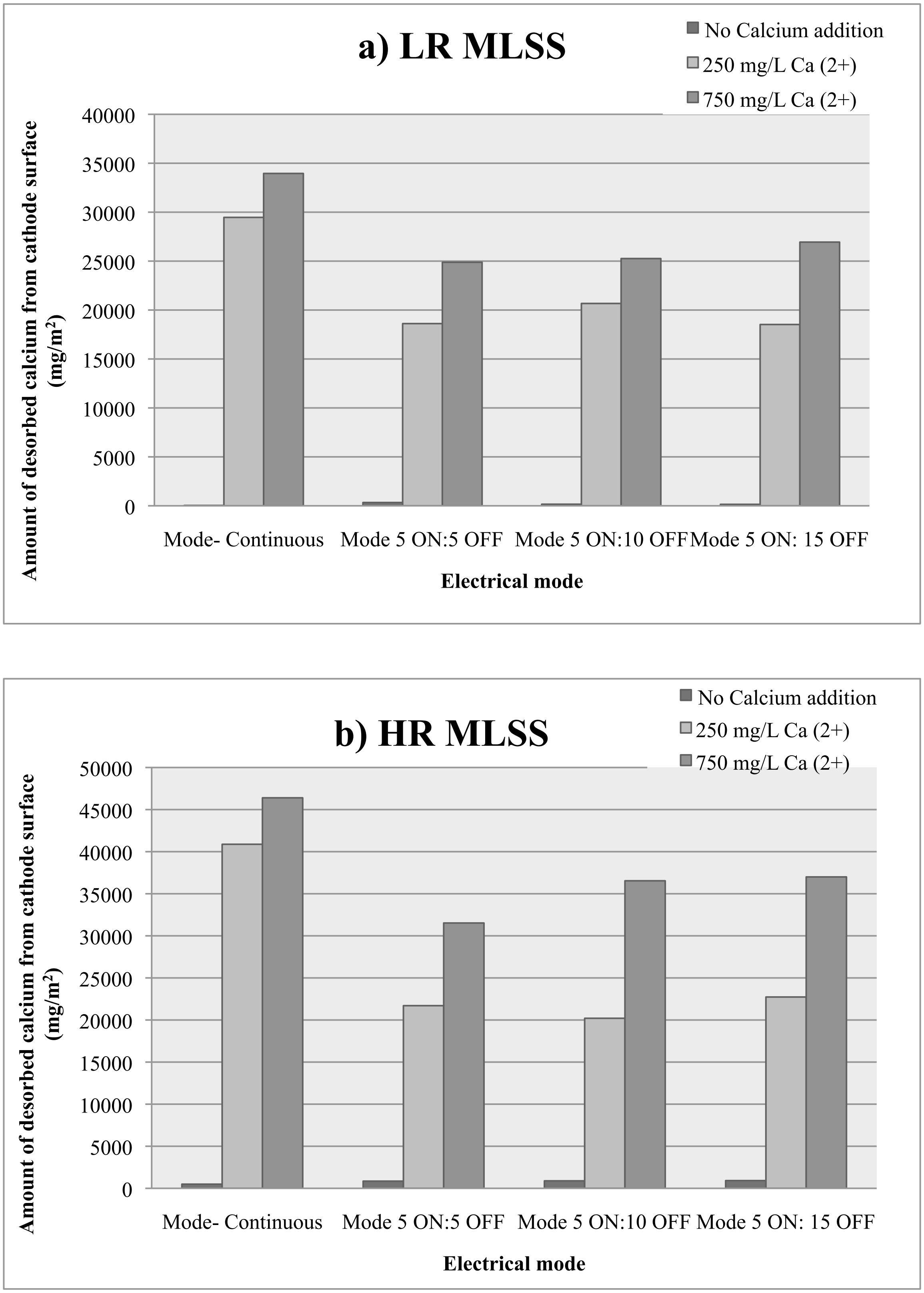


Figure 4-35 Amount of calcium desorbed from cathode surface a) LR MSS b) HR MLSS

In order to be able to better understand the behavior of calcium in the rectors, a comparison was made between the amount of calcium that was desorbed from anode and cathode surface. Figure 4-36 depicts the amount of calcium obtained from electrodes surface for LR MLSS when 250 mg Ca^{2+}/L was added.

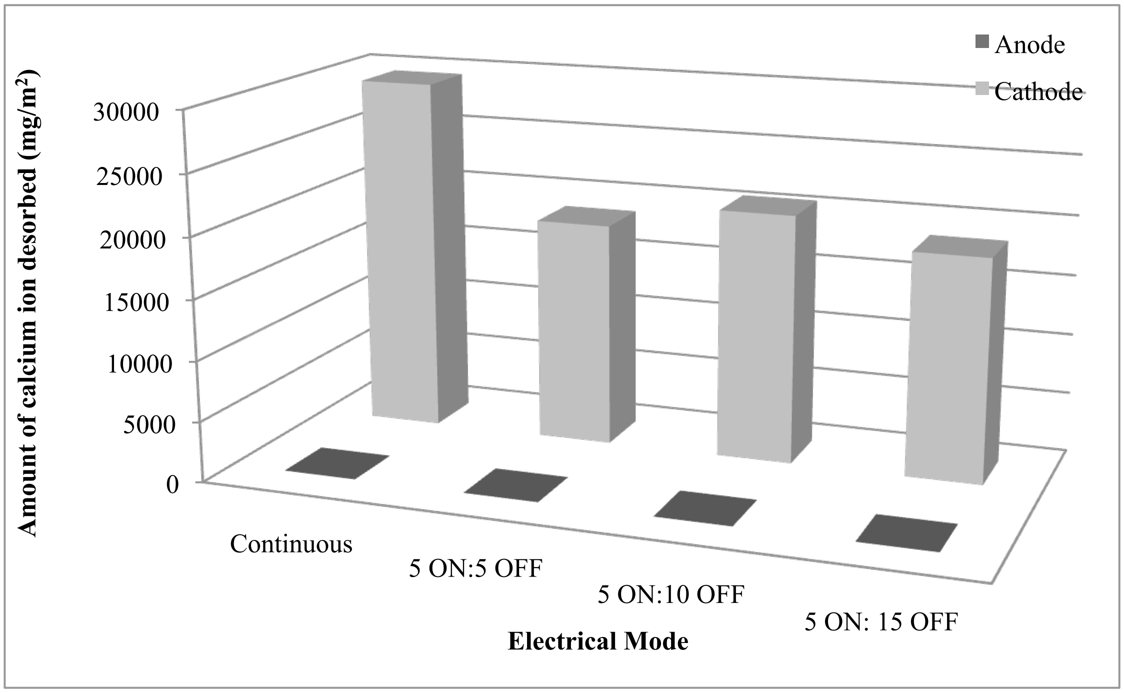
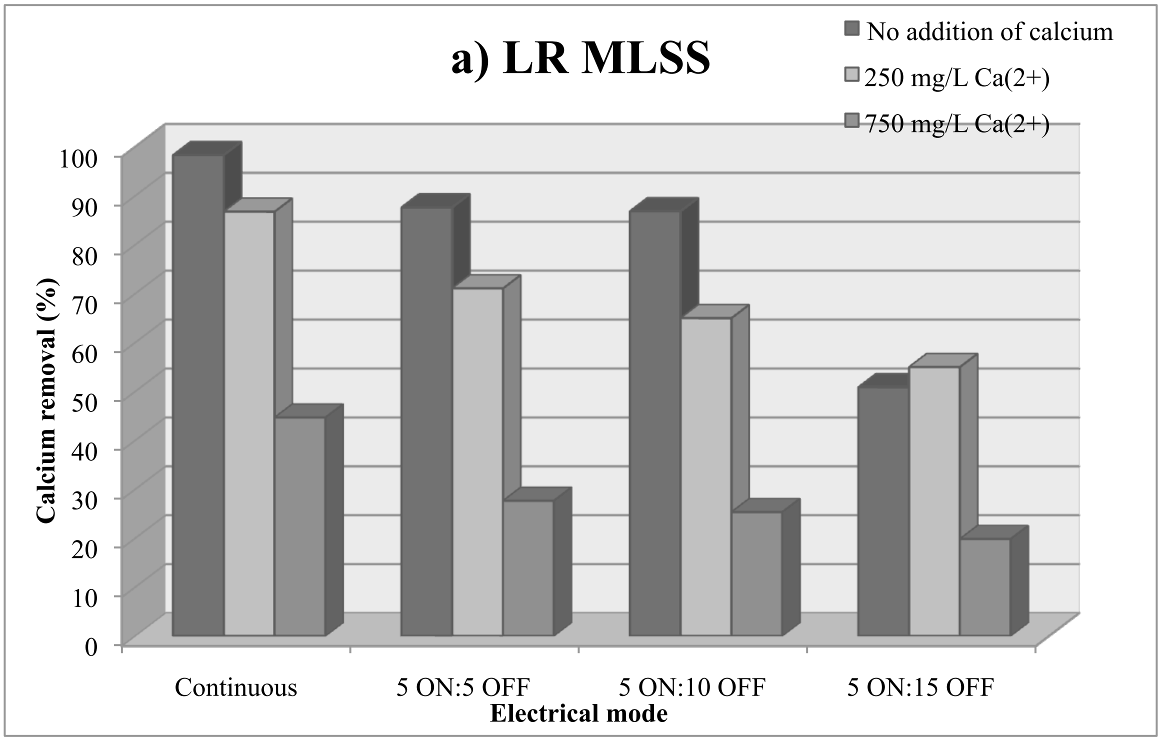


Figure 4-36 Amount of calcium desorbed from anode and cathode surface (LR MLSS, 250 mg Ca^{2+}/L)

It is apparent that the amount of calcium desorbed from the anode surface is negligible in comparison with the amount of calcium on cathode surface. Since calcium is a divalent cation, it has higher affinity to cathode that bears a negative charge and therefore much more calcium is observed on cathode surface.

The Variations in calcium concentration through different electrical modes for LR and HR MLSS have also been indicated in Figure 4-37.



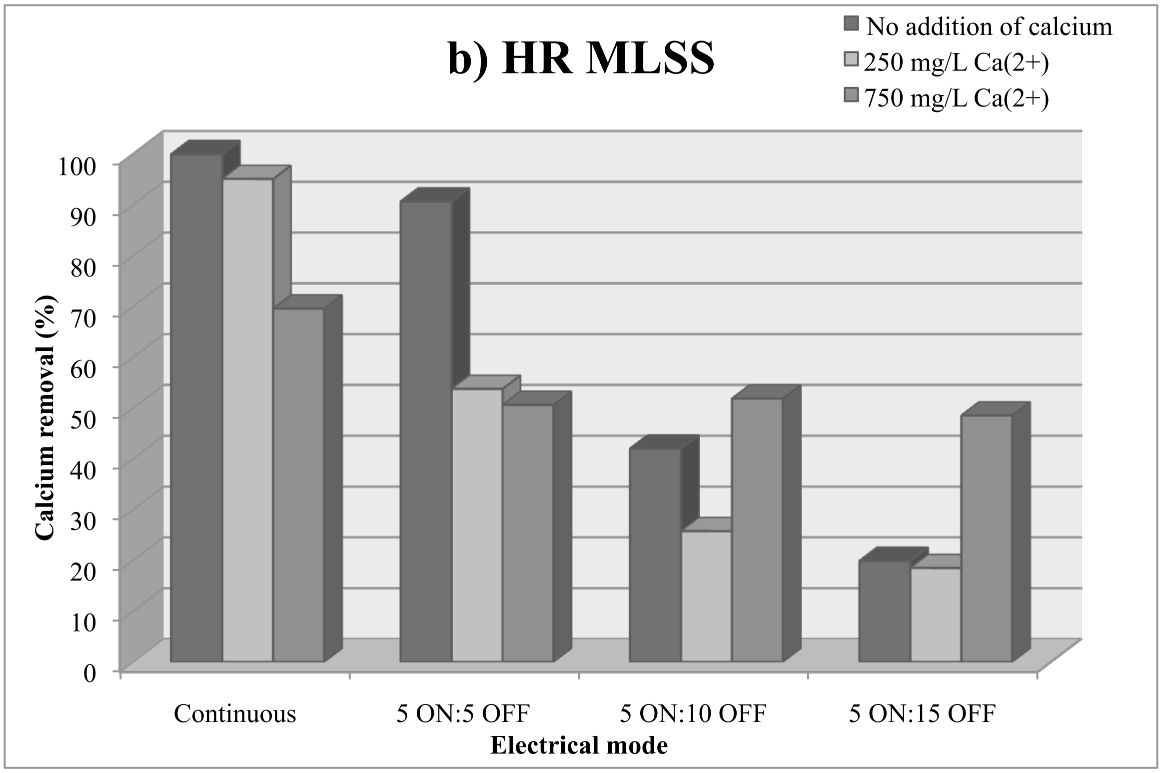
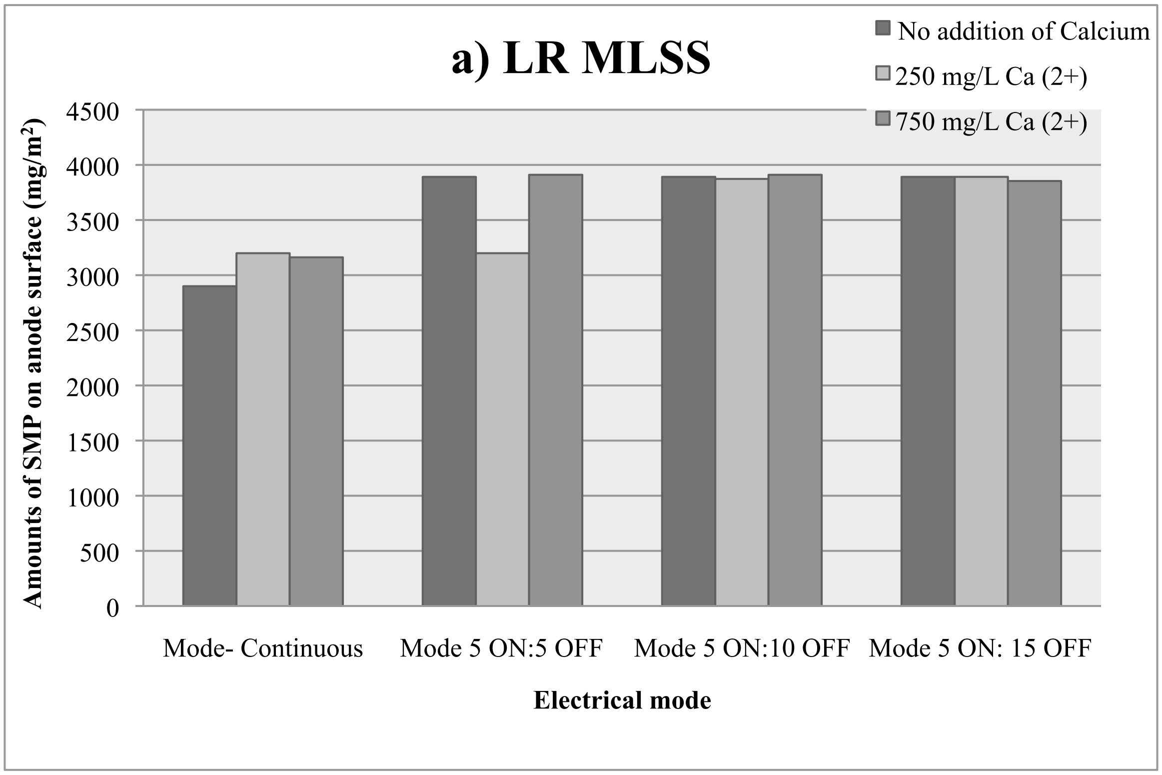


Figure 4-37 Variation in calcium removal after 48 hours

At LR MLSS (Figure 4-37a), at all electrical modes as the initial concentration of calcium increased, the amount of calcium removed from the activated sludge decreased. Among all electrical modes, continuous mode achieved the highest reduction in calcium concentration. Same trend was observed for HR MLSS (Figure 4-37b); however, when the initial calcium concentration was 750 mg/L, the amount of calcium removed from the activated sludge was the same among 5ON:5OFF, 5ON:10OFF and 5ON:15OFF electrical mode. These results are comparable to the results obtained from the impact of calcium on activated sludge properties.

4.4.2. Organic Fraction

The organic fraction of the attached materials on electrode surfaces was analyzed by measuring SMP as soluble COD from the solution obtained from immersion of electrodes (see Chapter 3, Section 3.4.4). Figure 4-38 and 4-39 indicate the amount of SMP extracted from the surface of the anode and cathode respectively. As indicated in Figure 4-38a, at LR MLSS continuous electrical mode had the lowest SMP amount (2900 mg/m^2) in comparison to other electrical modes. The SMP amounts, desorbed from the anode, in other electrical modes were not significantly different. It could be concluded that addition of calcium did not have a significant impact on the adsorption of SMP to the anode. Figure 4-38b also shows the same trend for SMP amount desorbed from anode for HR MLSS. Therefore, in this experiment no considerable difference was found between different electrical fields, calcium addition and sludge concentration in adsorption of SMP to the anode surface. Since during all the experiments, current density was kept constant, this behavior of SMP might be in accordance to the constant current density (CD).



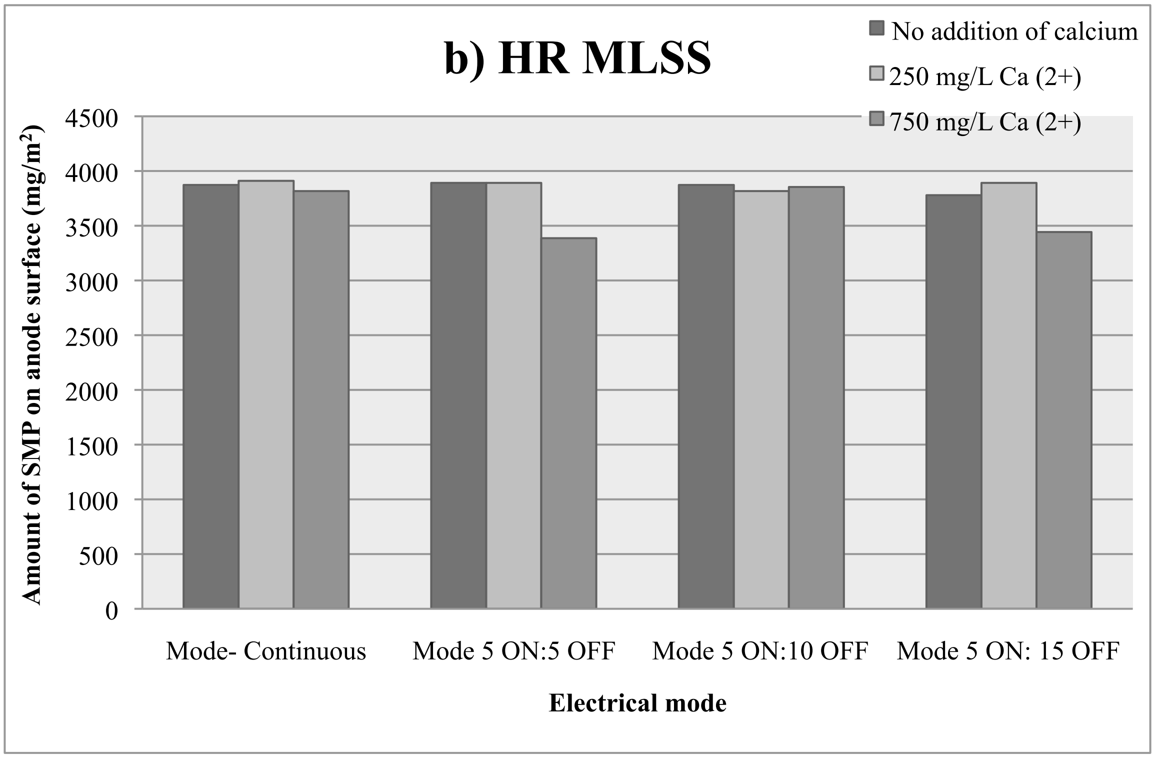
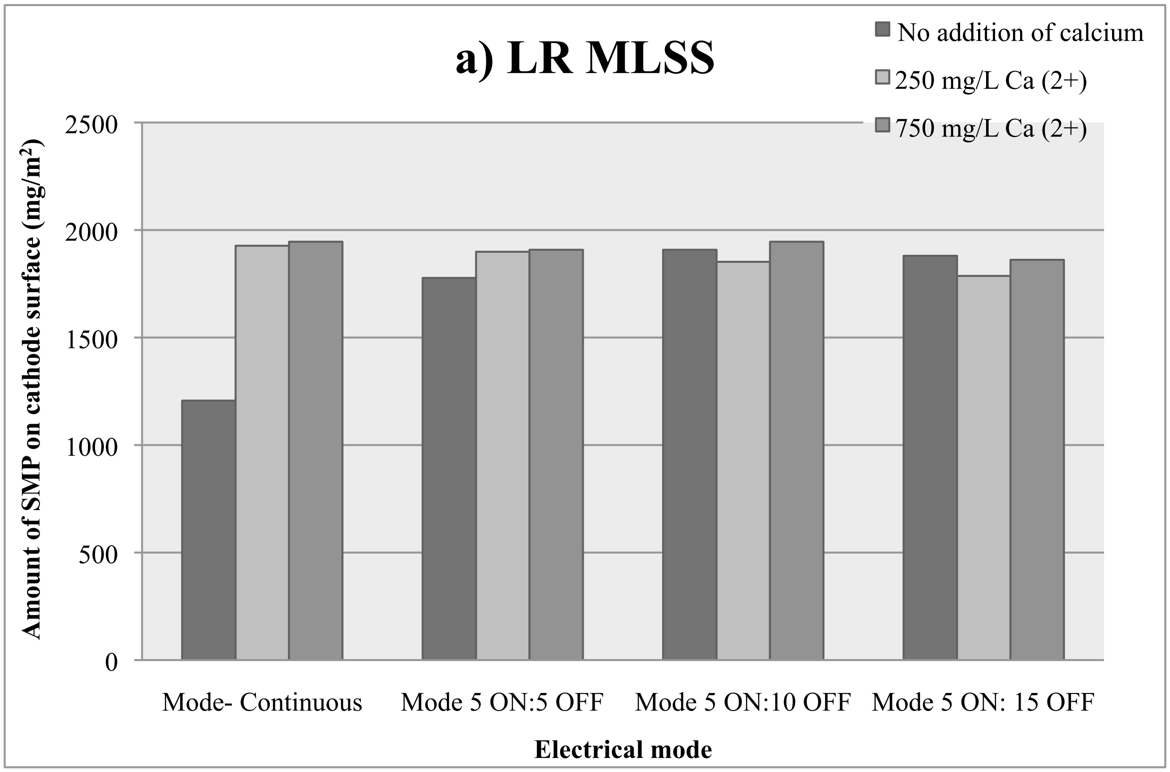


Figure 4-38 Amount of SMP on anode surface in mg/m^2 a) LR MLSS b) HR MLSS



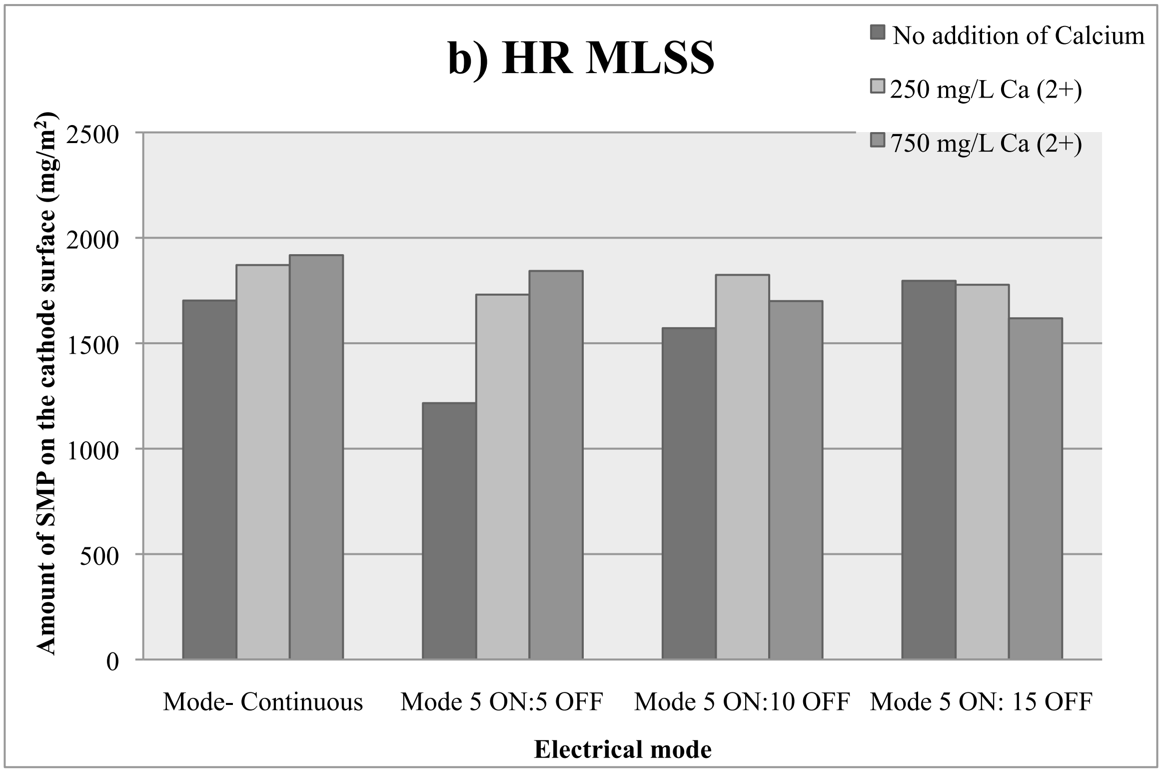


Figure 4-39 Amount of SMP desorbed from cathode surface (mg/m^2) a) LR MLSS b) HR MLSS

Figure 4-39a shows the amount of SMP desorbed from the cathode surface for LR MLSS. The lowest amounts of SMP desorbed from the cathode surface were found in the reactors with no addition of calcium. No significant difference was observed between 250 and 750 mg Ca^{2+}/L runs. Variation in the SMP amount for HR MLSS is shown in Figure 4-39b, which also had the same trend as LR MLSS. Overall, it can be assumed that adsorption of SMP to the cathode surface is related to the applied current density during the electrocoagulation process.

Figure 4-40 illustrates the amount of SMP that was deposited on the anode and cathode where 250 mg Ca^{2+}/L was added at low range sludge concentration.

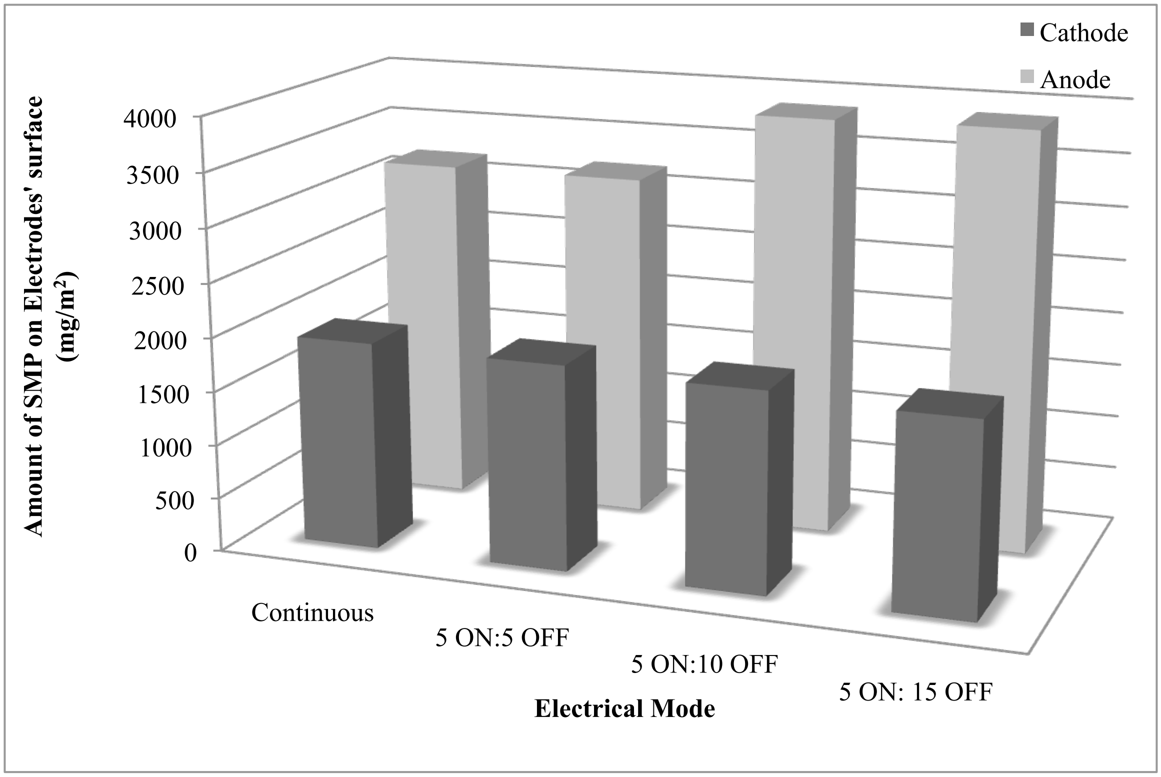


Figure 4-40 Amount of SMP deposited on the cathode and anode (LR MLSS, 250 mg Ca^{2+}/L)

An average amount of SMP desorbed from the cathode surface, among all electrical modes, was 1866 mg/m^2, whereas the concentration of SMP, found on the anode surface, in 5ON:10OFF and 5ON:15OFF modes were 3872 and 3891 mg/m^2 respectively; the continuous and 5ON:5OFF modes deposed the same amount (3199 mg/m^2) of SMP.

A comparison between the SMP values obtained for cathode and anode reveals that SMP have much higher affinity to the anode than to the cathode surface. This might be due to the effect of negatively charged functional groups within soluble EPS (SMP), which due to electrophoresis phenomenon migrate toward the oppositely charged electrode (anode).

Chapter 5 Conclusion

5.1. Conclusions

In this research the direct application of electrocoagulation process to activated sludge has been examined. EC has been applied to activated sludge in different electrical modes; continuous, 5ON:5OFF, 5ON:10OFF, and 5ON:15OFF at constant current density of 20-25 A/m^2. During each experiment, samples were taken from the bioreactors and were analyzed for their properties such as SVI, particle size, SMP and etc. Electrocoagulation experiments were carried out on both activated sludge alone and activated sludge mixed with different concentrations of calcium salt. The depositions of organics and inorganics on the electrodes were analyzed. Furthermore, the impact of different calcium concentrations (0, 250 and 750 mg Ca^{2+}/L) on activated sludge properties, without the application of electrical field, was also investigated. All experiments were performed for low range and high range MLSS concentrations. The obtained results and analyses from the above experiments fulfill the objectives of this research in the content of the following achieved conclusions:

Impact of electrocoagulation (EC) on activated sludge properties:

- From the overall performance of EC in different conditions, it could be concluded that EC has a high potential in improving the activated sludge characteristics.
- For all electrical modes, EC had higher impact on AS properties than reactors without EC.

- Continuous electrical mode had significant impact on the reduction of SVI: 58% and 37% at LR and HR MLSS respectively. For all electrical modes, EC had higher impact on LR MLSS than HR MLSS.
- As the exposure time to DC was increased, for both concentration ranges of mixed liquor, higher MLSS concentrations were obtained and therefore the VSS/TSS ratio was highly reduced.
- Aluminum dissolution from the anode to bulk solution was a function of the electrical mode.
- The exposure time of DC to activated sludge had a direct impact on the morphology of sludge particles. Longer exposure time to DC resulted in smaller particle size distribution. The continuous electrical mode achieved the highest reduction in particle size for both LR and HR MLSS (23 and 16% respectively); for HR MLSS and shorter DC exposure time, longer operation time is required to obtain smaller particles.
- EC had a significant impact on the reduction of TTF. At LR MLSS, all electrical modes achieved an average of 83% reduction in TTF, whereas at HR MLSS, the highest reduction (73%) was achieved in both 5ON:10OFF and 5ON:15OFF electrical modes.
- The highest SMP removal efficiency (53% and 78%) was achieved in 5ON:10OFF mode at both MLSS ranges. Furthermore, in all electrical modes, the impact of EC on SMP removal efficiency was higher at HR MLSS compared to LR MLSS.

- In all electrical modes, over 75% reduction in phosphate was achieved. The impact of EC on phosphate removal efficiency at LR MLSS was higher than at HR MLSS.
- EC had the potential to remove ammonia from activated sludge. As the exposure time to DC was decreased, more ammonia was removed. Application of 5ON:15OFF electrical mode achieved 56% and 50% ammonia removal at LR and at HR MLSS respectively.
- Longer exposure time to DC resulted in higher nitrate removal. Variation in nitrate removal was more considerable for HR MLSS.
- Bioactivity in activated sludge was affected by EC process. In this regard, 5ON:10OFF electrical mode had the lowest impact on SOUR.
- EC does not impede biological activity with respect to pH; during the experiments the pH values were situated between 6 and 9.
- Generally, 5ON:10OFF electrical mode had the highest impact on AS properties in terms of soluble microbial products, nitrates, ammonia, and phosphate removal efficiency and microorganism bioactivity at both ranges of MLSS.

From the this research, at LR MLSS, 5ON:10OFF electrical mode had the highest impact on activated sludge properties in terms of SMP removal and affecting the microbial bioactivity. Furthermore, it is expected that the application of EC into SMEBR system enhances its performance by reducing the membrane fouling.

Impact of calcium addition on activated sludge characteristics:

- Generally, the behaviour of calcium was different at LR and HR MLSS.

- At LR MLSS addition of 250 mg Ca^{2+}/L improved TTF, SMP removal efficiency and increased particle sizes; whereas at HR MLSS, 750 was more effective in terms of TTF reduction and SMP removal efficiency.
- At LR MLSS, the addition of 250 mg Ca^{2+}/L resulted in 39% higher TTF reduction in comparison to the reactor without the addition of calcium. Calcium concentrations higher than 250 mg/L did not have any further impact on this parameter. At HR MLSS, 750 mg Ca^{2+}/L was required to achieve 49% higher TTF reduction in comparison with reactor without addition of calcium.
- At LR MLSS, the addition of 250 mg Ca^{2+}/L resulted in 10% increase in particle size. This behaviour can be attributed to the bridging between calcium ions and negatively charged functional groups within EPS, and enhancement of bioflocculation. Calcium concentrations higher than 250 mg/L resulted in smaller particles. This might be due to the formation of calcareous flocs which have smaller sizes than microbial flocs. Calcium did not have any impact on particle sizes at HR MLSS.
- The addition of 250 mg Ca^{2+}/L, at LR MLSS, resulted in 33% higher SMP removal efficiency in comparison to the reactor without the addition of calcium. This behaviour might be the result of divalent cations bridging with negatively charged functional groups within EPS. At HR MLSS, higher calcium concentrations did not affect the SMP removal.
- At both MLSS ranges, as the concentration of calcium was increased higher phosphate removal efficiency was achieved.

- At both ranges of MLSS, higher calcium concentrations did not improve SVI value.

It is expected that addition of 250 mg Ca^{2+}/L could improve the performance of SMBR and reduce the membrane fouling.

Impact of calcium addition on EC process:

- Addition of 250 mg Ca^{2+}/L resulted in larger particles in comparison to the addition of 750 mg Ca^{2+}/L. At LR MLSS and HR MLSS, 5ON:5OFF and 5ON:10OFF electrical modes had the highest impact on the PSD increase.
- Generally, for continuous electrical mode, the activated sludge properties behave differently in comparison to other electrical modes.
- Comparison between different concentrations of calcium revealed that 250 mg Ca^{2+}/L had higher impact on TTF. The highest reduction was achieved in 5ON:5OFF electrical mode. As the exposure time to electricity decreased, the impact of calcium also decreased.
- At LR MLSS and in all electrical modes, addition of 250 mg Ca^{2+}/L resulted in higher SMP removal efficiency (over 72%) in comparison to 750 mg Ca^{2+}/L. This behaviour can be attributed to the bioflocculation phenomenon. At HR MLSS, addition of calcium did not have any significant impact on the SMP removal.
- At LR MLSS, the higher concentration of calcium did not have a considerable impact on the phosphate removal. However at HR MLSS, in all electrical modes higher calcium concentrations resulted in higher phosphate removal (over 87%).

- For both MLSS ranges, higher calcium concentrations did not improve SVI. Among all electrical modes and for all concentrations of calcium, the continuous mode acheived the highest reduction in SVI.
- Aluminum dissolution was independent from the calcium concentration in the activated sludge. It can be concluded that higher conductivities does not have any impact on amount of aluminum released to the reactor. Aluminum dissolution is a function of current density.

Overall, it can be concluded that in SMEBR systems, addition of 250 mg Ca^{2+}/L and application of 5ON:5OFF and 5ON:10OFF electrical mode might reduce the membrane fouling.

Deposition of organics and inorganics on the electrodes:

- The amount of calcium deposited on the anode was negligible in comparison to the amount of calcium adsorbed on the cathode.
- At LR MLSS and continuous electrical mode, increasing the calcium concentration from 250 mg/L to 750 mg/L had only resulted in 13% higher amount of calcium deposition on the cathode surface. The 5ON:10OFF electrical mode also provoked higher deposition of calcium on the cathode.
- The difference between the results obtained from the deposition of calcium on the cathode was much more evident for HR MLSS than LR MLSS.
- Deposition of SMP on the anode surface was approximately two times higher than the amount of SMP, which was deposited to the cathode surface.

- At both MLSS ranges, higher calcium concentrations did not have any significant impact on the deposition of SMP on both the cathode and the anode.

It is expected that at LR MLSS, the electrokinetically controlled conditions through electrocoagulation process (e.g. application of 250 mg Ca^{2+}/L and 5ON:10OFF mode at CD of 20-25 A/m^2) might have significant effects, in terms of SMP and inorganics reduction, and particle sizes, in reducing the membrane fouling.

5.2. Recommendation for Future Works

- Comparison between the changes in activated sludge properties generated in batch and continuous flow
- Evaluating the tests in the presence of the membrane module
- Studying the morphology of floc formation in different activated sludge conditions and under the application of DC field
- Studying nitrogen cycle in various activated sludge conditions under the application of DC field
- Studying the impact of different cations on the activated sludge properties

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Appendix I: Calculations

Calculation No.1: Removal Efficiency

$$RE\ (\%) = ((I-F)/I)\times 100$$

where,

I: Initial concentration

F: Final concentration

Calculation No. 2: Amount of organics and inorganics deposited on electrodes

$$W(mg/m^2) = (C \times D.F. \times 50ml \times 2) / A$$

where,

W: Amount of organics and inorganics

C: Concentration of calcium obtained from AA readings or concentration of sCOD obtained from Hach COD vials

D.F.: Dilution factor

A: Effective electrode’s surface area (0.0107 m^2)

Calculation No.3: Metal Analyses

$$\text{Metal concentration (mg/L)} = A\times(B/C),$$

where,

A = Concentration of metal in filtrate solution (mg/L)

B = Final volume of filtrate (mL)

C = Sample size (mL)

Calculation No.4: Aluminum concentration in supernatant

Concentration of aluminum (mg/L) = (D – H) / L

where,

D = Initial weight of aluminum electrode (mg)

H = Weight of aluminum electrode after the experiment (mg)

L = Volume of activated sludge used (1.5 L)

Calculation No.5: Percentage Error

Error (%) = ((Average value – Actual value) / Actual value) ×100

The absolute value of error was taken as the percentage error

Appendix II: Photographs

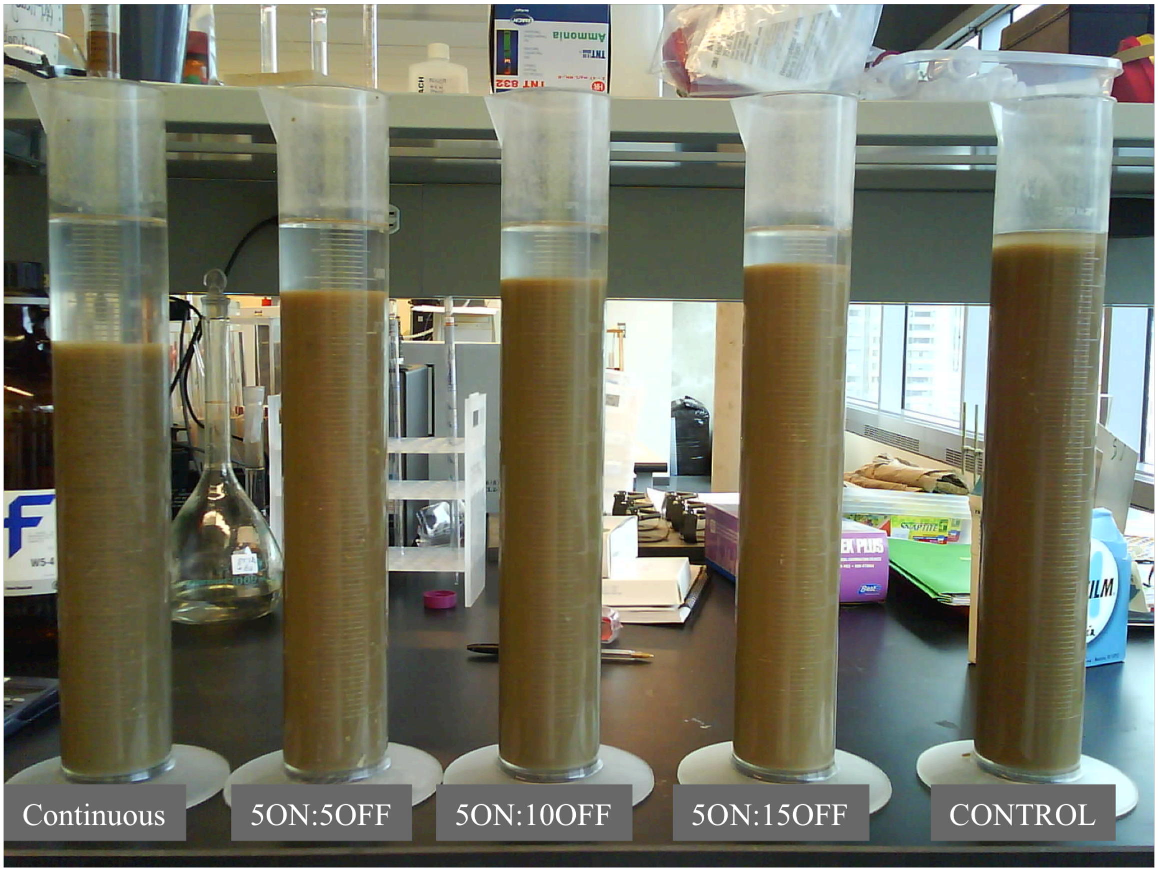

Figure A-1 Sample picture of variations in SVI after 48 hours of operation among different electrical modes

Glossary

Abbreviations and Symbols	Terms
5 ON: 10 OFF	Bioreactor which is connected to a automatic timer with 5 minutes ON and 10 minutes OFF operation mode
5 ON: 15 OFF	Bioreactor which is connected to a automatic timer with 5 minutes ON and 15 minutes OFF operation mode
5 ON: 5 OFF	Bioreactor which is connected to an automatic timer with 5 minutes ON and 5 minutes OFF operation mode
AS	Activated sludge
BOD	Biological oxygen demand
C1	Control reactor for Run 1 (no electrocoagulation), LR MLSS
C2	Control reactor for Run 2 (no electrocoagulation), HR MLSS
C3-4	Control reactor for Run 3 and 4 (no addition of calcium), LR MLSS
C5-6	Control reactor for Run 5 and 6 (no addition of calcium), HR MLSS
CAS	Conventional activated sludge process
CD	Current density (A/m^2)

COD	Chemical oxygen demand
Continuous	Bioreactor which is continuously connected to direct current
DC	Direct Current
DCB	Divalent cation bridging
DLVO	Double layer theory
DO	Dissolved oxygen
EC	Electrocoagulation
EDTA	Ethylene diamine tetra acetic acid
Electrocoagulation	In-situ generation of coagulant by electrolytic oxidation of an appropriate anode material.
Electromigration	Transport of ions and polar molecules in the direction of the opposite electrode under electrical field
Electroosmosis	Movement of water under the influence of imposed electric gradient. Due to the presence of more cations than anions in the water, the flow of water is toward cathod.
Electrophoresis	Transport of charged particles and colloids under the influence of an applied direct current
Elektrokinetic Phenomena	Application of direct-current electric field to across a section of contaminated soil to remove contaminants, which consist of three principle mechanisms: Electromigration, Electroosmosis and Electrophoresis

EPS	Exocelluar polymeric substances
F/M	Food to microorganisms ratio
FTIR	Fourier transform infrared spectroscopy
HR MLSS	High range mix liquor suspended solids (10000-12000 mg/L)
HRT	Hydraulic retention time
I	Current (A)
LC	Low calcium concentration
LR MLSS	Low range mixed liquor suspended solids (5000-7000 mg/L)
M/D	Monovalent to divalent cations ratio
MBR	Membrane bioreactor
MLSS	Mixed liquor suspended solids (mg/L)
MLVSS	Mixed liquor volatile suspended solids (mg/L)
OC	High calcium concentration
OUR	Oxygen uptake rate ((mg/L)/min)
PAC	Powdered activated carbon

PSD	Particle size distribution (μm)
$R_{(inorganic\text{-}f)}$	Resistance caused by inorganic fouling
$R_{(organic\text{-}f)}$	Resistance caused by organic fouling
R_c	Cake resistance
R_f	Membrane resistance
R_m	Membrane intrinsic resistance
sCOD	Soluble chemical oxygen demand
SEM	Scanning electron microscopy
SEM-EDS	Scanning electron microscopy with Xray microanalysis
SMBER	Submerged membrane electro-bioreactor
SMBR	Submerged membrane bioreactor
SMP	Soluble microbial products, Soluble EPS
SOUR	Specific oxygen uptake rate ((mg/g)/hr)
SRT	Sludge retention time
SVI	Sludge volume index

TDS	Total dissolved solids
TMP	Trans-membrane pressure
TS	Total solids (mg/L)
TSS	Total suspended solids (mg/L)
TTF	Time to filtration (sec)
V	Voltage (V)
VSS	Volatile suspended solids (mg/L)
XRD	X-Ray diffraction
WWTP	Wastewater treatment plant