Development of a Novel Submerged Membrane Electro-Bioreactor for Wastewater Treatment

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ABSTRACT

Development of a Novel Submerged Membrane Electro-Bioreactor for Wastewater Treatment

Khalid Qasem Bani-melhem, Ph.D.

Concordia University, 2008

The principle objectives of this research were to design and investigate a novel approach to generate an excellent quality effluent, while minimizing the size of the treatment unit and energy consumption. To achieve these objectives a submerged membrane electro-bioreactor (SMEBR) was designed and its performance was investigated. Membrane processes, electrokinetic phenomena, and biological processes take place simultaneously leading to the control of the problem of membrane fouling which has been considered one of the major challenges to widespread application of membrane bioreactor technology. This design is the first attempt to combine electrokinetic principles, using electro-coagulation (EC) processes and submerged membrane bioreactor in one reactor vessel.

Both water quantity and quality were monitored through different experimental phases to verify the feasibility of the SMEBR system for wastewater treatment under various operating conditions.

Firstly, a preliminary experimental phase was conducted on a small-scale electro-bioreactor (without the operation of the membrane module) to identify the best electrokinetic conditions in terms of the appropriate current density so as not to impede the biological treatment, and to determine the best exposure time of DC when it should be applied intermittently in the SMEBR system. DC field of 1 V/cm with an operational mode of 15 minutes ON / 45 minutes OFF of DC power supply were found to be the adequate electrical conditions to operate the SMEBR system.

Two different anode materials - iron and aluminum - were used to validate the SMEBR system for wastewater treatment.

At the operating mode of 15 minutes ON/ 45 minutes OFF, the applied DC field in the SMEBR system enhanced the membrane filterability up to 16.6 % and 21.3 % using iron and aluminum electrodes respectively. However, the significant improvement in membrane filterability was 52.5 % when using an aluminum anode at an operational mode of 15 minutes ON/ 105 minutes OFF, which indicated that the operational mode of DC supply is a key parameter in the operation of a SMEBR system.

In terms of pollutants removal, the overall removal efficiency for COD was greater than 96% and greater than 98% for phosphorus. In conjunction, the removal of NH_3-N was on average 70 %. It should be emphasized that the phosphorous removal efficiency was higher than other studies on MBR without the use of electrokinetics. Furthermore, the effluent of the SMEBR treatment, using synthetic wastewater, had no color and no odor.

The designed SMEBR system may find a direct application in the treatment of various wastewaters, including sewage, without an extensive pretreatment. Such a solution is required by several small municipalities, mining areas, agriculture facilities, military bases, and in cold regions. Finally, such a compact hybrid system can easily be adapted to a mobile unit.

To My Late Mother

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List of Abbreviations

ASP	Activated Sludge Process
BNR	Biological nutrient removal
CC	Chemical coagulation
COD	Chemical oxygen demand, [mg/L]
CVF	Cross flow velocity
DC	Direct Current, [A]
DO	Dissolved oxygen, [mg/L]
DOC	Dissolved organic carbon, [mg/L]
EC	Electrocoagulation
ENR	Enhanced nutrient removal
EPS	Extracellular polymeric substances,
F/M	Food to microorganisms ratio, [kg COD/ kg MLSS. day]
HRT	Hydraulic retention time, [day]
LRV	Log removal value
MBR	Membrane bioreactor
MF	Microfiltration
MLSS	Mixed liquor suspended solid, [mg/L]
MLVSS	Mixed liquor volatile suspended solid,[mg/L]
MT	Membrane technology
NH_3-N	Ammonia nitrogen concentration, [mg/L]
NO_2-N	Nitrite nitrogen concentration, [mg/L]
NO_3-N	Nitrate nitrogen concentration, [mg/L]
OLR	Organic loading rate, [kg/m^3.day]
OUR	Oxygen uptake rate , [mg O_2/ L .h]
PAC	Powdered active carbon
PO_4-P	Orthophosphate, [mg/L]
PRPF	Percentage reduction in permeate flux
R	Rejection efficiency
SMBR	Submerged membrane bioreactor

SMEBR	Submerged membrane electro-bioreactor
SMP	Soluble microbial products
SOUR	Specific oxygen uptake rate, [mg O_2/g MLVSS. h]
SRF	Specific resistance to filtration, [m/kg]
SRT	Sludge retention time, [day]
TMP	Transmembrane pressure, [Pa]
TN	Total nitrogen, [mg/L]
UF	Ultrafiltration

List of Symbols

A	Surface area of filtration, [m^2]
A_m	Membrane area, [m^2]
b	The slope from Equation (4.3), [s/m^6]
C	Weight of solids per unit volume of filtrate, [kg/m^3]
C_b	The bulk concentration of particles, [kg/m^3]
C_F	The concentration of the pollutant in feed stream, [mg/L]
C_p	The concentration of the pollutant in permeate stream, [mg/L]
C_r	The concentration of the pollutant in the supernatant in the electro-bioreactor, [mg/L]
d_p	Particle diameter, [m]
E	Energy consumption, [kWh]
F	Faraday's constant, 96,500 [C/mol]
HRT	Hydraulic retention time [day]
I	Current density, [A/cm^2]
J	Permeate flux, [$m^3/m^2.s$]
J_{AS}	The flux of activated sludge at steady state, [$m^3/m^2.s$]
J_i	Initial permeate flux, [$m^3/m^2.s$]
$J_{Stage\text{-}I}$	Permeate flux in Stage I after five days of continuous operation, [$m^3/m^2.s$]
J_{wf}	Final water flux, [$m^3/m^2.s$]
J_{wi}	Initial water flux, [$m^3/m^2.s$]
L	The distance between electrodes, [m]
M	The relative molar mass of the electrode, [g/mole]
m	The quantity of electrode material dissolved, [g/cm^2]
OUR	The oxygen uptake rate, [mg O_2/L.h]

P	Pressure, [kPa]
P_f	Pressure in the feed side, [kPa]
P_p	Pressure in the permeate side, [kPa]
ΔP	Transmembrane pressure, [kPa]
$PRPF$	Percentage reduction in permeate flux
Q_e	Effluent flow rate, [m^3/s]
r	Specific resistance to filtration, [m/kg]
R	Removal efficiency
R_c	Cake resistance, [m^{-1}]
R_f	Fouling resistance due to irreversible adsorption and pore blocking, [m^{-1}]
R_m	Membrane resistance, [m^{-1}]
R_t	Total resistance, [m^{-1}]
$SOUR$	The specific oxygen uptake rate, [mg O_2/g MLVSS. h]
T	Temperature, [^oC]
t	Time, [s]
U	The applied voltage, [V]
V	The total volume of collected permeate, or volume of the treated wastewater,[m^3]
V_r	The electro-bioreactor volume, [m^3]
Z	The number of electrons in oxidation/reduction reaction

Greek Symbols

ε	Porosity of cake layer
ξ	Zeta potential, [mV]
η	Viscosity of solution, [N.s/m^2]
μ	Permeate viscosity, [N.s/m^2]
ν	Speed of particles, [m/s]
Π	The electrophoretic mobility
ρ_p	Particle density, [kg/m^3]
σ	Dielectrical constant

Chapter 1

Introduction

1.1 Thesis Statement

One of the major challenges facing many countries around the world is to provide clean water for various human activities (e.g. drinking, agricultural and industrial) and to cover the needs of the population growth. Although the needs for clean water are a critical issue in developing countries, the developed countries are also suffering from the continuous shortage in freshwater resources due to water pollution from industrial processes and urbanization. Consequently, the needs for wastewater treatment in developed countries have become a pressing environmental issue due to the regulation requirements for increasing effluent quality (Philips et al., 2003; Smith et al., 2002).

For example, an important environmental issue is the biological nutrient removal (BNR) (Kimura et al., 2008). Although many of the existing wastewater treatment plants are capable of biological nutrient removal, the regulations are changing in some areas to take wastewater treatment to a higher level requiring enhanced nutrient removal (ENR). For example, in Germany, future stringent phosphorus regulations are expected for wastewater discharge, aiming on a limit of 50 μg/L in the receiving water bodies in order to prevent increased algae growth (Genz et al., 2004).

Excess sludge treatment and disposal represents another challenge for wastewater treatment plants due to economic, environmental and regulations factors (Wei et al., 2003). Therefore, there is a considerable interest in developing technologies for reducing sludge production in wastewater treatment plants.

Consequently, the currently available conventional wastewater treatment technologies are no longer responding to new standards, and there is an increasing desire for the development of innovative, more effective and inexpensive techniques for wastewater treatment (Al-Malack, 2007; Poyatos et al., 2007).

On the other hand, the continuous pollution of the receiving bodies highlights the trend to further manage treated wastewaters by changing the total water recycle approach, which promotes ecological sustainability by recognizing the treated wastewater as a water resource instead of a wasted medium (Kimura et al., 2008). This new view may lead to a reduction of the demand for water from existing water sources (Jefferson et al., 2001).

To fulfill the above requirements, a focus on advanced wastewater treatment has become an international hot issue during the last years. Membrane processes belong to this group and attract a high degree of attention from researchers (Jang et al., 2006). In the last decades of the 20th century, membrane technology (MT), especially the pressure driven membrane group (Bagga et al., 2008; Bruggen et al., 2003), has been given great attention and it has been proven to be a promising technology for the purification of drinking water, for wastewater treatment and for reuse applications (Bagga et al., 2008; Choi et al., 2006; Van Dijk and Roncken, 1997).

Membrane technology was firstly limited to the tertiary treatment stage of disinfection and polishing of the effluent from the secondary treatment (Cicek, 2003). However, in 1969, membrane technology was integrated directly with the activated sludge process to form one technology called membrane bioreactor technology (MBR) (Smith et al., 1969). The idea of MBR technology was first developed to replace the secondary clarifier in the activated sludge process (ASP) in order to overcome the settling difficulties associated with the process and to obtain a good quality effluent (Cicek, 2003). Although MBR solved many problems associated in ASP, fouling of the membrane is the major factor in reducing the wide-spread use of the process (Li and Wang, 2006; Le-Clech et al., 2006; Chang et al., 2002; Judd, 2005). Originally, the membrane module was utilized outside the reactor, but further development of the process made the membrane module integrated inside the bioreactor. This new configuration was called a submerged membrane bioreactor (SMBR). Therefore, the MBR technology has two configurations in terms of process operation: external and submerged membrane bioreactors. The SMBR overcomes the limits of the external configuration by the lowering the energy costs (Ueda et al., 1997; Yamamoto et al., 1989); hence, most of the recent studies focus on the development of this type of configuration.

The SMBR as a second generation MBR technology can lead to a revolution in wastewater treatment methods if the fouling problem can be reduced. Le-Clech et al. (2006) reported that SMBR would be a good alternative for wastewater treatment plants in comparison with ASP when the fouling problem is finally eliminated.

Furthermore, because MBRs are often operated with minimum sludge removal (Rosenberger et al. 2000b), holding high concentrations of the sludge by maintaining long sludge retention time (SRT), enhanced biological phosphorous removal would be limited in MBRs applications (Song et al., 2008; Adam et al., 2002).

Accordingly, for SMBR systems to be commercially competitive in comparison with ASP, further development of the process is required to decrease the fouling rate of the membrane. In this domain, many studies have been conducted to address this problem. In general, there are many methods to reduce fouling in SMBR technology. Those methods can be grouped by three distinct approaches: cleaning the membrane unit, optimizing the operating parameters and improving the wastewater characteristics. Membrane cleaning is the common approach used in most of the SMBR applications.

Cleaning the membrane is achieved physically by backwashing the permeate or back flushing using a high flow rate stream of air. This technique results in an increase in the operating costs and the high flow rate of air may cause damage for the membrane module (Le-Clech et al., 2006). In the long run, membranes can be washed chemically to recover its permeability.

Optimization the operating parameters includes the selection of the best operating conditions in terms of aeration, sludge retention time (SRT), hydraulic retention time (HRT) and MLSS concentration in the bioreactor to minimize the fouling on the membrane.

Improving the characteristics of the treated wastewater has been proven an effective approach in reducing the fouling in SMBR applications (Wu and Huang, 2008). This approached includes the addition of chemical coagulant such as alum and iron salts to increase the floc size of the MLSS solution (Song et al., 2008; Wu and Huang, 2008; Wu et al., 2006; Lee et al.; 2001) or the addition of adsorptive materials like high concentration of powdered activated carbon (Guo et al., 2008; Lesage et al., 2008; Hu and Stuckey, 2007; Munz et al., 2007; Lee et al., 2006; Seo et al., 2004) and zeolite (Lee et al., 2001).

Increasing the size of the MLSS floc solution by coagulation has been proven to be an effective method (Wu and Huang, 2008). However, the addition of chemicals to the wastewater may cause side effects by producing by-products or increasing the volume of sludge in the reactor (Clark and Stephenson, 1998). An alternative technology to create coagulation inside the system, suggested by the author, is by introducing electrokinetic processes to the biological process. In this case, one of the electrokinetic processes is electro-coagulation (EC). EC has been proven to be a good method for coagulation in wastewater (Mollah et. al., 2001). In comparison with the chemical coagulation (CC) processes, electrocoagulation (EC) has many advantages: no liquid chemical is added, alkalinity is not consumed, and the EC process requires less coagulant and produces less sludge (Zhu et al., 2005). Thus, in the proposed design, no coagulate addition is planned, leading to the minimization of operation costs and to an increase in the quality of both effluent and wasted solids.

The proposed design integrates three main processes in one unit: a biological process, a membrane filtration process and an electrokinetic process. The overall configuration of this system is named the submerged electro-bioreactor (SMEBR). For this design to be successful, the treatment of wastewater within the SMEBR system process should include biodegradation, electro-coagulation, sedimentation and filtration through the membrane.

To the best knowledge of the author, no previous work has been reported to integrate MBR system with electrokinetics in one unit as a hybrid technology. Although the work done by Chen et al. (2007) reported using a direct electrical current (DC) field to enhance the membrane flux in a SMBR system, the membrane module in their work was separated from the bioreactor zone and the applied DC field was at a high voltage which is costly and may have negative effects on the microbial community.

1.2 Research Objectives

As it was mentioned in the previous section, presently designed WWTPs have difficulties producing effluents with the quality requested by environmental norms. Therefore, there is a need to design a novel method for more efficient wastewater treatment.

The principle objective of this PhD research was to design and investigate a novel advanced method for wastewater treatment where the three main processes: biological treatment, electrocoagulation and membrane filtration would function in one hybrid unit and their combination would produce an excellent quality effluent. The detailed objectives of this research include:

1) Designing a new hybrid unit - "Submerged Membrane Electro-Bioreactor" (SMEBR)- which permits the interactive actions of three fundamental wastewater treatment processes (biological, electrokinetics and membrane filtration).

2) Investigation of the best combination of electrical parameters for the newly designed SMEBR system (electrodes specification, voltage gradient, DC field distribution, mode of operation).

3) Investigation of the performance of the SMEBR system as a new design for reducing fouling problems associated with membrane filtration.

4) Investigation of the impact of the SMEBR operation in reducing the COD and nutrient content of the effluent.

5) Investigation of the performance of the SMEBR system with regards to "electro–flocs" formations.

It is expected that this new method of treatment would not only generate a high quality effluent and decreases the operation costs, but also decreases the capital costs by considering the lower footprint for the eventual treatment facilities and the possibility of its application as a mobile system.

1.3 Organization of the Thesis

This thesis consists of nine chapters. The remainder of this thesis is organized as follows:

In Chapter 2, general literature review about the main topics of this thesis is discussed. Chapter 3 highlights the major considerations in designing the SMEBR system. Chapter 4 presents the theoretical background of the thesis. It includes the methods used in this thesis to assess the performance of the SMEBR system. Chapter 5 introduces a detailed description for the experimental work such as research strategy, experimental set-up, equipment, materials and chemicals, and analytical methods.

Since the experimental work of this thesis was divided into three phases, the output results of each phase will be discussed in separate chapters. Then, Chapter 6 presents the results of the Phase I, where the effect of applying direct current (DC) fields on the characteristics of activated sludge mixed liquor (MLSS) solution was studied by using a small scale laboratory electro-bioreactor without the membrane module. The objective of Phase I was to identify the best electrokinetic conditions in term of the appropriate current density so as not to impede the biological treatment, and to determine the best exposure time to the DC field, that is to say, when it should be applied intermittently in the SMEBR system.

The results of the experimental work in Phase II were presented in Chapter 7, where the impact the SMEBR operation system on the decrease in fouling rate was investigated. In Phase II, the variation of the physiochemical and biochemical parameters were studied with iron used for both the cathode and anode electrodes.

In the experimental Phase III, the SMEBR system was investigated using aluminum as the anode material. The results of this phase were presented in Chapter 8.

Finally, the conclusions and a general evaluation are given in Chapter 9, outlining the directions for further research and optimization.

Chapter 2

Literature Review

This chapter presents a literature review of the previous works related to the topics of this thesis. Section 2.1 introduces a short description of wastewater treatment plants. In section 2.2, a general introduction of membrane technologies is presented. Section 2.3 presents an overview of membrane bioreactor (MBR) systems. Advantages and disadvantages of MBR systems, in comparison with activated sludge process (ASP), were highlighted. Also, section 2.3 discuses the general methods of reducing fouling in MBR systems. Section 2.4 gives an overview of electrocoagulation (EC) process, its advantages, and its applications in wastewater treatment. Finally, Section 2.5 summarizes the conclusions in the previous sections.

2.1 Conventional Wastewater Treatment Plants

Conventional wastewater treatment plants consist of three stages: Primary, secondary and tertiary (Figure 2.1). In the primary treatment stage most of the large objects are removed. The secondary treatment stage consists of biological treatment technologies that have been utilized in wastewater reclamation for over a century (Cicek, 2003).

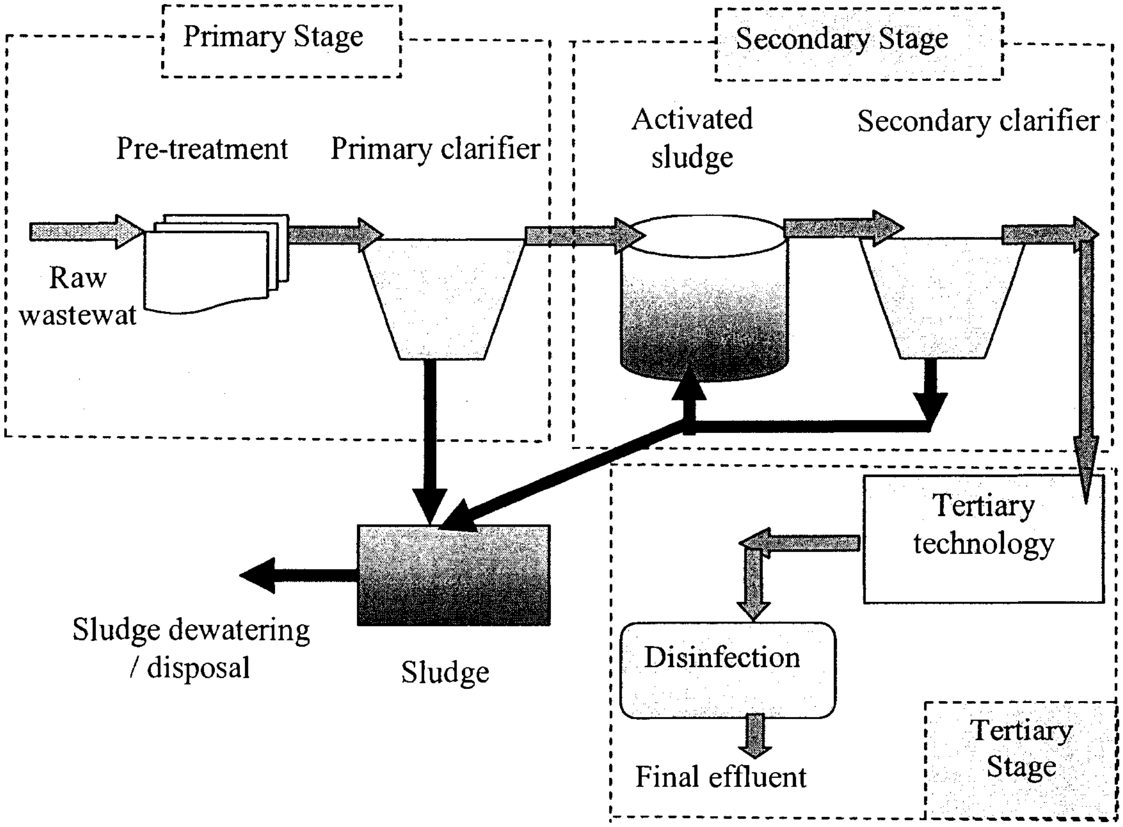


Figure 2.1 Simplified schematic diagram of conventional wastewater treatment plant

Among the many different biological processes, activated sludge process (ASP) has proved to be the dominant process for more than a century (Tchobanoglous et al., 2003; Tay et al., 2003). However, conventional biological treatments have several disadvantages. For example, the production of biomass is high and the amount of biomass that can be maintained is limited because the settling qualities are poor at high sludge concentrations (Muller et al., 1995). Also, ASP produces a large amount of excess sludge, of which the treatment and disposal represents 50% to 60% of the total treatment cost (Tay et al., 2003; Egemen et al., 2001). Furthermore, in conventional treatment plants, nutrients are insufficiently removed and a large surface area is required as volumetric capacities are low (Muller et al., 1995).

In the tertiary treatment process, the effluent from the secondary clarifier is further disinfected. Usually, there are more than one tertiary treatment process used at any treatment plant (e.g. UV, colonization, ionization and membrane filtration). The selection among these methods depends on the required quality of the final effluent which is discharged into the receiving environment (sea, river, lake, ground, etc.).

As membrane filtration is one of the methods used in this research, this technology will be highlighted in the next section.

2.2 Membrane Technology

Figure 2.2 shows a simple schematic for the membrane technology. A membrane process can be defined as splitting a feed stream by a membrane module into two streams: a retentate (or concentrate) and a permeate fraction. During the past few decades, researchers gave membrane separation technologies great attention as one of the most effective and promising methods in water purification. Various types of membrane separation processes have been developed for specific industrial applications. Based on the driving forces across the membrane, membranes could be classified into four groups (Figure 2.3).

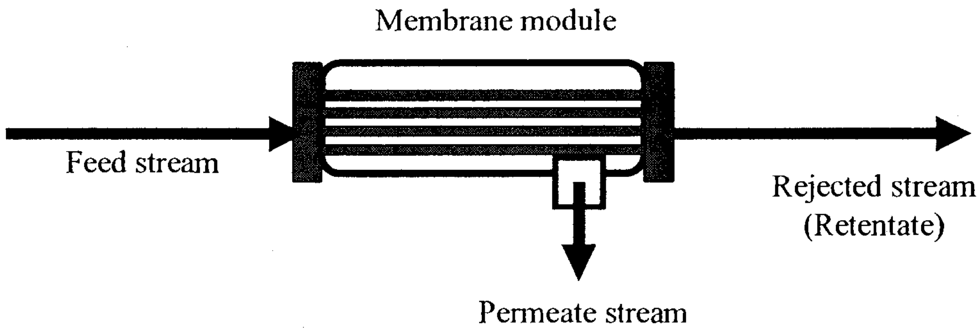


Figure 2.2 Concept of membrane technology

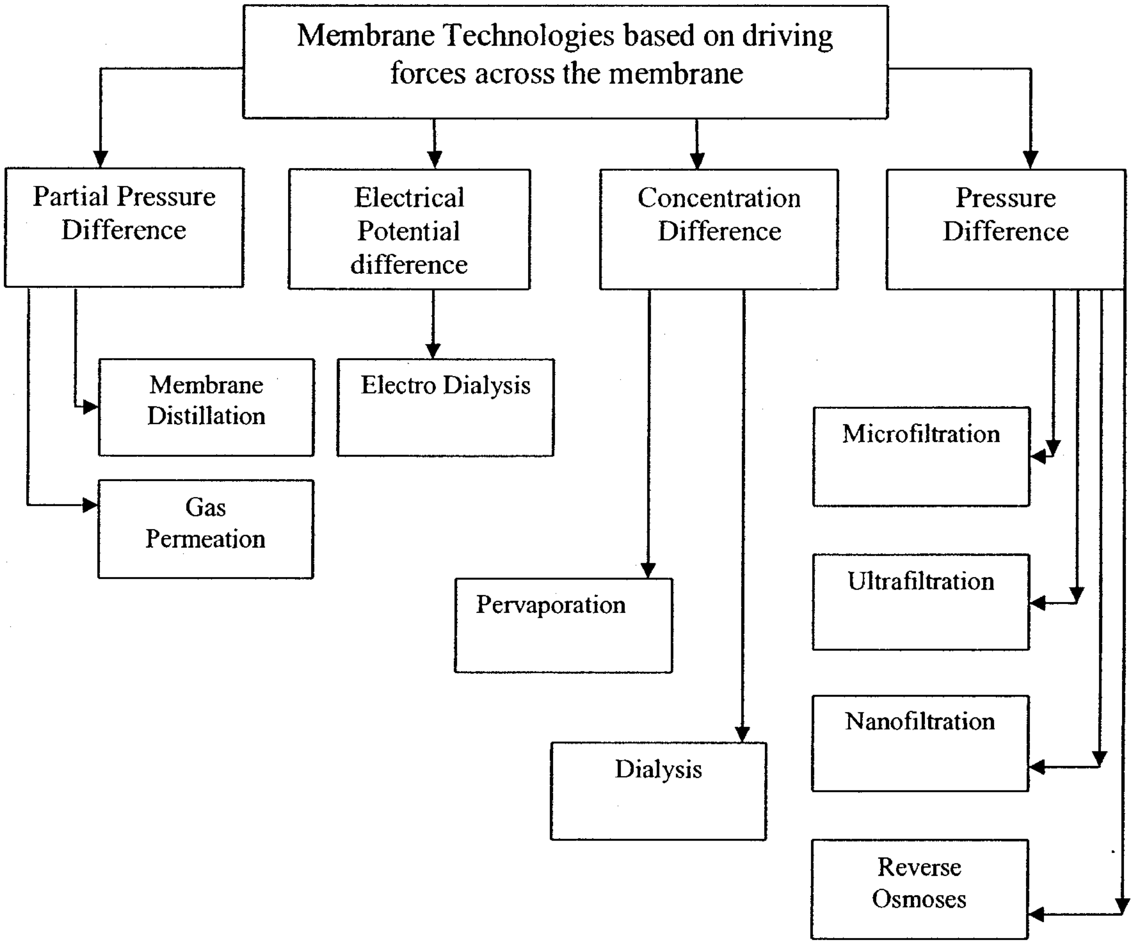


Figure 2.3 Classification of membrane technology based on driving forces across the membrane

The first group is pressure driven membrane process and includes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Bruggen et al., 2003; Laine et al., 2000, Ripperger and Altmann, 2002). The second group, which is based on concentration difference across the membranes, includes dialysis (Sakai, 1994) and pervaporation (Shao and Huang, 2007). The third group, which contains electro-dialysis membranes, is based on an electrical potential (Bazinet, 2004; Tongwen, 2002). The fourth group includes gas permeation (Dolan et al., 2006; Ismail and David, 2001) and membrane distillation (MD) (Lawson and Lloyd, 1997), in which the partial pressure is the driving force across the membrane. Membrane technologies could also be classified based on membrane types or based on membrane configurations and modules.

Membrane technologies (MT) have a long history that began in 1748, however the golden age (1960-1980) of this technology began in 1960 when Loeb and Sourirajan developed the first asymmetrically integrated skinned cellulose acetate RO membrane for seawater desalination. The full description of this event is reported by Matsuura (2001).

The first use of membrane technology was initially limited to tertiary treatment and polishing (Cieck, 2003). Insufficient knowledge of membrane applications and the high capital and operating costs were considered negative factors and limited the spread of membrane technologies (Cieck, 2003).

The applications of membrane technologies have covered many fields. Membrane technologies have been used in the field of drinking water (Jacangelo et al., 1997), water purification (Phelps et al., 2008), treatment of pesticide industry effluents (Shaalan et al., 2007), endocrine disrupting compounds and pharmaceuticals products

(Yoon et al., 2006), virus removal (Madaeni et al., 1995; Bechtel et al., 1988) and sterilization (Kong et al., 2006).

In general, using membrane technologies has many basic advantages in comparison with other traditional treatment processes; some of these advantages include (Bodzek and Konieczny, 1998; Aptel et al., 1993):

i) Production of water of invariable quality;
ii) Smaller quantity of added chemical substances;
iii) Lower consumption of energy;
iv) Compactness of the installation and the possibility to fully automate the process.

Alternately, using the conventional methods of water treatment also has certain disadvantages. For example, chlorine treatment leads to the formation of byproducts like chlorine by-products, such as trihalomethanes and haloacetic acids (Chang et al., 2000), commercial UV and ozone based water treatment units do not guarantee the deactivation of all the pathogenic microorganisms (Ma et al., 1998). The fouling of membrane modules is seen as a major problem in all applications of membranc technology.

2.3 Membrane Bioreactor Technology

2.3.1 General Description

The membrane bioreactor (MBR) is a relatively new technology. The first reported use of membranes combined with biological wastewater treatment was in 1969 (Smith et al., 1969). In that process an ultrafiltration membrane was used for the separation of activated sludge from the final effluent with the recycling of biomass to the aeration tank (Ng and Kim, 2007).

The process of this technology is not fully formed and is largely still in the development stage. Although the concept has been known for almost forty years, the numbers of large-scale commercial plants do not grow as fast as expected due to some limitations. For example, in Europe, the first full-scale MBR plant for treatment of municipal wastewater was constructed in Porlock (UK, commissioned in 1998, 3,800 p.e.), soon followed by WWTPs in Büchel and Rödingen (Germany, 1999, 1,000 and 3,000 p.e., respectively), and in Perthes-en-Gâtinais (France, 1999, 4,500 p.e.). In 2004, the largest MBR plant worldwide so far was commissioned to serve a population of 80,000 p.e. in Kaarst, Germany (Lesjean and Huisjes, 2008).

However, due to the recent stringent restriction in effluent regulations and the continuously decreasing costs of membrane systems, MBR systems have been a subject of keen interest and rapid development in the past 10 years. The developments of MBR technology were reviewed by many researchers (Ng and Kim, 2007; Le-Clech et al., 2006; Yang et al., 2006).

The rapid development of the technology resulted in regular technology reviews, among which some of the most informative were published by Judd (2006), Nieuwenhuijzen (2005) and Stephenson et al. (2000). Moreover, a recent market study was also completed together with a literature survey on research activities and trends for Europe (Lesjean and Huisjes, 2008), China (Wang et al., 2008) and North America (Yang et al., 2006).

2.3.2 MBR Suppliers

Currently, MBR designs are proposed by the leading membrane suppliers such as GE-Zenon (Canada), USFilter (USA), X-Flow (The Netherlands), Siemens-Australia (Australia) and Mitsubishi and Kubota (Japan). In each case, the process proposed is very specific. The membrane material and configuration used are different for each supplier. The operating conditions, cleaning protocols and reactor designs also change from one company to another. For example, the flat sheet membrane provided by Kubota does not allow backwash operation, while hollow fiber membrane type from Memcor (USFilter) have been especially designed to hydraulically backwash the membrane at a given frequency (e.g. around every 10 min) and some membrane undergo relaxation as opposed to backwashing, like GE-Zenon.

2.3.3 MBR Configurations

Figure 2.4 shows the first concept of membrane bioreactor systems that was based on a combination between two individual treatment methods (activated sludge process and membrane filtration) to form an integrated method (membrane bioreactor, MBR).

As demonstrated in Figure 2.4, the idea of an MBR technology was based on replacing the secondary clarifier in the ASP by a membrane module. As a result of this improvement, the space required for treatment was reduced; this was considered a great contribution of MBR technology in comparison with covenantal ASP (Cornel et el., 2003). It was reported that omitting the secondary clarifier can reduce the land requirements by 50 % (Chae et al., 2006).

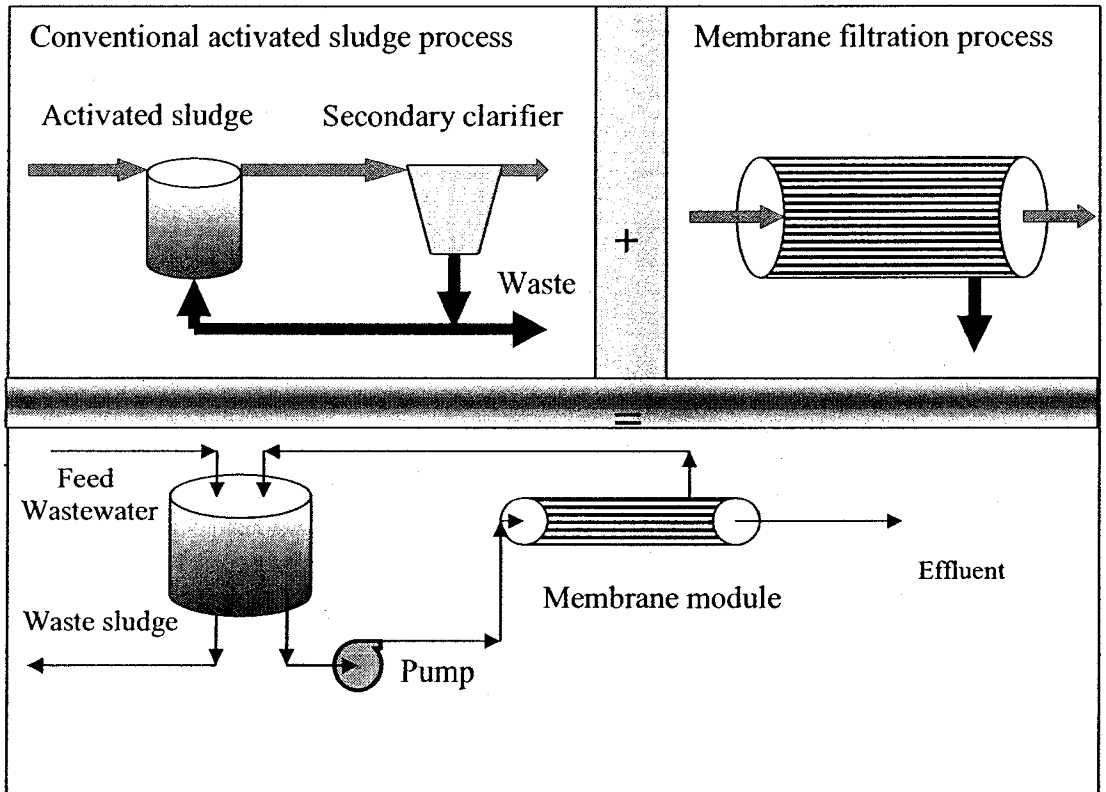


Figure 2.4 The first concept of MBR technology

Physically, MBR includes a biological reactor and a membrane module to separate the liquid phase from the solid phase. Usually microfiltration (MF) and Ultrafiltration (UF) membranes are used in this type of process (Ramesh et al., 2006; Geissler et al., 2005) with pore sizes ranging from 0.05 µm to 0.4 µm (Le-Clech et al., 2006). Based on the classification in Figure 2.3, MBR systems follow the first group in which the pressure difference is the driving force across the membrane.

There are two types of configurations in which the membrane bioreactors (MBRs) can be operated (Figure 2.5). The first one, appearing in 1969, is the external operation that represents the original idea of MBR systems in which the second clarifier in ASP was replaced by a membrane unit (Figure $2.5_{(a)}$). In this type of configurations, the mixed liquor is pumped from the aeration tank to the membrane module.

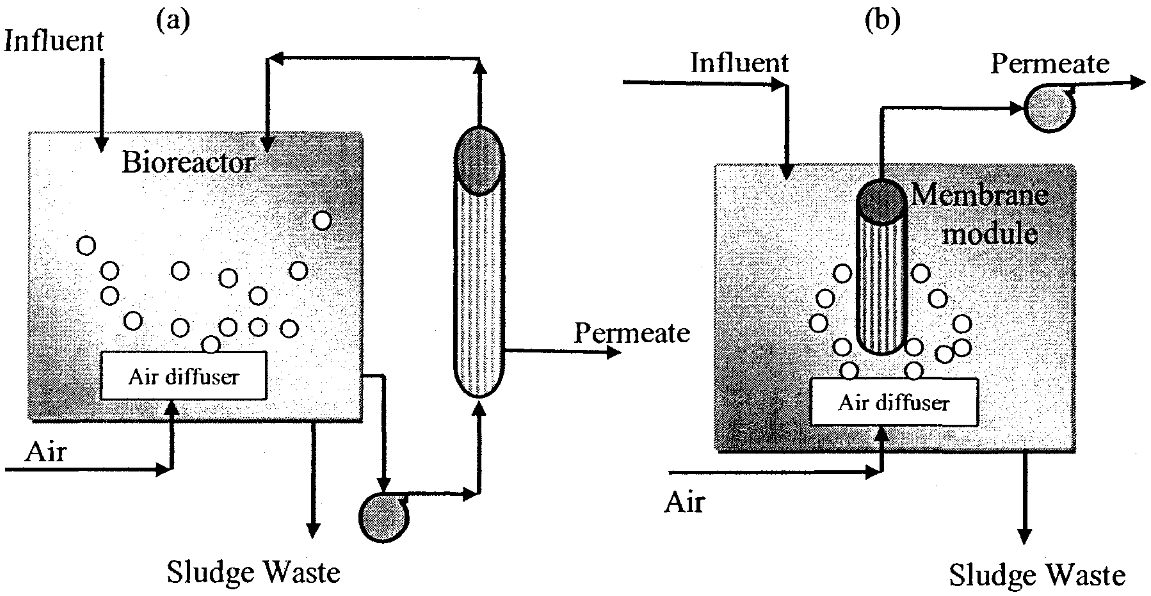


Figure 2.5 Schematics of external re-circulation (a) and submerged MBR system (b)

The second type of MBR configurations was a breakthrough and it was invented in Japan in 1989 (Yamamoto et al., 1989). In this type (Figure $2.5_{(b)}$), the membrane module was submerged directly in the aeration tank, while permeate is obtained by applying low vacuum or by using static head of the mixed liquor. Submerged membrane bioreactors have lower power requirements than the external MBR configurations (Gehlert et al., 2005; Ueda et al., 1996). The energy demand of the submerged system can be up to 2 orders of magnitude lower than of the side stream systems (Gander et al., 2001). Full comparison between the two configurations is shown in Table 2.1.

2.3.4 Advantages and Disadvantages of MBR Systems

Advantages of MBR applications are well documented (Stephenson et al., 2000). Usually MBR system is compared with conventional activated sludge process (ASP).

Table 2.1 Comparison between MBRs configurations

Item	External MBR	Submerged MBR
Shape	Figure 2.5(a)	Figure 2.5(b)
Cost	High	Low
Energy consumption	The energy demand is high	The energy demand is low (can be up to two order of magnitude than external MBR
Space	Need more space	Need less space
Flux	Operate at high flux	Operate at low flux (need more membrane area)

In comparison with ASP, the advantages of MBR applications can be summarized by the following points:

- Small footprint and reactor requirements (Judd, 2006; van Dijk and Roncken, 1997). The main contribution from MBR system in comparison with conventional ASP is the saving in the space required for treatment. This is achieved because the secondary clarifier is replaced by a membrane unit (Cornel et al., 2003). The land requirement could be reduced by 50% with this improvement (Chae et al., 2006). Moreover, MBRs eliminate the difficulties associated with settling solids in the effluent from the second clarifier in activated sludge processes (Cicek, 2003).
- Excellent retention for all the suspended solids and most of soluble organic matter can be achieved by the membrane module used in the process. This increases the quality of the permeate stream in terms of organic and nutrients materials (Cicek, 2003).

- MBR system has the capability to retain all the bacteria and viruses (Clech et al., 2006). Usually, the membrane has an effective pore size <0.1 μm which is significantly smaller than the pathogenic bacteria and viruses in the sludge (Judd, 2008). This decreases the need for further treatment by using other chemicals for disinfection and results in a decrease in the cost and the hazardous effects that could occure from byproducts produced from the disinfection process.
- It was reported that the conventional activated sludge process (ASP) of a wastewater treatment plant is operated in a short sludge retention time (SRT) to keep low MLSS concentration for better gravity separation of sludge (Bhatta et al., 2004), while the MBR systems can minimize sludge wastage by maintaining a high biomass concentration in the reactor (Wagner and Rosenwinkel, 2000; Chang et al., 1999). Accordingly, operating parameters like hydraulic retention time (HRT) and solid retention time (SRT) can be controlled independently in MBR systems (Judd, 2008, Busch et al., 2006), while it is more difficult to control these parameters in ASP (Chae et al., 2006).

On the other hand, the disadvantages associated with MBR are addressed by the following points:

- Disadvantages associated with MBR systems are mainly cost related, in terms of high capital cost and energy cost, reflecting the expensive membrane units and the need for a pressure gradient (Judd, 2008; Cicek et al., 1999a, 1999c).
- As in other membrane technology, Membrane fouling and concentration polarization are considered important problems in MBR systems (Judd, 2008; Le-Clech et al., 2006).

- The harmful of the microbial population and membrane structure are other problems in MBR systems which are resulted from the possible accumulation of non-filterable inorganic compounds in the bioreactor (Cicek et al., 1999a).

2.3.5 MBR Applications

It was estimated that the MBR market in 2006 was around $ 216 million and this number will rise to US$ 363 million in 2010 (Atkinson, 2006).

The reported applications of MBR systems vary from numerous pilot scale studies to full scale units (Cicek, 2003, Brindle and Stephenson, 1996). In the pilot scale, membrane bioreactor (MBR) systems covered many applications in wastewater treatment technology. The process has been used in domestic wastewater treatment (Seo et al., 2004; Liu et al., 2000; Ueda et al., 1999; Ueda et al., 1996; Kishino et al., 1996), municipal wastewater (Wintgens et al., 2003; Rosenberger et al., 2002), industrial wastewater (Lesage et al., 2008), tannery wastewater (Munz et al., 2007; Yamamoto and Win, 1991), oily wastewater (Knoblock et al., 1994, Zaloum et al., 1994), hospital wastewater (Wen et al., 2004) and bath wastewater (Rui et al., 2005).

2.3.6 MBR Fouling

Although MBR systems have been proven to solve many problems associated with activated sludge processes (ASP) like, for instance, the settling difficulties associated in secondary clarifier, the fouling problem of membranes is still the major factor in hindering the wide-scale applications of this process (Li and Wang, 2006; Le-Clech et al., 2006; Trussell et al., 2006; Judd, 2005; Chang et al., 2002).

The highly heterogeneous nature of the bioreactor mixed liquor suspension makes the fouling phenomenon in the MBR system more difficult to predict and control (Chang et al., 2007; Chang et al., 2002).

The negative impacts of membrane fouling are represented by the increase in energy and operating costs as a result of continuous maintenance. This reflects the fact that controlling the membrane fouling is of great importance for a stable operational performance.

2.3.7 Factors Affecting Fouling in MBR

In general, membrane fouling in MBR systems is attributed to many factors and can be classified under four groups (Le-Clech et al., 2006). The first group is related to the membrane's characteristics, the second group is related to feed-biomass characteristics, the third group is related to the operating conditions, and the fourth group is related to the operational mode. Figure 2.6 summarizes all the parameters that affect the fouling in the MBR technology as it was adapted from the literature by Le-Clech et al. (2006). A brief discussion of each parameter is provided in the following subsections.

2.3.7.1 Membrane Characteristics

The physical and chemical characteristics of the membrane module have a significant contribution on the fouling phenomenon in the MBR technology. Physical parameters like pore size and distribution, configuration, roughness and porosity are the key parameters of membrane and have different impact on fouling rates depending on the characteristics of the biomass (Le-Clech et al. 2006).

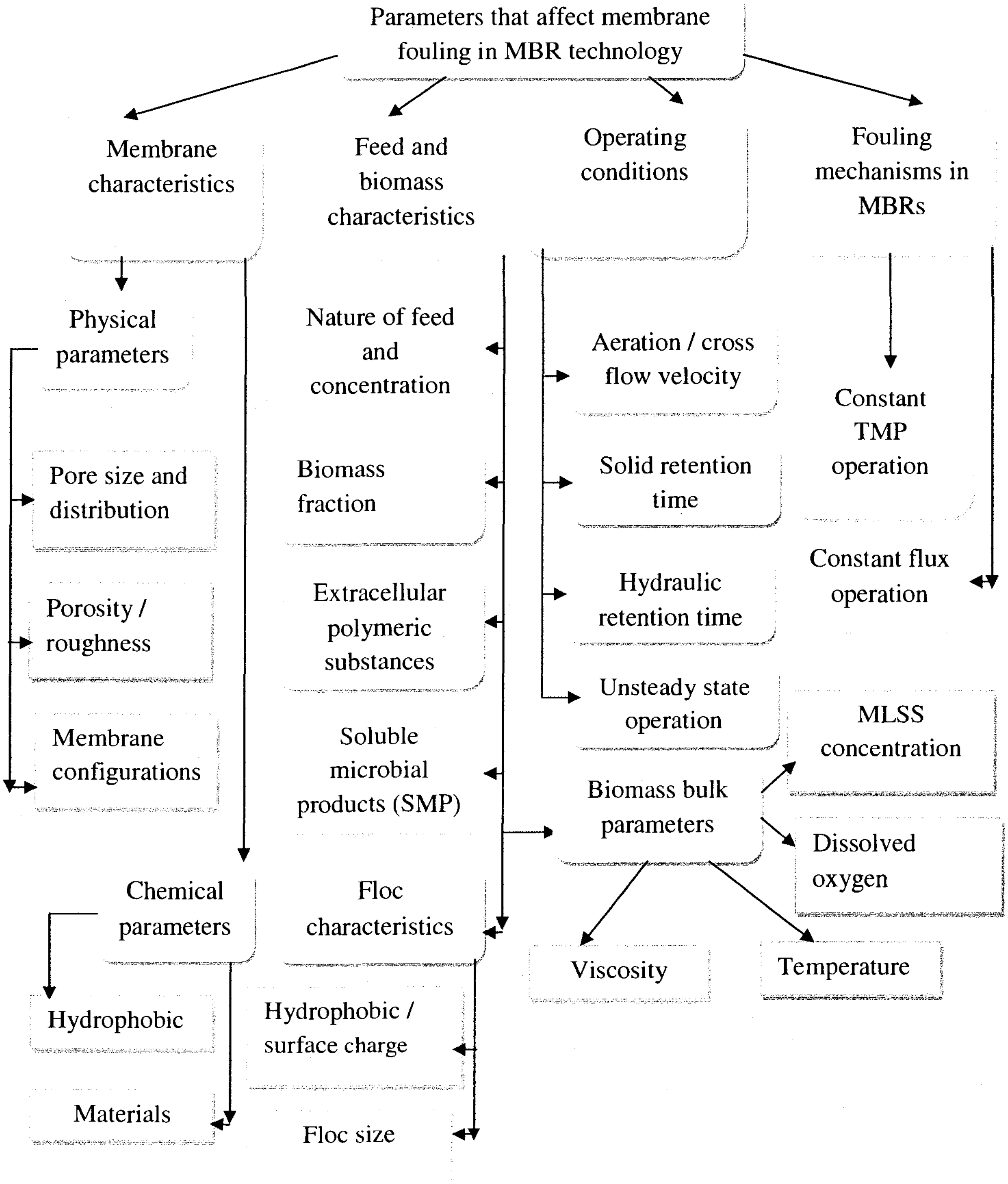


Figure 2.6 Parameters that affect membrane fouling in MBR technology (adapted from Le-Clech et al., 2006)

On the other hand, chemical parameters such as hydrophobicity and membrane construction material also have an important contribution on fouling. Studies demonstrated that polyvinylidene fluoride (PVDF) membranes are better at preventing irreversible fouling than those membranes composed of polyethylene (PE) membranes used in treatment of municipal wastewater. The composition of the fouling cake layer is dependent on the membrane material because of the different affinities of some portions of the organic matter in the biomass on the different polymeric materials, and consequently, this higher affinity leads to greater irreversible fouling of the membrane (Yamato et al., 2006).

2.3.7.2 Feed-Biomass Characteristics

- **Natural of Feed Wastewater**

Fouling propensity in the MBR technology is affected by the nature of feed wastewater and its characteristics. Feeding the MBR with synthetic wastewater produces a relatively higher fouling rate than real sewage wastewater. This is due to the variation in the physical and chemical characteristics in biological suspension. For example, a higher concentration of COD and TN in the synthetic feed could lead to a higher propensity to fouling (Le- Clech et al., 2003).

Feeding the MBR with saline sewage requires more frequent membrane cleaning. However, no significant difference was observed in membrane performance (Tam et al., 2006).

- **Fractionation of the Feed**

In the activated sludge process, the feed is usually classified into three fractions: i) suspended solid, ii) colloids and iii) solutes. The fouling rate in MBR is affected by the filtration resistance of these three fractions in different mechanisms. No standard method to quantify this resistance was reported. However, in their review, Le-Clech et al. (2006) presented a schematic diagram to understand the filtration resistance of the different fractions of feed. In their approach, the feed is first centrifuged with a dead-end filtration carried out with the supernatant to estimate the filtration resistance (R_{sup}) which represents the combined resistance of colloids and solute. Some part of supernatant was filtrated through a 0.5 μm nominal size microfilter and then dead-end test was conducted in order to estimate the resistance of solutes. Another portion of biomass was directly tested in a dead-end cell to calculate the total filtration resistance which represented the accumulated value of the suspension solid resistance (R_{ss}), colloid resistance (R_{col}) and solute resistance (R_{sol}).

It was reported that the relative contribution of the biomass supernatant, which is a combination of the solute and colloids (generally defined as soluble microbial products or SMP), to the overall membrane fouling ranged from 17% (Bae and Tak, 2005) to 81% (Itonaga et al., 20004). The wide range of SMP contribution to fouling may be due to the different operating conditions and biological states of the suspension used in the reported studies. In terms of the fouling mechanisms, Itonaga et al. (20004) reported that the soluble and colloidal materials are assumed to be responsible for the pore blockage of the membrane, while the suspended solids account mainly for the cake layer resistance.

2.3.7.3 Biomass Characteristics

- **Mixed Liquor Suspended Solid (MLSS) Concentration**

The MLSS is the concentration of suspended solids in the mixed liquor sludge solution. It is often believed that the MLSS concentration is one of the main fouling parameters which may affect the MBR performance due to the complex interaction of mixed liquor solution in the bioreactor with the membrane module (Le-Clech et al., 2006; Meng et al., 2006). However, the exact influence of the MLSS concentration on membrane fouling is not yet clear. Some of the recent studies reported that the MLSS seems to have a mostly negative impact on the MBR hydraulic performance represented by a high TMP and a low flux (Meng et al. 2006; Chang and Kim, 2005), while other studies have reported a positive impact (Brookes et al., 2006; Defrance and Jaffrin, 1999), and some observed an insignificant impact (Hong et al., 2002; Lesjean et al., 2005). It appears that the level of MLSS concentration plays an important role on the fouling rate. According to Yamamoto et al. (1994), the flux decreases abruptly if the MLSS concentration exceeded 40,000 mg/L in a submerged membrane bioreactor. Le-Clech et al. (2003) investigated the effect of three distinct levels of MLSS concentrations (4000, 8000, and 12,000 mg/L) on membrane fouling in a submerged membrane bioreactor. They found that there was no significant difference in the concentrations of 4000 to 8000 mg/L, but that a significant decrease of permeate rate was observed when the MLSS concentration increased to 12,000 mg/L.

- **Dissolved Oxygen (DO)**

Dissolved Oxygen (DO) is a significant parameter in MBR technology. The oxygen is not only required for the microorganisms but it also reduces the fouling tendency of membrane surface which is dependent upon air scouring rates. It was reported that under the same hydraulic condition, the fouling rate of the membrane is 5 times faster in the presence of low DO (< 0.1 mg/L) than of high DO (6 mg/L) concentrations in the MBR (Kim et al., 2006).

In another study by Jin et al. (2006), the effect of dissolved oxygen (DO) concentrations on biofilm structure and membrane filterability in SMBR was analyzed. They found that the rate of membrane fouling in low DO reactor was 7.5 times faster than those in high DO reactor.

- **Viscosity**

Fouling in MBR applications is strongly affected by the viscosity of suspension which is strongly affected by the level of the MLSS concentration (Itonaga et al., 2004). However, at critical value of MLSS concentration, the viscosity remains low and slightly increases with higher MLSS concentrations. Itonaga et al. (2004) reported that the viscosity of suspension exponentially rises above the critical value of 11 when the range of study was between 10 and 17g MLSS/L. Watanabe et al. (2006) found that at higher concentration of MLSS (between 8 and 12 g/L), reversible membrane fouling rate increases with increasing F/M ratios. They attributed these results to the increase of suspension viscosity caused by an increased in the size and volume of the activated sludge at higher concentrations.

- **Temperature**

The temperature strongly affects the permeate viscosity, thus its impact on the membrane fouling is significant (Mulder, 2000). Jiang et al. (2005) reported that at low temperature (13-14 °C) greater resistance has been observed due to an increase in sludge viscosity, floc size reduction, particle back transport, lower biodegradation of COD than at high temperature conditions (17-18 °C). Chiemchaisri and Yamamoto (1994) reported that a temperature decrease affected the permeate flux not only by increasing the viscosity of mixed liquor but also by changing the properties of the cake layer (cake layer thickness and/or porosity). Pore size will also be reduced at lower temperature, particularly for organic membranes.

2.3.7.4 Extracellular Polymeric Substances (EPS)

In aquatic environments, bacterial extracellular polymeric substances (EPS) exist as a part of the dissolved organic matter and in particulate matter such as microbial mats, biofilms, etc. (Bin et al., 2008). The predominant components of EPS are carbohydrate, protein, lipids, nucleic acids and various heteropolymers (Lazarova and Manem, 1995). EPS is the construction material of biofilm and flocs. EPS have been found at or outside cell surfaces and in the intercellular opening of microbial aggregates. EPS are one of the major components that produce membrane resistance, and carbohydrates and proteins are the foremost components in extracted EPS and are responsible for membrane fouling and for the decline in flux in MBRs (Meng et al., 2006, Nagaoka et al., 1998). It has been reported that in SMBR, EPS accumulated both in the mixed liquor and on the membrane, which may cause an increase in the viscosity of the mixed liquor and in the filtration resistance of the membrane (Nagaoka et al., 1996). Moreover, the result demonstrated that EPS is the predominant contributor to membrane fouling, by analyzing the soluble and colloidal organic material in the activated sludge of MBR, and by spectrophotometer and size exclusion chromatography (SEC) methods (Lesjean et al., 2005). EPS provide a highly hydrated gel where microorganisms are embedded and where they hamper permeate flux in MBRs. Specific EPS resistance could be estimated from filtration resistance divided by EPS density on membrane surfaces. In a study for Meng et al. (2006), they reported that proteins are the most important factor influencing membrane flux and the behavior of membrane fouling, whereas carbohydrates have a moderate correlation due to their lower amounts.

2.3.7.5 Soluble Microbial Products (SMP)

Soluble microbial products (SMP) can be defined as the pool of organic compounds produced as a result of microbial activities (Barker and Stuckey, 1999). The SMP level in biological wastewater treatment systems are of crucial importance because of their significant impacts on both effluent quality and treatment efficiency (Liang et al., 2007). It is well established that the majority of soluble organic substances come from SMP in the effluent in biological treatment systems and its concentration determines the discharge level of chemical oxygen demand (COD) and dissolved organic carbon (DOC) in the effluent (Liang et al., 2007). Furthermore, some SMP have certain characteristic like toxicity and metal chelating properties that affect the metabolic activities of microorganisms both in the receiving water and in the treatment process. Therefore, for a better efficiency of treatment systems, a lower concentration of SMP is desirable (Liang et al., 2007). SMP could be again categorized into two categories: as utilization associated products which are associated with substrate metabolism, and as biomass growth and biomass associated products which are associated with biomass decay. Although humic substances (humic and fulvic acids), carbohydrates and proteins have been successfully identified as the major components of SMP, its precise composition remains unclear (Liang et al., 2007). However, most of the previous studies concentrated on SMP in conventional biological treatment plants but few studies have focused on the impact of SMP in MBR systems. It was found from studies that depending on the operation conditions, SMP are responsible for 26 to 52% of the membrane fouling in microfiltration and ultrafiltration membranes in MBRs, and they play a major role as organic foulants (Bouhabila et al., 2001; Wisniewski and Grasmick, 1998). In addition, it has been seen that the SMP concentration is higher in the supernatant in MBR mixed liquors rather than in the effluent, which indicates that some SMP components accumulated into membrane surface. For better understanding of the SMP fouling mechanism and the accumulation of SMP on membranes in MBRs, more information are required concerning the apparent molecular weight distribution of SMP in the MBR's effluent (Liang et al., 2007).

Song et al. (2007), experimentally and theoretically, investigated the impact of an accumulation of SMP in a membrane bioreactor. The results of their study demonstrated that the simulation results were in good agreement with the experimental data, indicating that the accumulation of SMP in the MBR could be attributed to the retarded transport of SMP through the membrane. Furthermore, the proposed model in their studies provided a new conceptual framework for evaluating the fate of SMP and the performance of MBR.

2.3.7.6 Floc Characteristics

Floc characteristics have a particular role in the membrane fouling processes. As it is the case in full-scale wastewater treatment plants, sludge flocs characteristics have an important impact on settleability and compressibility of activated sludge in MBR operation.

These flocs could be characterized by morphological, structural (floc size distribution, fractal dimension, and filament index) and physical (flocculating ability, viscosity, hydrophobicity, and surface charge) parameters. Polymeric constituents & metal content are considered chemical parameters (Le-Clech et al., 2006). Compressibility and settleability are largely improved in the presence of chemical coagulations like Al and Fe cationic ions in the sludge (Jin et al., 2003).

Although it is normally assumed that large flocs do not settle on membrane surface due to drag force and have no role in blocking pore entrances directly, biological flocs have an important role in the formation of the cake layer on the membrane surface. Generally, particles penetration into membrane pores can be reduced by increasing the particle size, and this will enhance particle back transport from the membrane surface to the bulk solution (Lee et al., 2001). It was reported that the permeate flux in submerged membrane reactors can be increased by increasing the particle size of flocs, this is because the shear-induced diffusion increases with increase in particle size (Jinsong et al., 2006).

2.3.7.7 Operating Conditions

- **Aeration and Cross Flow Velocity**

The aeration intensity plays an important role in controlling membrane fouling in MBRs configurations. However, control of fouling in SMBR is still more challenging than in cross flow configuration because the liquid feed could be managed precisely in the latter case. In SMBR, aeration is induced to provide oxygen to biomass, to maintain the activated sludge in suspension, and to mitigate fouling by the constant scouring of the membrane surface with flow circulation and shear stress. Bubbles flowing near the membrane surface provide local shear transients and liquid flow fluctuations that increase the back transport of fouling components (Le-Clech et al., 2006). Meng et al. (2008) investigated the impact of different aeration intensities (150, 400 and 800 L/h) on membrane fouling mechanisms. The impact of aeration on membrane fouling was interpreted from two aspects: the evolution of biomass characteristics and the formation mechanism of the cake layer. The results showed that either small or large aeration intensity had a negative influence on membrane permeability. The large aeration intensity resulted in a severe breakup of sludge flocs, and promoted the release of colloids and solutes from the microbial flocs to the bulk solution. The sludge supernatant would thus become heterogeneous as the aeration intensity increased. As the MBR operated under a high aeration intensity of 800 L/h, colloids and solutes became the major foulants. In addition, the back transport mechanism of membrane foulants in the three MBRs was different from each other. Aeration had a positive effect on cake layer removal, but pore blocking became severe as aeration intensity increased to 800 L/h.

Hwang et al. (2002) demonstrated that improving aeration resulted in enhanced filtration efficiency. Adjusting the aeration rate from 2 L/min to 4 L/min at 5.6 g/L of sludge and 50 kPa of pressure increased the flux from 10 $L/m^2.hr$ to 13 $L/m^2.h$. However, in their study, the aeration rate was not enough to maintain the flux lower than that of the critical flux.

Aeration rates can also affect the activated sludge properties. For example, Ji and Zhou (2006) reported that the quantity and composition of soluble EPS, bound EPS and total polymers in flocs in the MBRs is influenced by aeration rates. Moreover, they found that soluble EPS underwent an initial accumulation and a subsequent degradation. Also, the increase of aeration rates increased the amount of soluble protein, and EPS increased while the amount of carbohydrate of soluble EPS generally decreased. For bound EPS and polymers in sludge flocs, the amount of protein/ carbohydrate both generally decreased with increased aeration rates.

However, aeration technique is still a challenge for MBR designers to find the effective aeration system throughout the population of fibers in the bundles (Le-Clech et al., 2006). Another alternative to limit the fouling of membranes is using cross flow velocity (CFV). In a small cross flow module, Choi et al. (2005) reported that permeate flux increased linearly with increasing CFV and a cross-flow velocity was more effective at reducing fouling for MF (0.3μm) membrane than for UF (30kDa) membrane. A cross-flow velocity of around 3.0 m/s for MF membrane and 2.0 m/s for UF membrane was sufficient to prevent the formation of a reversible fouling layer.

- **Solid Retention Time (SRT) and Hydraulic Retention Time (HRT)**

SRT is probably the most important operating parameter impacting the membrane fouling tendency in MBRs. The SRT cannot be varied without important changes in sludge composition. The direct impact of the SRT variations is on MLSS concentration (Chang et al., 2002). The MLSS concentration increased from 2.5 to 15 g/L when the SRT increased from 5 to 30 days (Xing et al., 2000).

At longer SRT, decreases in EPS concentration (Chang and Lee, 1998) and slight increases in mean particle size (Huang et al., 2001) have been reported. At low SRT, the fouling propensity of membrane was found to increase and the fouling rate got nearly 10 times higher when SRT was dropped from 10 days to 2 days (representing F/M ratios from 0.5 to 2.4 g COD/g MLVSS/day) (Trussell et al., 2006).

Ahmed at al. (2007) investigated the effect of SRT on membrane bio-fouling in a membrane bioreactor (MBR) equipped with a sequential anoxic/anaerobic reactor. They reported that as the SRT decreased to 20 days, the bound-EPS per unit of biomass increased, and consequently, the value of specific cake resistance increased, which resulted in the rise of TMP. When the system operated at longer SRTs (above 60 days), a significant decrease in the value of specific cake resistance was observed.

Han et al. (2005) reported that the membrane fouling increased with SRT because sludge particles were more severely deposited on the membrane surface at longer SRT.

Like the SRT, the HRT is also an important parameter in MBRs operation. Although the HRT has no direct effect on membrane fouling, the different HRT can cause various OLRs (Meng et al., 2007). Short HRT can induce large OLR. Therefore, the HRT related not only to the treatment efficiency of the MBRs (Ren et al., 2005), but also to the characteristics of the MLSS solution (Cho et al., 2005; Yoon et al., 2004).

Visvanathan et al. (1997) observed that the membrane fouling reduced at higher HRT values (no TMP increase) postulating that a rapid formation of a compact layer on the membrane surface took place at longer HRTs.

- **Unsteady State Operation**

Changes of operation conditions are very common in MBR applications. For example, shifts in aeration intensity, fluctuation in the HRT and changing in the SRT result in unsteady state conditions. Sudden change in operation state might lead to a change in the nature and/or structure of the polysaccharide and consequently membrane fouling could be deteriorated (Le-Clech et al., 2006). For example, Cho et al. (2005) reported that the levels of bound EPS were changed when the SRTs were altered (8, 20 and 80 days).

2.3.7.8 Mode of Operation

The current trend in MBR applications is to operate the MBRs at constant flux (Le-Clech et al., 2006). However, MBRs can be operated at constant pressure or constant flux. At the constant pressure mode, a rapid decline is expected to occur as a result of fouling during the initial stages of operation. It was reported that the operation of the membrane bioreactor at constant flux below the critical flux avoids over fouling of the membrane in the initial stage and thus is more advantageous (Defrance and Jaffrin, 1999).

2.3.8 Methods of Reducing MBR Fouling

The various methods to minimize the effects of membrane fouling on membrane performance in MBR technology can be grouped into three approaches. These approaches are: membrane cleaning, improvement in biomass characteristics and optimizing operating conditions. The different techniques in these approaches are discussed in detail in this section.

2.3.8.1 Membrane Cleaning

- **Physical Cleaning**

During physical cleaning, the membrane module in the bioreactor is relaxed when the filtration process is paused and the membrane is backwashed by pumping permeate in the reverse direction to remove some of the reversible foulants that have accumulated onto the membrane surface or within the membrane pores. Most of the reported studies on SMBR system used this technique to reduce the fouling problem.

The efficiency of backwashing has been area of research for many investigators (Psoch and Schiewer, 2006 & 2005; Bouhabila et al., 2001). In general, the membrane backwashing efficiency depends on the frequency and the duration time. For example, Jiang et al. (2005) found that the efficiency of backwashing was better with less frequent, but longer backwashing (600 s filtration/45 s backwashing) in comparison with more frequent backwashing (200 s filtration/15 s backwashing).

Schoeberl et al. (2005) compared the SMBR system in terms of suction time, aeration intensity and the backwash time based on factorial design. They found that suction time (between 8 and 16 min) was more effective in controlling fouling than both the aeration intensity (0.3–0.9m^3/m^2.h) and the backwash time (25–45 s).

Although the backwash technique has proved to be an effective method in reducing the fouling, 5 to 30 % of the produced permeate is consumed in this process which increases the energy cost (Le-Clech et al., 2006). Accordingly, optimization of this technique is required to save energy in terms of the operating cost and the permeate consumption. In this area, Smith et al. (2005) designed a generic control system that automatically optimized the duration of the backwash according to the monitored value of the TMP.

Water as permeate is not the only physical medium used for backwashing the membrane, air can also can be used as the backwashing medium. Air backwashing in SMBRs can increase the flux from 6 to 30 $l/h/m^2$ which corresponds to a 400 %

improvement in the flux (Visvanathan et al., 1997). However, 15 min of air backwash was required every 15 min of filtration to obtain this result. On the other hand, air backwashing is an efficient method for flux recovery; it may also present potential issues in terms of membrane breakage and rewetting.

- **Chemical Cleaning**

When increasing irreversible fouling accumulates on the membrane surface during the operation, the physical cleaning efficiency decreases and therefore chemical cleaning is required. Different types and intensities of chemical cleaning may also be recommended. They include (Le-Clech et al., 2006):

- Chemically enhanced backwash (on a daily basis);
- Maintenance cleaning with higher chemical concentration (weekly);
- Intensive (or recovery) chemical cleaning (once or twice a year).

Each of the four main MBR suppliers (Mitsubishi, Zenon, Memcor and Kubota) proposes their own chemical cleaning recipes, which differ mainly in terms of concentration and methods (Le-Clech et al., 2006).

2.3.8.2 Improvement the Biomass Characteristics

The performance of SMBRs can be enhanced by improving the wastewater characteristics. Theoretically, it was reported that the permeate flux in SMBR systems can be increased by increasing the particle size of the flocs in suspension. This is due to the shear-induced diffusion increases with the increase in particle size (Jinsong et al., 2006). In general, particles penetration into the membrane pores can be reduced by increasing the particle size, and this will enhance particle back transport from the membrane surface to the bulk solution (Lee et al., 2001).

- **Chemicals Additives**

The floc size of the MLSS solution can be increased by adding chemical flocculation-coagulation agents such as aluminum salts, iron salts and organic polymer prior to the membrane filtration processes. For example, Zhang et al. (2008) investigated the effect of adding iron (Fe (III)) in the form ferric chloride ($FeCl_3$) on fouling in a membrane bioreactor. They found that an optimal concentration of 1.2 mM of Fe (III) was effective in improving the mixed liquor filterability in MBR, and at the optimal concentration of Fe (III), the fraction of flocs with a MW greater than 10 kDa in the SMP and floc particle sizes 1-10 μm were reduced.

In another study conducted by Song et al. (2008), they confirmed that the addition of ferric chloride directly into the aerobic tank in a membrane bioreactor process was efficient in causing a decrease in the specific resistance to filtration.

Wu and Huang (2008) investigated the effect of iron addition in the form of polymeric ferric sulfate (PFS) on the membrane filterability performance of the mixed liquor in the membrane bioreactor. They found that membrane fouling was effectively retarded by PFS addition in the long-term operation of the MBR. They found that the suitable dosage and dosing interval were 1.0 mM Fe and 15-30 days for the MBR with an MLSS of 7-10 g/L. Moreover, the effluent quality was not affected after PFS addition although PFS addition influenced microbial activity as a result of pH reduction.

Song et al. (2008) found that the addition of alum directly in the aeration tank not only had a positive effect on the minimization of membrane fouling but was also associated with increasing phosphorus removal. They found that the addition of 30 mg/L of alum was effective in removing 3 mg/L of phosphorous in the feed of the MBR process with a reduction in the membrane fouling factor without deteriorating the nitrogen removal efficiency. Moreover, the particle size analysis further confirmed that coagulation with alum could minimize membrane fouling because of the relatively small particle sizes in the MBR, which are considered a cause of membrane fouling, could increase in size due to the addition of coagulants.

Fan et al. (2007) investigated the effect of adding different chemical coagulants (ferric chloride, alum, and an organic polymer) on the fouling potential of the mixed liquors on submerged membrane bioreactor processes in treating municipal wastewater. The filterability was evaluated at constant permeate flux mode. The results showed that coagulation pretreatment can reduce fouling rates when MBRs were operated above the critical flux. Even though coagulation with the organic polymer formed larger mixed liquor suspended solids particles and had shorter time-to-filtration than those with ferric chloride and alum, the filterability during membrane filtration were similar, indicating that membrane fouling in MBR applications was mainly controlled by the concentration of smaller colloidal particles.

Wu et al. (2006) used inorganic coagulants to control membrane fouling in a SMBR system. Among four types of congratulants (monomeric and polymeric) used in their study: $Al_2(SO_4)_3$, $FeCl_3$, PAC (polymeric aluminum chloride) and PFS (polymeric ferric sulfate), they found that the polymeric coagulants had a better effect on filterability enhancement of mixed liquor than the monomeric coagulants.

Holbrook et al. (2004) investigated the effect of aluminum sulfate (alum) addition on membrane performance in a submerged membrane bioreactor process. The results from their study demonstrated that that direct alum addition to bioreactor improved the membrane performance by reducing the organic fouling material and improving floc structure and strength.

Other studies showed that the addition of adsorptive material such as activated carbon PAC (Guo et al., 2008; Lesage et al., 2008; Hu and Stuckey, 2007; Munz et al., 2007; Lee et al., 2006; Seo et al., 2004) and zeolite (Lee et al., 2001) and zeolite (Lee et al., 2001) can also enhance the overall performance of SMBR system by increasing the surface area available for biological growth. Seo et al. (2004) found that the membrane fouling in submerged membrane bioreactor system can be decreased by adding high concentrations of powdered activated carbon (PAC).

Lee et al., (2001) investigated the effects of adding zeolite and alum to improve the performance of submerged membrane bioreactor. They found that the addition of alum reduced the membrane fouling rate and raised the rate of suction pressure. On the other hand, they found that the addition of natural zeolite enhanced the membrane permeability.

- **Using Direct Current DC Field**

Using the concept of electrical fields to prevent membrane fouling in membrane filtration technology was conducted by many researchers (Tarazaga et al., 2006; Visvanathan and Ben Aim, 1989; Jagannadh and Muralidhara, 1996) However, most of the studies reported in the literature focused on the cross flow and dead end membrane filtration. To the best of the author knowledge, the works of Chen et al. (2007) were the only studies reported in the literature regarding the integration of DC fields with SMBR system. They used a direct electrical current (DC) field to enhance the membrane flux. In their work the membrane module was separated from the bioreactor zone, and the reported MLSS was within the range 400-800 mg/L. Furthermore, they used high voltage which may affect the cost of the process.

2.3.8.3 Optimizing the Operating Conditions

It is recognized that optimization of the operating conditions is another approach in reducing the fouling on the membrane surface (Judd, 2006). Operating parameters that may primarily affect the overall hydraulic performance of the SMBR system include the aeration intensity, sludge retention time (SRT) and hydraulic retention time (HRT), and MLSS concentration in the reactor.

2.4 Electrocoagulation

2.4.1 General Description

Electrocoagulation is an electro-chemical process that simultaneously removes many contaminants (heavy metals, suspended solids, emulsified organics...etc) and many other from wastewater using electricity and sacrificial metal electrodes (usually iron and aluminum) instead of expensive chemical reagents. The basic operation is based on applying a direct current (DC) electrical filed between immersed electrodes in wastewater. The electrochemical reaction involving the iron and the contaminants in the waste stream produces insoluble hydroxides - flocs- that are easily separated from the treated water by settling.

The first appearance of using electricity in water treatment systems was in the UK in 1889 (Chen, 2004). Different techniques and applications of electrochemical technologies can be used in water and wastewater treatment like electrocoagulation (EC), electrodepsition, electroflotation (EF) and electro oxidation (Chen, 2004). This section introduces some important aspects of electrocoagulation as it is the focus in this research. The theoretical details of electrokinetic phenomenon as well as EC technology are discussed in Chapter 4. More details about the electrocagulation process can be found in the literature (Chen, 2004; Mollah et. al., 2001).

In 1909 electrocoagulation was recorded as a patent in USA. In 1946 EC of drinking water was first applied on a large scale in the USA (Chen, 2004). However, large capital investment and the expensive electrical supply were considered negative factors to make this technology spread worldwide during that period.

2.4.2 Advantages and Disadvantages of Electrocoagulation

Generally, Electrocoagulation (EC) has proven to be an effective method for wastewater treatment during the 20th century, especially in these last decades (Kobya et al., 2006).

The major advantages of using EC in comparison with chemical coagulation (CC) processes are: simple operation, relatively high quality of effluent, low sludge production, less total dissolved solids content, efficient in removing the smallest colloidal particles, no chemical is required, alkalinity is not consumed, and less energy demand (Zhu et al., 2005; Mollah et al., 2001; Horner and Duffey, 1983). Moreover, the space required for EC is less than CC because EC does not require chemical storage, dilution, and rapid mixing (Mills, 2000).

However, EC also suffers from some problems presented by (Mollah et. al., 2001):

- The fast corrosion of electrodes that requires regular replacement;
- The formation of oxide film on the cathode may reduce the overall efficiency of the process;
- The process needs high conductivity for the solution to be treated;
- Expensive electricity can be one of the drawbacks in using EC in some locations.

2.4.3 Applications of Electrocoagulation Processes

EC has shown the capability to remove a large range of pollutants under a variety of conditions. Table 2.2 summarizes some of the applications found in the literature.

2.5 Summary and Conclusion

The integration of two or more wastewater treatment methods in a hybrid technology is becoming a competitive trend to increase the overall performance of wastewater treatment technologies.

As it was outlined throughout the literature review presented in this chapter, the membrane bioreactor (MBR) technology has proven to be an efficient technology and it is a feasible alternative to conventional activated sludge processes. However, membrane fouling was addressed as a major problem in MBR operations which increases the maintenance and operating costs. This problem limits the widespread application of MBR technologies. For this reason further research and development are required in this domain.

Table 2.2 Some applications of EC technology

Application of wastewater by EC	References
Domestic wastewater	Kurt et al., 2008
Slaughterhouse wastewater	Asselin et al., 2008; Bayramoglu et al., 2006
Baker's yeast wastewater	Kobya and Delipinar, 2008
Textile industries	Bayramoglu et al., 2007 ; Zaroual et al., 2006 ; Bayramoglu et al., 2004; Lin and Chen, 1997
Heavy metals	Gomes et al., 2007; Parga et al., 2005; Mills, 2000; Horner and Duffey, 1983
Decolourization of water	Daneshvar et al., 2004; Can et al., 2003; Do and Chen, 1994
Removal of fluoride ions from industrial wastewaters	Shen et al., 2003
Treatment of restaurant wastewater	Chen et al., 2000
Potable water	Vik et al., 1984
Oil-in-water emulsions	Cañizares et al., 2008
Removal of nitrate from water	Koparal et al., 2002

Furthermore, for MBR systems to be commercially competitive the life-span of membrane module in MBR system should be increased; this would require decreasing the fouling rate. Consequently, the performance of the whole process would increase.

To decrease the fouling rate in MBR applications, a coagulation approach has been applied as mentioned in the literature. In most of the conducted studies, chemical coagulation was the target method. However, the addition of chemicals to the MBR system may cause undesirable side effects (e.g. increasing the amount of sludge, producing byproducts, lowering the quality of biosolids).

Therefore, in order to overcome many common problems found in present wastewater treatment technologies, a new approach was proposed. The proposed hybrid system combines membrane reactor, biological treatment and electrokinetic processes (where electro-coagulation is a leading process). In Chapter 3, the concept of this new method is introduced in greater detail.

Chapter 3

Development of the SMEBR – Design Criteria

Chapter 3 introduces a new method of wastewater treatment by developing a novel SMEBR (the submerged membrane electro-bioreactor) system. This chapter provides a detailed description of the proposed work to provide the reader with the required knowledge of the SMEBR design, configurations, and theoretical analysis of the process.

3.1 A Framework for Developing the SMEBR System

The original design of the SMEBR system appears to lies at the intersection of three more fundamental technologies: biodegradation, electrochemistry (in majority represented by the electro-coagulation phenomenon) and membrane filtration. One possible conceptual framework for the proposed design of the SMEBR is shown in Figure 3.1. Each defined area brings a certain perspective to the SMEBR system, as represented by each lobe of this diagram.

Each of these processes was studied separately. Each intersection between two lobes shows the possible interaction of two processes during wastewater treatment. For

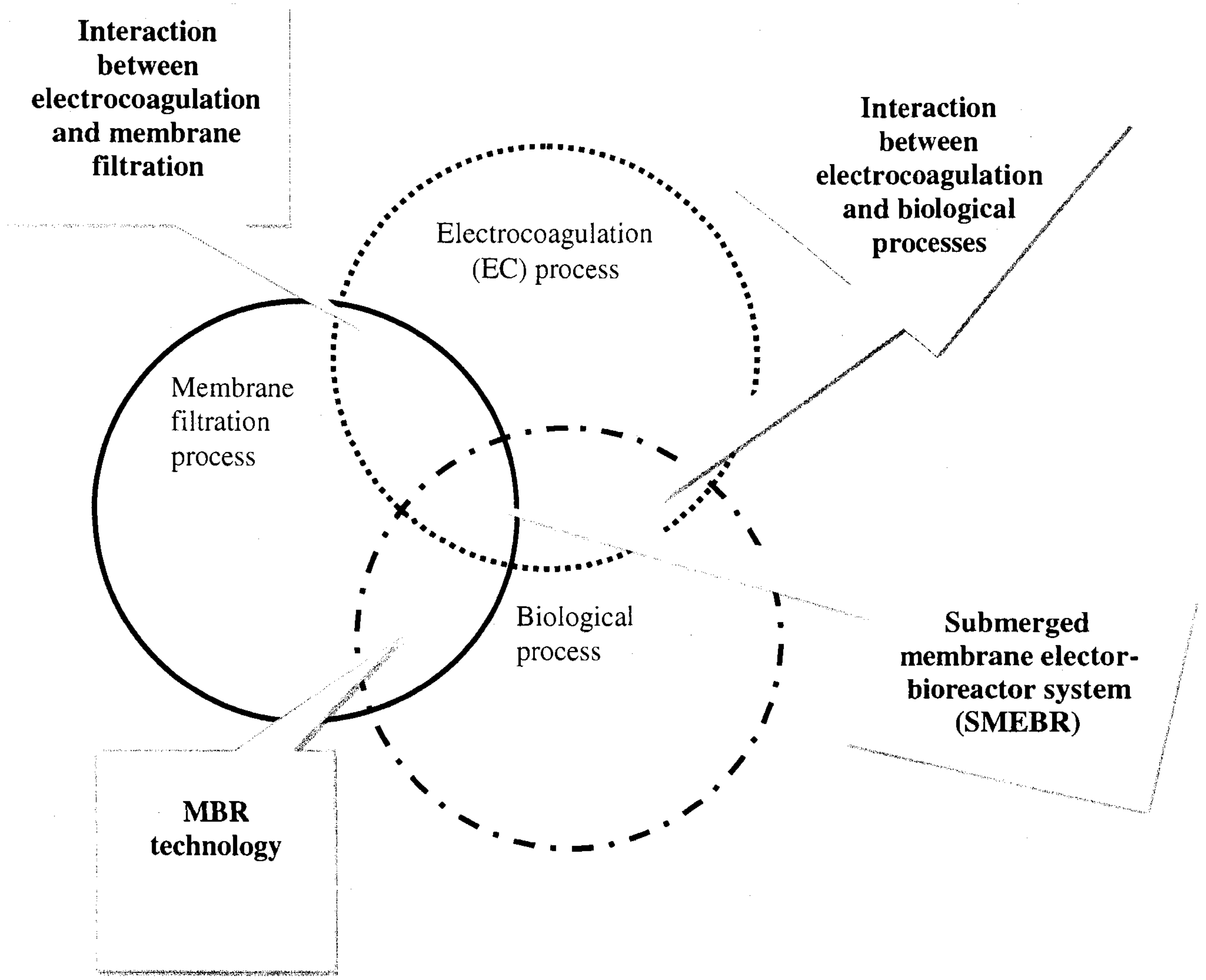


Figure 3.1 Conceptual framework of the submerged membrane electro-bioreactor (SMEBR) system

example, when the lobe of the biological process intersects with the lobe of membrane filtration, a membrane bioreactor technology (MBR) is established. The intersection of the three lobes forms a central area that characterizes the behavior of the SMEBR system.

Consequently, the distinguishing point between the proposed designed method in this research and the other studies in the literature is the integration of three processes, that is to say, biological, electrokinetic and filtration into one hybrid unit as an advance wastewater treatment method.

3.2 Considerations for the SMEBR Design

3.2.1 Electrodes Configurations Constraints

Designing the electrodes in the SMEBR system is important for the uniform distribution of the DC field strength on the mixed liquor solution inside the electro-bioreactor. During the designing stage of the SMEBR system, the design of electrodes was governed by the following constraints:

- The electrodes should be arranged inside the bioreactor that also includes a membrane module. This means that the place of the membrane module in the reactor must not affect the current density between the electrodes.
- The electrical field cannot affect the longevity of membrane material, for example through advance oxidation of the polymeric materials.
- Electrodes should be designed so as not to decrease the efficiency of the electrical current between the electrodes.
- The DC field should be identical in all directions in the bioreactor to get homogeneous flocs formation in the ML solution, which means that the electrodes

should be designed in a way such that the ML solution should be in contact with the electrodes by the same order of magnitude as the electrical current distribution.

- The electrodes assembly in the electro-bioreactor should be designed in a way such that they would not interfere with the feed and the flow toward membrane module.
- Electrode assembly is the heart of the present treatment invention; therefore, the appropriate selection of its materials is very important. The most common electrode materials for electro-coagulation are aluminum and iron. They are cheap, readily available, and proven effective because they introduce M (III) ions into media and accelerate the coagulation process. Thus both metals were tested in this research.
- The SMEBR design and configuration should take into consideration the requirements of the different simultaneous processes taking place inside the electro-bioreactor such as biodegradation, electro-coagulation and sedimentation. During these processes, the SMEBR is governed by the following fluid motions.
    i) Supply of wastewater from outside and across to the anode.
    ii) Air flow from bottom to the top.
    iii) Electro-formation of flocs and their settling.
    iv) Treated water flow through cathode and toward membrane module.

Solutions to solve the above constrains mean the successful design of the SMEBR system. To operate the SMEBR in a better way and to meet the above requirements, the SMEBR system should be designed according to the following criteria:

- The membrane unit must be placed in the center of the reactor;
- The electrodes must be placed around the membrane module with an appreciable distance from the membrane;
- An accurate distance between the electrodes should be kept in order to minimize the potential effect of an acidic (oxidation) zone on microbial community;
- Perforated electrodes should be used in the design but not interfere with the feed and the flow toward the membrane module.

The schematic diagram in Figure 3.2 illustrates the idea of the SMEBR configuration that is in agreement with the above mentioned constrains. The selected design of the SMEBR system divides the hybrid reactor into two zones, shown in Figure 3.3. Zone I (electro-bioreactor) is boarded between the external wall of the reactor to the cathode and Zone II is boarded from the cathode to the membrane module.

Generally in Zone I, three processes take place: biodegradation, electro-coagulation and electro-sedimentation, while Zone II has two processes: further biodegradation and membrane filtration.

3.2.2 Electrical Parameter Constraints

In addition to the design constraints related to the electrodes system, as mentioned in the section 3.2.1, the SMEBR system is governed by several electrical parameters during the operation of the SMEBR system. The selected DC field and the operating mode to supply this DC field into the ML solution are significant constraints in the SMEBR operation.

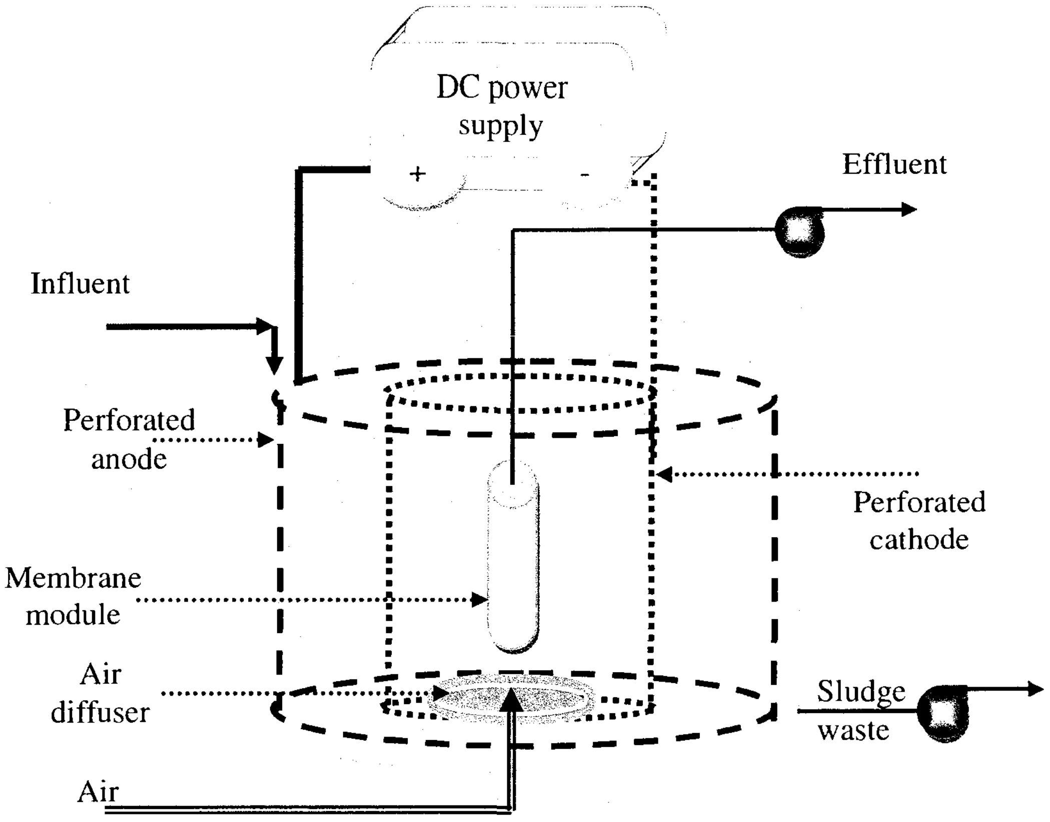


Figure 3.2 Simplified design configuration of the SMEBR system

It is very important to identify the best electrolysis conditions in terms of the appropriate DC density. Furthermore, the selected DC field could not be supplied in a continuous mode to the ML solution; therefore, the DC field should be applied intermittently in the SMEBR system. For this reason, a preliminary experimental phase (Chapter 6) was conducted to identify the best electrolysis conditions in terms of the appropriate current density so as to not impede the biological treatment, and to determine the best exposure time to DC when electrolysis should be applied intermittently to the SMEBR system.

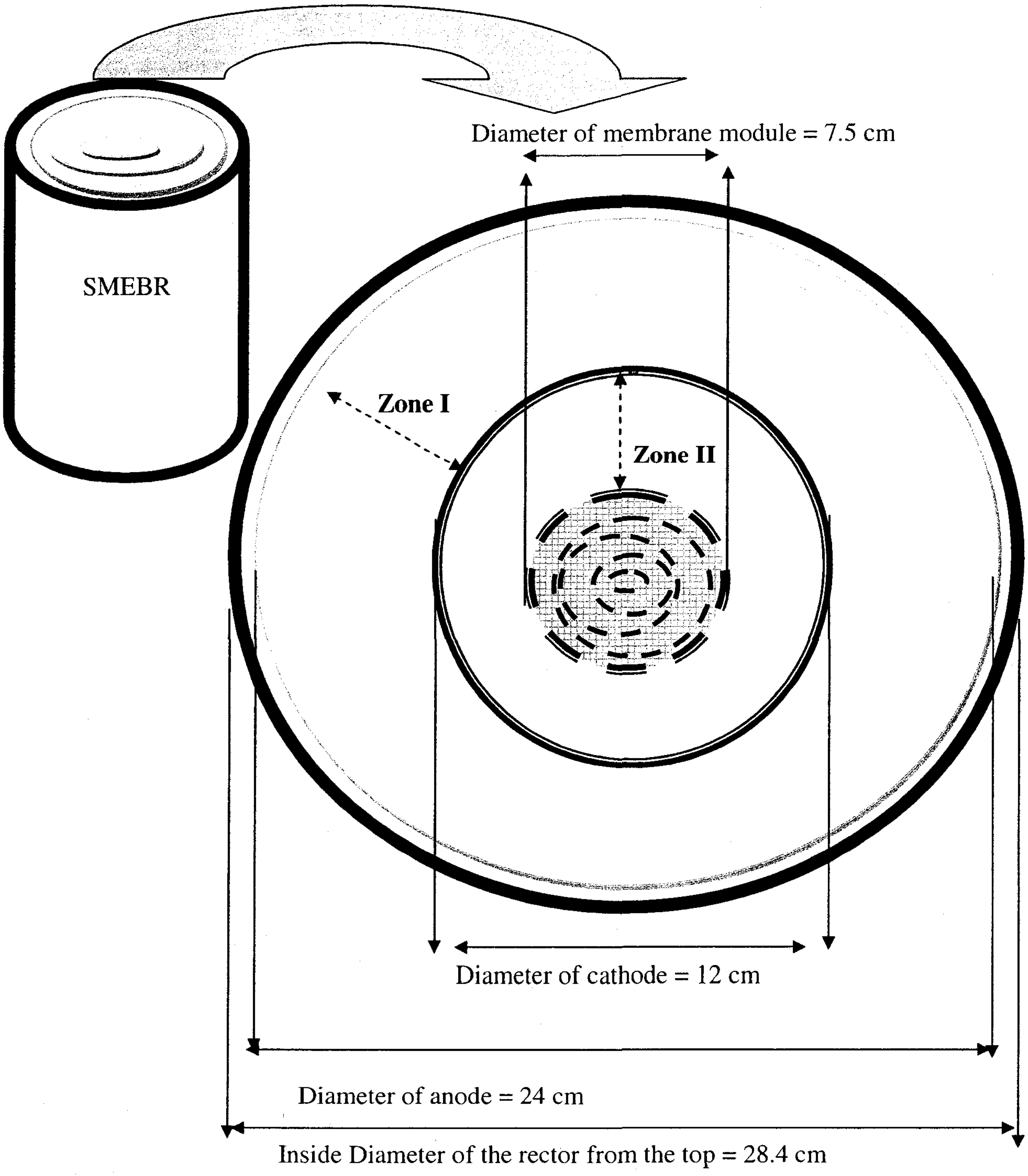


Figure 3.3 Top view of the submerged membrane electro-bioreactor (SMEBR)

Moreover, the distance between the electrodes should be designed to prevent the overlap between the acid and base conditions in Zone I that results from the electrochemistry occurring on the anode and the cathode (see Chapter 4). Also, an optimal distance should be selected between the cathode and the membrane module in Zone II to prevent any possibility of membrane surface damage.

3.3 Theoretical Approach and Hypothesis

3.3.1 Fluid Motions in the SMEBR System

The SMEBR is governed by the following fluid motions (Figure 3.4):

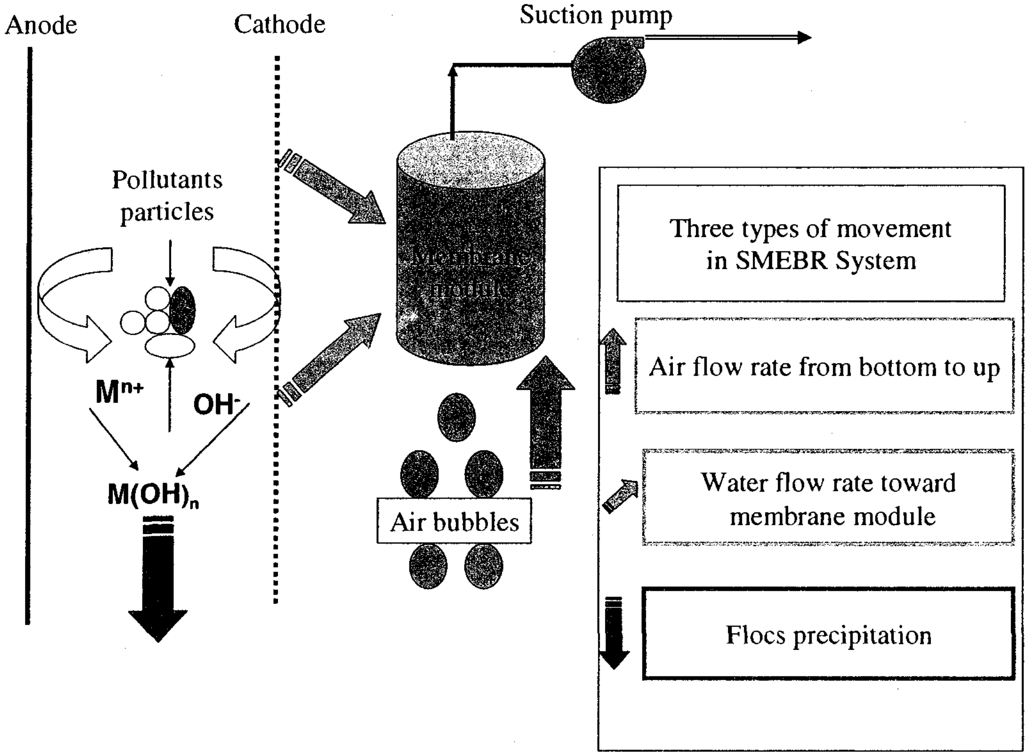


Figure 3.4 Major types of fluids motion occurring in the SMEBR system

i) Supply of wastewater from the outside and across the perforated anode in order to undergo biological and electrochemical treatment between the electrodes.

ii) Air flow from bottom to the top.

Air is used in SMEBR systems for three main reasons: i) supplying sufficient oxygen for the microorganism to achieve the biological process, ii) achieving a good mixing of the ML solution in the electro-bioreactor's zones and iii) reducing the fouling rate of the membrane. Methods of providing air to the SMEBR system are described in Chapter 5.

According to the above explanations, air bubbles are transferred from the bottom toward the top of the reactor.

iii) Electro-formation of flocs and electro-settling.

According to the principles of electrokinetic phenomena, a direct current (DC) field is formed between two electrodes: the anode and cathode. At the anode, the electrolysis of the anode material (M) into its cation (M^{n+}) and the formation of O_2 takes place under oxidation condition; simultaneously, water is reduced to hydrogen gas and the formation of hydroxyls (OH^-) take place at the cathode. Subsequently, flocs are formed in the mixed liquor, which accelerate the settling and the removal of solids bonded to pollutants (organic and inorganic). Details description about the theory of electrocoagulation is discussed in Chapter 4.

iv) Treated water flows through the perforated cathode toward the membrane module.

According to the suction pump connected to the membrane module, the treated water flows from the bulk solution toward the membrane as shown in Figure 3.5. This hydraulic force also drives the particles onto the membrane surface due to the movement of liquids out of the membrane.

3.3.2 Controlling Operational Parameters

Successful design of the SMEBR system should be based on assessing accurate operational parameters that would be able to simultaneously control all the preferential processes: biodegradation, electro-coagulation, sedimentation, and filtration within the system.

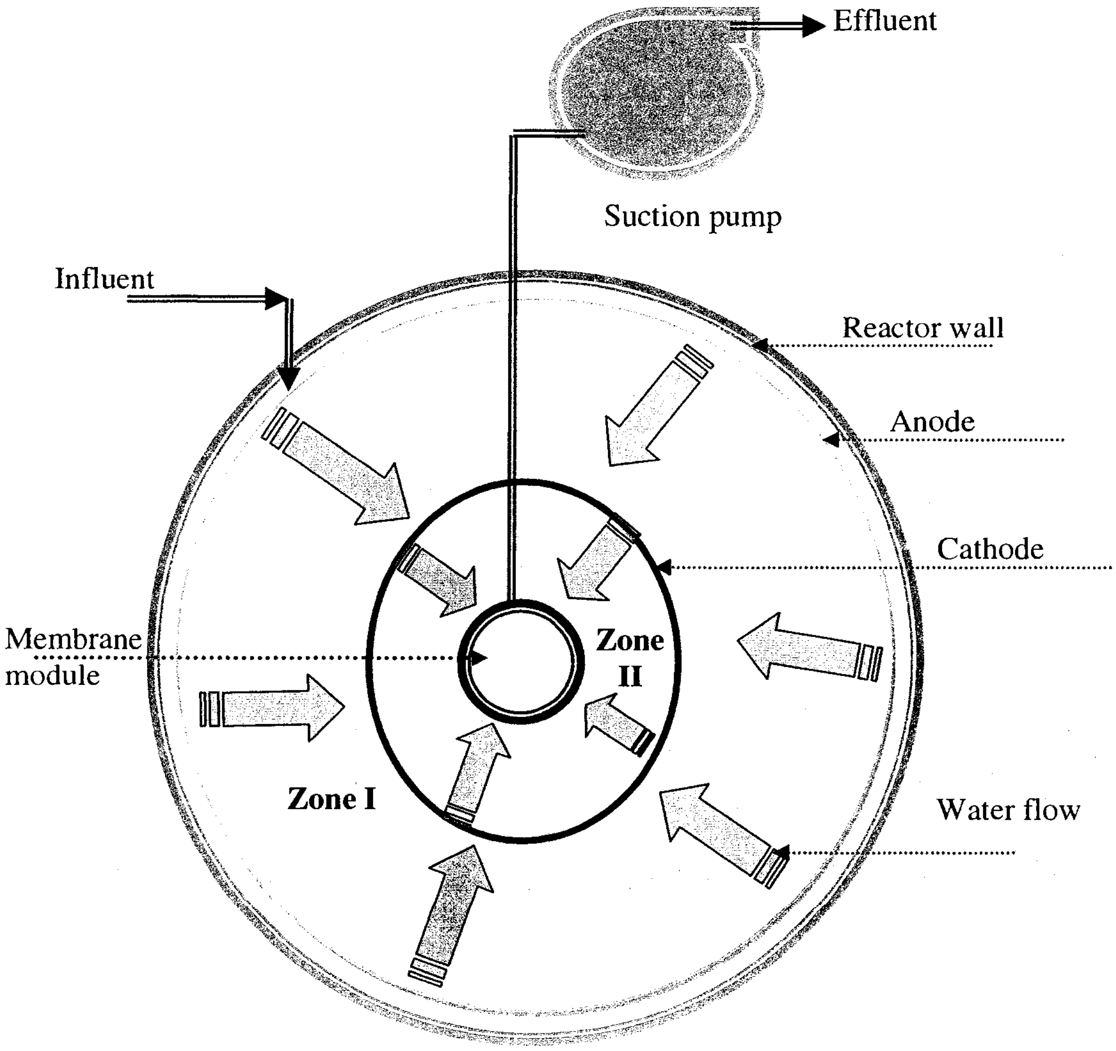


Figure 3.5 Top view of the SMEBR system: Effect of suction on water flow

Biodegradation processes are affected by the surrounding environmental conditions (temperature, pH, O_2 concentration) in the bioreactor. Appling a DC electrical field onto mixed liquor solution will affect all of these conditions in different ways (e.g., temperature may rise, pH would decrease closed to the anode and increase closed to the cathode). The recommend range for pH for microorganism is within the range 6-9 (Alshawabkeh et al., 2004). Subsequently, an interrupted supply of electrical field is needed to preserve the viability of microorganisms. However, at the same time, a DC (at an accurate voltage gradient) is required for an effective electro-coagulation process to create flocs in the bioreactor so the small particles can aggregate and can move away from the membrane module.

On the other hand, the supplied oxygen might also affect the behavior of the microorganisms in the bioreactor; however, an excess of air may breakdown the flocs' formation. Therefore to achieve the overall objectives of the designed configuration, five parameters should be controlled and optimized during the SMEBR operation, those are:

i) Electrical gradient;
ii) Exposure time to DC;
iii) Air supply;
iv) Hydraulic retention time (HRT);
v) Sludge retention time (SRT).

3.4 Conclusion

In conclusion, the feasibility of the designed SMEBR system for wastewater treatment needs to be verified and the operating conditions need to be optimized. Because the selected design criteria for the SMEBR system requires relatively large circular electrodes to be compatible with the membrane module, it might be time consuming to perform the optimizing work directly on a designed system. Therefore in this initial stage of the research, a small scale elector-bioreactor was used to simulate the exact design of the SMEBR system without using the membrane module in order to select the best operating conditions in terms of the electrical parameters. This was conducted during the preliminary tests in Phase I of this research.

After selecting the best electrical parameters in Phase I, the performance of the up-scaled SMEBR was investigated in two separate phases. In Phase II iron was used as both electrodes materials, while in Phase III an aluminum anode was utilized.

Chapter 4

Theoretical Background for Determination the Performance of the SMEBR System

As the submerged membrane electro-bioreactor (SMEBR) system has been designed for the first time in this work and in order to verify its feasibility for wastewater treatment, the SMEBR was monitored for some periods of time (around two months in each phase). Both water quantity and quality were monitored to analysis different physicochemical and biochemical parameters to assess the performance of the SMEBR system under various operating conditions.

In this chapter, the theoretical analysis required to assess the SMEBR's performance was discussed. Section 4.1 presents a theoretical background on membrane filtration process, which includes a description of the fouling mechanism occurring in membrane technology. Section 4.2 includes the calculation methods in membrane efficiency, description of electrokinetic phenomena, and electrocaogulation process. Section 4.3 describes the theory of electrocoagulation. Section 4.4 summarizes briefly the methods used to assess the performance of the SMEBR system.

4.1 Membrane Filtration Performance in the SMEBR System

In any membrane process, the performance of the membrane module is measured quantitatively by the amount of flux produced through the membrane area. The process efficiency of membrane performance often depends on the operating conditions and their susceptibility to fouling, which may reduce the effective size of the pores and decrease the permeability of the membrane. In order to assess the membrane filtration process in the SMEBR system, a brief discussion about the fouling phenomenon was described in next section.

4.1.1 Theory of Membrane Filtration Mechanisms

Microfiltration (MF) and ultrafiltration (UF) are the common types of membranes used in MBR filtration applications. The permeation flux (J), which is defined as permeate volume per unit membrane surface area and filtration time, through MF and UF filtration systems can be described by Darcy's law as follows (Lee et al., 2003):

$$J(t) = \frac{1}{A_m}\frac{dV}{dt} = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu(R_m + R_c + R_f)} \tag{4.1}$$

Where J is the permeate flux ($m^3/m^2.s$), V the total volume of permeate (m^3), A the membrane area (m^2), ΔP is the transmembrane pressure (Pa) (TMP) (TMP = $P_f - P_p$), μ the permeate viscosity ($N.s/m^2$), R_t is the total resistance in the system (m^{-1}), R_m is the membrane resistance (m^{-1}), R_c is the cake resistance (m^{-1}), and R_f is the fouling resistance (m^{-1}) due to irreversible adsorption and pore blocking (Figure 4.1).

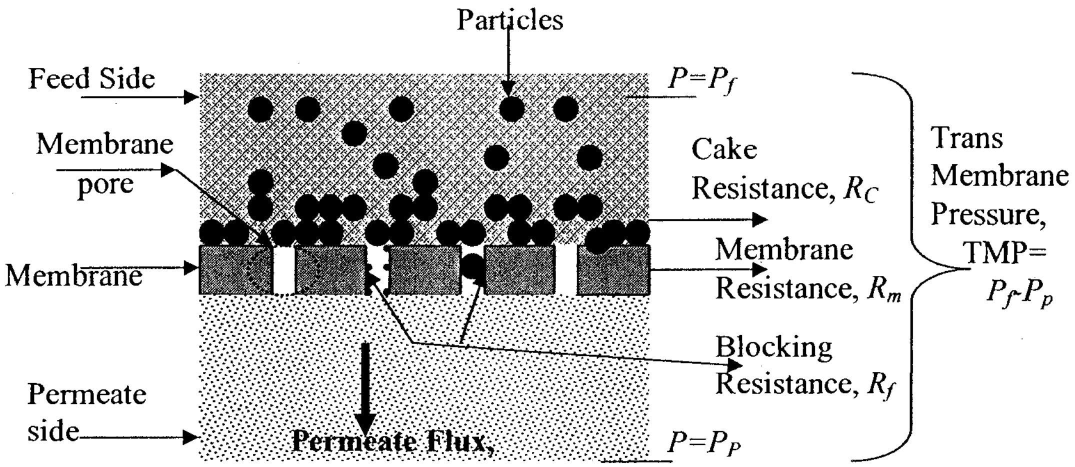


Figure 4.1 Fouling phenomena occurring in membrane technology
(Adapted from Evenblij H., 2006)

For microfiltration and ultrafiltration at a constant TMP, the initial permeate flux, J_i; will mainly depend on R_m as R_f and R_c are initially zero. With the proceeding of filtration operation, pore blocking and cake formation will cause R_f and R_c to increase, and change the relative significance of R_m, R_f, and R_c, and the filtration process can transfer from a membrane resistance-limited to a pore blocking resistance-limited or a cake resistance-limited process. As a result, the permeate flux (J) decreases with time.

The cake resistance, R_c, is related to the specific cake resistance (r) and the mass of cake deposited on the membrane surface, M, as in the following equation:

$$R_c = \frac{rM}{A_m} = \frac{rVC_b}{A_m} \tag{4.2}$$

Where A_m (m^2) is the membrane area, V is the cumulative filtrate volume (m^3), C_b is the bulk concentration of particles (kg/m^3), and r is the spesific cake resistance (m/kg) normalized to the mass of materials deposited per unit of membrane surface area. The value r can be determined experimentally and Equation (4.3) can be used if the applied

(ΔP) is constant; it also can be estimated theoretically using the Carman-Kozeny Equation (Equation 4.4).

$$\frac{t}{V}=\frac{\mu R_m}{A_m \Delta P}+\frac{r\mu C_b}{2A_m^2 \Delta P}V \tag{4.3}$$

$$r=\frac{180(1-\varepsilon)}{\varepsilon^3 \rho_p d_p^2} \tag{4.4}$$

Where ε is the cake porosity, ρ_p is the particle density (kg/m^3), and d_p is the particle diameter (m).

4.1.1.1 Determination of Fouling Resistances

In order to determine the fouling mechanism in any membrane filtration process, all the resistances (R_m, R_c, R_f) should be determined. This can be done experimentally when the operation would be at constant pressure. Usually, dead end filtration cell is used for this purpose.

From Equation (4.1), at constant TMP, the total resistance throughout the system is given by:

$$R_t=\frac{\Delta P}{\mu J} \tag{4.5}$$

Where R_t is the total resistance in the system. The membrane resistance (R_m) can be determining by the following equation:

$$R_m=\frac{\Delta P}{\mu J_{wi}} \tag{4.6}$$

Where J_{wi} is the initial water flux, and the fouling resistance (R_f) can be determined by the following equation:

$$R_f = \frac{\Delta P}{\mu J_{wf}} \tag{4.7}$$

Where J_{wf} is the final water flux after removing the cake layer by flushing with tap water. Finally the cake resistance (R_c) can be determined from the following equation:

$$R_c = \frac{\Delta P}{\mu J_{AS}} - R_m - R_f \tag{4.8}$$

Where J_{AS} is the flux of activated sludge at steady state.

The viscosity of water μ in the above equations is a function of temperature and it can be normalized to 20 °C using the following equation, which is accurate within 5% error for a temperature range of 5-40 °C (Trussell et al., 2005).

$$\frac{\mu\ (T)}{\mu\ (20^{o}C)} = e^{(-0.0239(T-20))} \tag{4.9}$$

Where T is the temperature of water (^{o}C); $\mu(T)$ is the absolute viscosity of water at T (N.s/m^2); $\mu(20^{o}C)$ is the absolute viscosity of water at 20 °C (N.s/m^2).

4.2 Determination the Water Quality in the SMEBR System

4.2.1 Pollutants Removal Efficiency

Usually, the faster way to calculate the membrane efficiency is to measure the pollutants concentrations of the input and the output streams of the membrane module (Figure 4.2). In general, there are two terms to measure the efficiency of membrane filtration process in terms of pollutants concentrations. The first term is called the percentage rejection or the removal efficiency (*% R*) and the second term is the log removal value (LRV). The removal efficiency (*% R)* is given by the following equation:

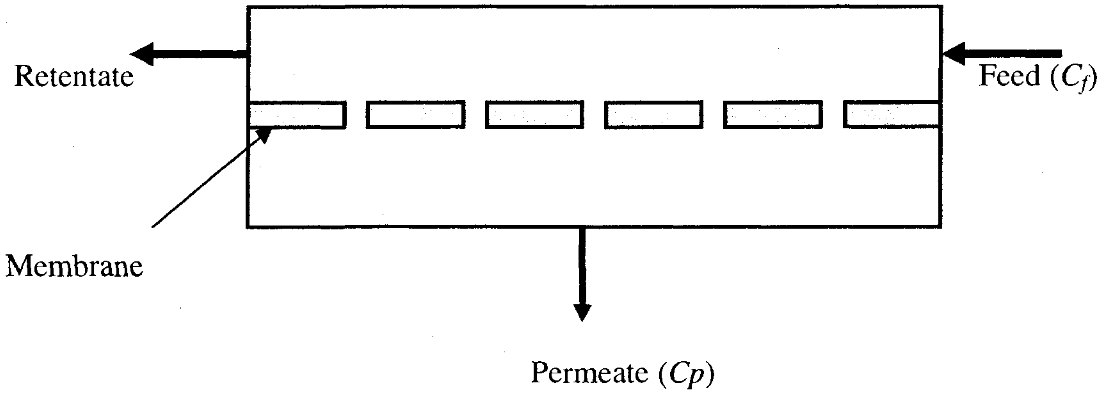


Figure 4.2 Concept of membrane filtration

$$\%R = (\frac{C_F - C_P}{C_F}) * 100\% \tag{4.10}$$

Where C_F is the concentration of the pollutant in feed stream (mg/L) and C_p is the concentration of the pollutant in permeate stream (mg/L). The LRV is mainly used to calculate the efficiency of removing microorganisms and particles (bacteria, viruses....etc) by membranes (Zhu et al., 2005). The LRV is given by the following equation:

$$\text{LRV} = \log(\frac{C_F}{C_p}) \tag{4.11}$$

Because the SMEBR has two units: the electro-bioreactor, and membrane module, sometimes it may be required to measure the removal efficiency of the electro-bioreactor alone which is expressed by:

$$\%R_{reactor} = (\frac{C_F - C_r}{C_F}) * 100\% \qquad (4.12)$$

Where C_r is the concentration of a specific pollutant in the supernatant in the electro-bioreactor (mg/L). In the SMEBR system, C_F, C_P and C_r can be the concentrations of COD, ammonia nitrogen (NH_3–N), nitrate nitrogen (NO_3–N), nitrite nitrogen (NO_2–N), orthophosphate (PO_4-P) and TKN.

Equation (4.10) describes the removal efficiency of the whole system of the SMEBR (the membrane module and the electro-bioreactor).

Because the SMEBR system has been designed to have two zones, it might be interesting to calculate the removal efficiency of the pollutants in each zone based on equation (4.12).

4.2.2 Measuring the Sludge Characteristics in the SMEBR System

Different wastewater treatment processes are taking place in the electro-bioreactor unit of the SMEBR system as mentioned in Chapter 3. It is well known that applying direct electrical current (DC) filed into the mixed liquor suspended culture affects its physiochemical and biochemical parameters. Accordingly, measuring the changes of these parameters is of great importance to give indication of the impact of the applied DC on these parameters which is reflected on the overall performance of the SMEBR system.

Because the selected design of the SMEBR system permitted for generation of various electrokinetic phenomena, a brief discussion is presented in the next section about these phenomena.

4.2.2.1 Electrokinetic Phenomena

4.2.2.1.1 Double Layer and Zeta Potential

As the SMEBR system is designed on applying DC filed between two immersed electrodes throughout the treated solution, subsequently various electrokinetic phenomena occur in the treated solution.

A colloidal system consists of liquid and solid particles (like mixed liquor activated sludge solution) and most colloidal particles in an aqueous colloidal dispersion carry an electric charge due to their ionic characteristics and/or dipolar attributes. The magnitude of the surface charge depends on the acidic or basic strengths of the surface groups and on the pH of the solution.

Each colloidal particle dispersed in a solution is surrounded by oppositely charged ions called the fixed layer (Figure 4.3). Outside the fixed layer, there are varying compositions of ions of opposite polarities, forming a cloud-like area. This area is called the diffuse double layer (Lindquist, 2003), and the whole area is electrically neutral. The boundary that separates the diffuse double layer from the bulk solution is called the slipping plane (sometimes it is called the surface of hydrodynamic shear). The potential that exists on the slipping plane, or, which separates the diffuse layer from the bulk solution is called zeta potential. When a particle moves (e.g. due to gravity), ions within the slipping plane move with it, but any ions beyond the slipping plane do not travel with the particle. Therefore, the magnitude of the zeta potential gives an indication of the potential stability of the colloidal system.

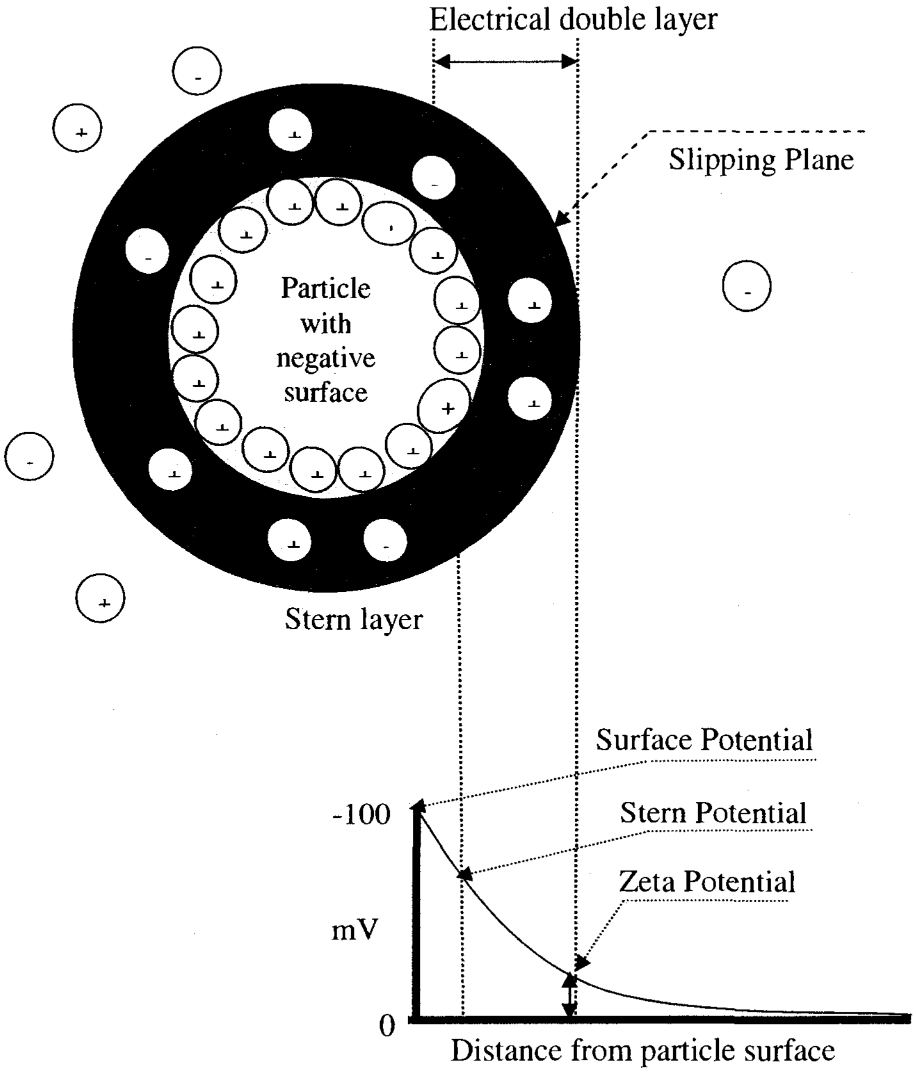


Figure 4.3 Electrical double layer (Source: http://www.nbtc.cornell.edu)

Theoretically, the zeta potential is the overall charge a particle acquires in a specific medium. If all the particles have a large negative or positive zeta potential they will repel each other and there is dispersion stability. If the particles have low zeta potential values then there is no force to prevent the particles coming together and there is dispersion instability. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as shown in Table 4.1 (ASTM Standard, 1985). In general, a dividing line between stable and unstable aqueous dispersions is generally taken at either +30 or -30 mV, (Figure 4.4). Particles with zeta potentials more positive than +30 mV are normally considered stable. Particles with zeta potentials more negative than -30 mV are normally considered stable.

Table 4.1 Stability behavior of the colloidal system (adapted from ASTM Standard, 1985)

Zeta Potential [mV]	Stability behavior of the colloid
From 0 to ± 5	Rapid coagulation or flocculation
From ± 10 to ± 30	Incipient stability
From ± 30 to ± 40	Moderate stability
From ± 40 to ± 60	Good stability
More than ± 60	Excellent stability

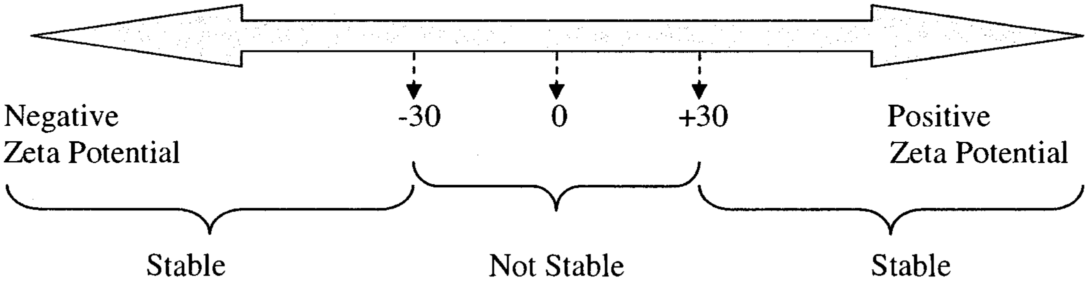


Figure 4.4 Zeta potential scale

Zeta Potential is usually measured by a specific chamber containing the colloidal solution between two electrodes. Schematic diagram of zeta potential measurement is presented in Figure 4.5. The zeta potential can be computed using the Smoluchowski's formula (Equation 4.13)

$$\xi = (\frac{4\pi\eta}{\sigma} \times \Pi \times 300 \times 300 \times 1000) \tag{4.13}$$

Where:

ξ : Zeta potential (mV)

η : Viscosity of solution (N.s/m^2)

σ : Dielectrical constant

Π is the electrophoretic mobility and it is given by:

$$\Pi = (\frac{v}{U / L}) \tag{4.14}$$

Where:

v : Speed of particles (m/s)

U: Voltage (V)

L: The distance between electrodes (m)

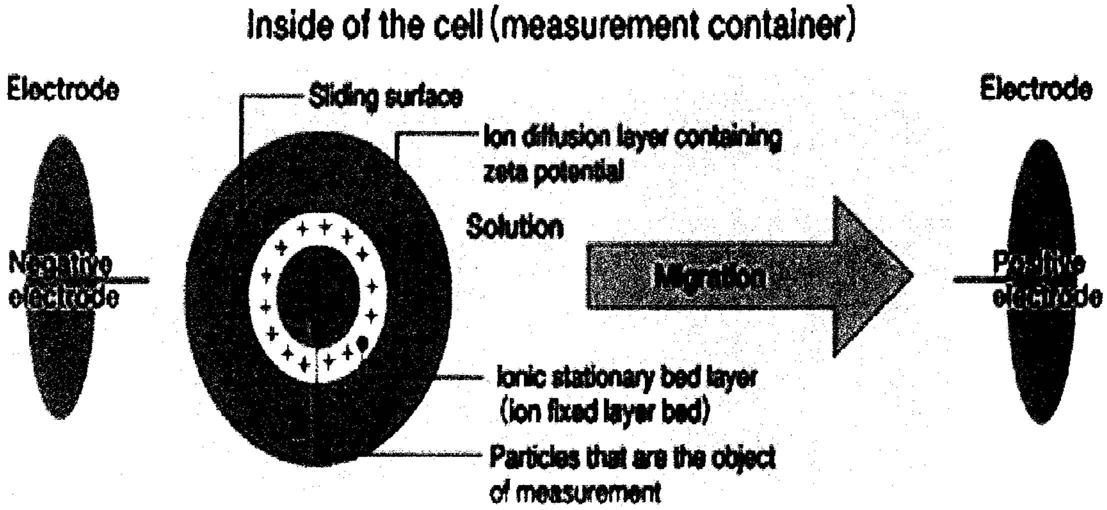


Figure 4.5 Zeta potential of colloidal particles dispersed in a solution
(Source: http://nition.com)

The most important parameter that affects zeta potential is pH. A zeta potential value quoted without a definition of its environment (pH, ionic strength, concentration of any additives) is a meaningless number.

Theoretically, when particles in suspension with a negative zeta potential, adding more alkali to this suspension makes the particles tend to acquire more negative charge, whileif acid is added to this suspension then a point will be reached where the charge will be neutralized. Further addition of acid will cause a buildup of positive charge.

A typical zeta potential versus pH curve will be positive at low pH and lower or negative at high pH as shown in Figure 4.6.

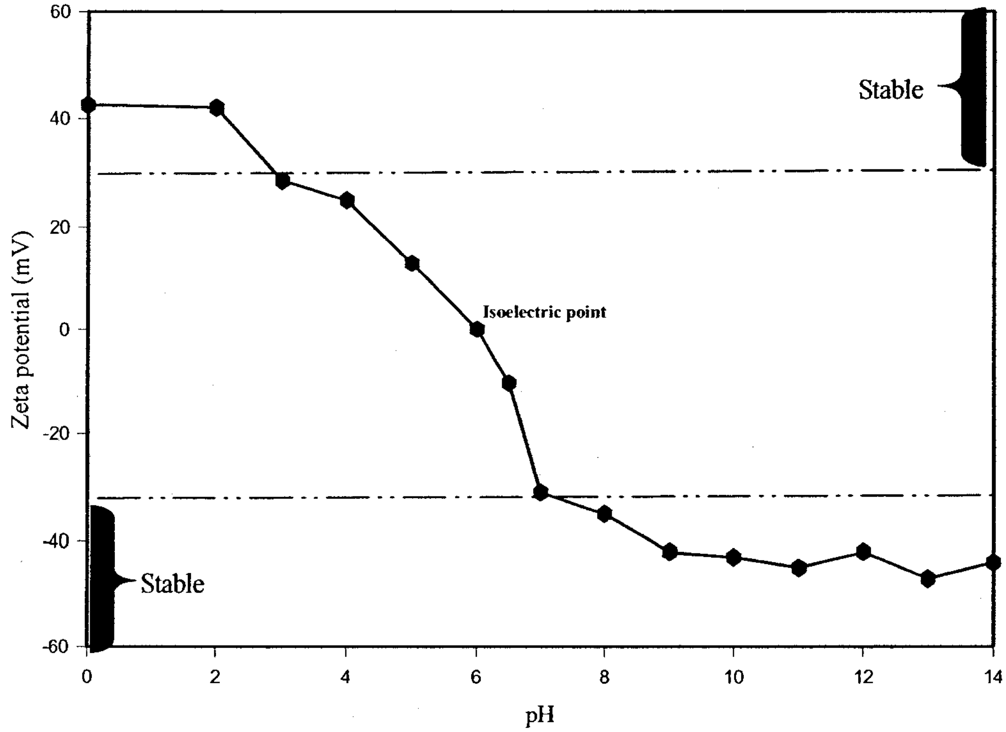


Figure 4.6 A typical zeta potential curve versus pH
(Source:http://www.silver-colloids.com)

As shown in Figure 4.6, if the dispersion pH is below 4 or above 8 there is sufficient charge to form colloidal stability. However if the pH of the system is between 4 and 8 the dispersion may be unstable. Also, Figure 4.6 shows that at pH around 6, the zeta potential is closed to zero, the point at which the colloidal particles are least stable. This point is called the isoelectric point. However, the isoelectric point depends on each suspension, it changes with the type of colloids, therefore with their charge. For example, the isoelectric point for silica (silicon oxide, SiO_2) in water at 25 °C is within the range 1.7 and 3.5 and for magnetite (iron (II, III) oxide, Fe_3O_4) between 6.5 and 6.8 (Kosmulski, 2001).

4.2.2.2 Electrophoresis and Electroosmosis Phenomena

When an electric field is applied into mixed liquor solution in which particles are dispersed, charged particles are attracted towards the electrode of the opposite charge, accompanied by the fixed layer and part of the diffuse double layer, or internal side of the "sliding surface". The particles move with a characteristic velocity which depends on the strength of the electric field, the dielectric constant and the viscosity of the medium and the zeta potential. The velocity of a particle in a unit electric field is referred to as its electrophoretic mobility.

An important consequence of the existence of electrical charges on surfaces is that particles will be affected by an applied electric field. These are collectively defined as electrokinetic phenomena. There are two distinct phenomena depending on the way in which the motion is induced:

- Electrophoresis: the movement of a charged particle relative to the liquid under the influence of an applied electric field. In other words, electrophoresis is related to the movement of the solids or charged species, e.g., the migration of particles through a relatively stationary fluid.
- Electroosmosis: the movement of a liquid relative to a stationary charged surface under the influence of an electric field. Or, the electroosmosis phenomenon is about the movement of the fluid such as the permeation of fluid through a porous medium (membrane).

4.3 Electrocoagulation Process

4.3.1 Theory of Electrocoagulation Process

Electrocaogulation (EC) is considered as a complex process with a multitude of mechanisms operating simultaneously and synergistically to remove pollutants from water (Holt et al., 2002). Simplified description can stand for application of a direct current between metallic anode and cathode through wastewater solution. As a result, the metal (M) is oxidized to its cation (M^{n+}) at the anode (Equation 4.15), while water is reduced to hydrogen gas and the hydroxyl ion (OH^-) at cathode (Equation 4.16). The dissolution of metal from the anode is simultaneous with formation of hydroxyl ions and hydrogen gas occurring at the cathode (Figure 4.7). Generally, aluminum or irons are used as sacrificial anodes in EC processes (Chen et al., 2004) and both materials were used in the SMEBR system operation in this research. In the following section, the electrochemistry reaction associated with EC processes by iron and aluminum were highlighted.

$$M \longrightarrow M^{n+} + ne^- \quad (4.15)$$

$$2\,H_2O + 2e^- \longrightarrow 2\,OH^- + H_2 \quad (4.16)$$

Electocoagulation process can involve many steps. Mollah et al. (2001) summarized the main steps in EC processes in the following three steps:

- Formation of coagulants by electrolytic oxidation of the "sacrificial electrode";
- Destabilization of the contaminants;
- Breaking of emulsions.

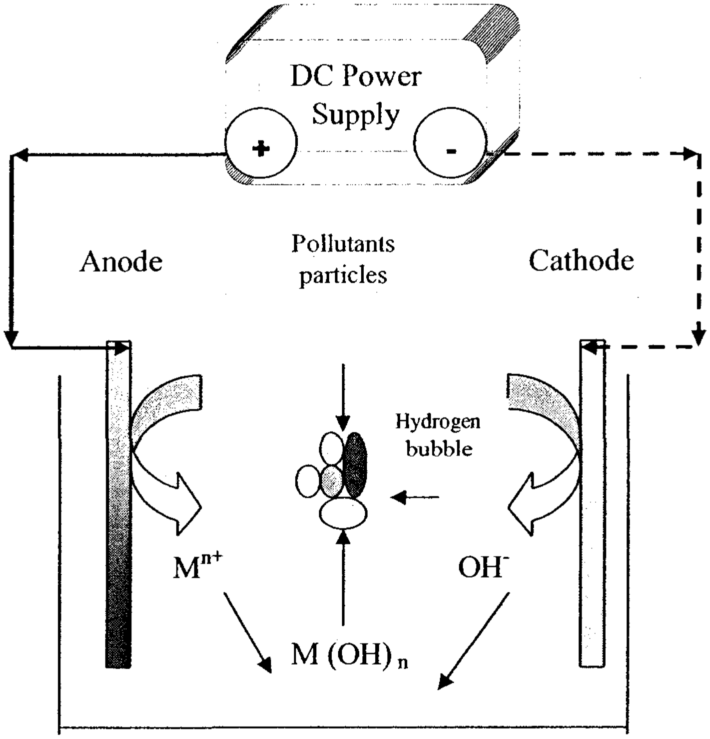


Figure 4.7 Principle of electrocoagulation
(Adapted after Holt et al., 2002)

While Kobya et al. (2006) described the EC process by the following main processes which occur serially:

- Electrolytic reactions at electrode process;
- The formation of coagulants in aqueous phase;
- The adsorption of soluble or colloidal pollutants on coagulants.

Generally, the overall mechanism of EC process is affected by many parameters like the aqueous medium characteristics as conductivity, pH, particle size and the concentration of the chemical consistent. So, a combination of multi mechanisms may be occurring during the operation. The dominant mechanism may vary throughout the dynamic process as the reaction progresses. The dominant mechanism will almost certainly shift with changes in operating parameters and pollution types. In conclusion, many factors associated with EC process may affect the final efficiency. Those factors can be summarized by the following:

- Wastewater characteristics (The pH value, components of the suspension and their concentrations, the bubble size and position, floc stability and agglomerate size).
- Type of electrodes.

Material of electrodes; aluminum and iron are the major sacrificed electrodes used in EC processes. Electrocoagulation of wastewater using aluminum and iron has been reported by number of authors (Kurt et al., 2008; Bayramoglu,et al., 2007 Gomes et al., 2007; Daneshvar et al., 2004; Can et al., 2003). In the following subsections, the mechanism of EC using those two electrodes are reviewed as it was reported in literature.

4.3.2 Theory of EC Using Iron and Aluminum Electrodes

Different reaction mechanisms may occur during the SMEBR system operation when iron and aluminum are used as electrodes. Therefore, understanding the theory of electrocoagulation by using iron and aluminum should be highlighted.

4.3.2.1 Iron Electrodes

A series of reactions take place when iron is used as electrodes material. According to Kurt et al. (2008), the following main reactions occur in the EC cell when iron is used as electrode material:

- Reactions in a cathode environment:

$2H_2O\,(l) + 2e^- \rightarrow H_2\,(g) \uparrow + 2\,OH^-\,(aq)$ (4.17)

$8\,H^+(aq) + 8e^- \rightarrow 4\,H_2\,(g) \uparrow$ (4.18)

- Reactions in an anode environment:

$2H_2O\,(l) \rightarrow O_2\,(g) \uparrow + 4H^+\,(aq) + 4e^-$ (4.19)

$Fe\,(s) \rightarrow Fe^{2+}\,(aq) + 2e^-$ (4.20)

Due to the production OH^- ion near the cathode as in shown from equation (4.17), the pH of the medium is expecting to increase. Meanwhile, the anode electrolyses and dissolves ferrous ions into solution as shown in the following equations:

$Fe^{2+}\,(aq) + 2OH^- \rightarrow Fe\,(OH)_2\,{}^{(}s)$ (4.21)

$2Fe^{2+}\,(aq) + 1/2\,O_2\,(g) \uparrow + 5\,H_2O\,(l) \rightarrow 2Fe\,(OH)_3\,(s)\,{}^{+}\,4H^+ \uparrow (aq)$ (4.22)

The detailed theory of electrocoagulation using iron electrodes was discussed in Chapter 7 of this thesis in which the experimental Phase II of this research was conducted using cylindrical tubes iron mesh.

4.3.2.2 Aluminum Electrodes

When aluminum is used as an anode material, the main reactions are as follows (Kobya et al., 2006):

- At the anode:

$Al \rightarrow Al^{3+} + 3e^-$ (4.23)

- At the cathode:

$3H_2O + 3e^- \rightarrow 3/2H_2\,(g) + 3OH^-$ (4.24)

- In the solution:

$Al^{3+}\,(aq) + 3H_2O \rightarrow Al\,(OH)_3 + 3H^+\,(aq)$ (4.25)

The amorphous Al $(OH)_{3(s)}$ formed is characterized by "sweep flocs" that have large surface areas which are beneficial for the rapid adsorption of soluble organic compounds and entrapping colloidal particles (Kobya et al., 2006). These flocs are removed easily from aqueous medium by sedimentation.

Section 4.3.2.2 forms the theoretical part of Chapter 8 in which the experimental Phase III of this research was conducted using perforated cylindrical aluminum sheet.

4.4 Methods of Assessment the SMEBR System

Based on the theoretical analysis presented in this chapter, the SMEBR system was assessed in this research according to the following points:

4.4.1 Assessment of Permeate Flux in the SMEBR System

Since the SMEBR system was operated under constant transmembrane pressure mode, the simple method to assess the SMEBR system quantitatively by measuring the variation of the permeate flux (*J*) with time. The permeate flux (*J*) expected to decrease with time due to fouling phenomenon as it was explained in Figure 4.1. In addition, the corresponding percentage reduction in permeate flux (*PRPF*) calculated from the following equation:

$$PRPF = (1 - \frac{J}{J_i}) \times 100\% \tag{4.26}$$

Where J_i is the initial permeate flux and J is the permeate flux at any time during the membrane filtration process.

The change in the hydraulic retention time (HRT) during the SMEBR operation is considered another indication for the performance of the SMEBR system. The HRT is defined by the following equation:

$$HRT = (\frac{V_r}{Q_e}) \tag{4.27}$$

Where, V_r is the reactor volume (m^3) and Q_e is the effluent flow rate (m^3/s). The HRT gives indication about the SMEBR operation to reach the steady state conditions.

4.4.2 Measuring the Physiochemical Parameters

- **Change in pH**

Applying direct electrical current (DC) thought mixed liquor culture will result in rodox reaction at the electrodes (anode and cathode). When two electrodes are used in water, water oxidation generates hydrogen (H^+) and oxygen gas at the anode while water reduction produces hydroxyls (OH^-) and hydrogen gas at the cathode as follows (Alshwabkeh et al., 2004):

$$\frac{1}{2} H_2O \Longrightarrow e^- + H^+ + \frac{1}{4} O_2 \quad \text{Anode} \tag{4.28}$$

$$H_2O + e^- \Longrightarrow OH^- + \frac{1}{2} H_2 \quad \text{Cathode} \tag{4.29}$$

This will increase the acidity at the anode due to (H^+) production and reduce the pH, and at the same time, the base will increase at the cathode and pH will increase.

Accordingly, in the SMEBR system, measuring pH in the mixed liquor culture after introducing a DC thought the culture is an important parameter because most of the bacterial growth needs a specific optimum range of pH in which they can grow. This range is usually closed to neutrality with limits in minimum and maximum near 5 and 9 respectively (Gaudy and Gaudy, 1988).

- **Specific resistance to filtration (SRF)**

Specific resistance to filtration (SRF) of the mixed liquor sludge is an index representing the filterability of mixed liquor when it is dewatered through filter medium. Physically, it gives an indication of the resistance of biomass to filtration (Ng and Hermanowicz, 2005). It is defined as resistance distributed to the unit filter area when specific weight sludge is filtered at a given pressure. A higher sludge specific filtration resistance reflects worse filterability.

The SFR can be used in this research to assess the effect of applying DC fields on mixed liquor activated sludge. Theoretically, it was reported that the permeate flux in submerged membrane reactors can be increased by increasing the particle size of flocs, this is because the shear-induced diffusion increases with increase in particle size (Jinsong et al., 2006).

Generally, particles penetration into membrane pores can be reduced by increasing the particle size, and this will enhance particle back transport from the membrane surface to the bulk solution (Lee et al., 2001). However, Sun at al. (2006) reported that there is an optimal mean size at which the filtration performance will be at maximum condition.

Theoretically, increasing the applied voltages (DC) throughout the mixed liquor will result an increase in the floc sizes and correspondingly the SFR will decrease (Ng and Hermanowicz, 2005). The filtration process is described in the following equation (Ng and Hermanowicz, 2005):

$$r = \frac{2bPA^2}{\mu C} \tag{4.30}$$

Where:

r = Specific resistance to filtration (m/kg);

P = Pressure across filter medium and cake layer (N/m^2);

A = Surface area of filtration (m^2);

μ = Dynamic viscosity of filtrate (N.s/m^2);

C = Weight of solids per unit volume of filtrate (kg/m^3).

The value of b in equation (4.30) is obtained experimentally. Usually the filterability test to determine the value of b is done under vacuum pressure or using pressurized dead end trill cell. In this research, the experiment test to determine b was done at a given vacuum pressure (vacuum kept constant) A series of data V–t was measured, and a curve for t/V–V was obtained (See Equation 4.3). The slope coefficient from the graphic method is b (s/ m^6). Detailed description of the filterability test is shown in Appendix A.

- **Measuring Zeta Potential**

The potential for particle aggregation in the electro-bioreactor's zones can be checked by measuring the zeta potential of floc particles. Zeta potential is considered the most easily measured electrokinetic parameter defining the concept of double layer as it was mentioned before. In this research, zeta potential was used to provide a quantifiable basis for estimating the impact of applying an external DC electric field to enhance the membrane filtration in the SMEBR system.

- **Microbial Activity**

Applying DC field into a mixed liquor solution might have an adversely affect the microbial activity (Maillacheruvu and Alshawabkeh, 2000). Therefore, the oxygen uptake rate (OUR) of the activated sludge was determined in each zone in order to determine the effect of applying DC field on microbial activity. The oxygen uptake rate is calculated by the following equation (Hasar et al., 2002):

$$OUR = \frac{d[O_2]}{dt} \tag{4.31}$$

Where *OUR* is the oxygen uptake rate (mg O_2/L.s), *d[O_2]* is the change in dissolved oxygen concentration (mg/L) and *dt* is the change of time (s).

The specific oxygen uptake rate (*SOUR*) is calculated as follows:

$$SOUR = \frac{OUR}{MLVSS} \tag{4.32}$$

Where MLVSS is the concentration of the mixed liquor volatile suspended solid (mg/L) in each zone of the electro-bioreactor. The value of SOUR is expressed as (mg O_2 /g MLVSS. h).

4.4.3 Measuring the Biochemical Parameters

In addition to the physicochemical parameters, The SMEBR system was closely monitored for different biochemical parameters (COD, ammonia nitrogen (NH_3–N), nitrate nitrogen (NO_3–N), nitrite nitrogen (NO_2–N) and orthophosphate (PO_4-P)).

4.4.4 Measuring the Electrical Parameters

The application of DC field in the designed SMEBR system associated with changes in the electrical parameters in the system. When electrocaogulation process forms a basic root as wastewater treatment method in the designed SMEBR system, the efficiency of using electrocoagulation is determined by the amount of the dissolved metal which is dependent on the quantity of electricity passed through the electrolytic solution. In any electrocaogulation process, the electrodes assembly is usually connected to an external DC source. A relationship between the current density (A/cm^2) and the amount of substances (M) dissolved (g of M/cm^2) can be derived from Faraday's law:

$$m = \frac{I \times t \times M}{ZF} \tag{4.33}$$

Where m is the quantity of electrode material dissolved (g of M/cm^2), I is the current density (A/cm^2), t is the time in s; M is the relative molar mass of the electrode concerned (g/mole), Z is the number of electrons in oxidation/reduction reaction, F is the Faraday's constant, 96,500 (C/mol).

Furthermore, the electricity consumption (E) during wastewater treatment by electrocaogulation process is calculated by (Kobya et al., 2006):

$$E = U \times I \times t \tag{4.34}$$

The energy consumption (E) is expressed as kWh. U is the voltage (V), I is current (A) and t is the EC time (s).

As the electrocaogulation process is a basic process in designing the SMEBR system in this research. Equations (4.33) and (4.34) were used in this research to evaluate the performance of the SMEBR system theoretically in terms of changing in the electrical parameters.

Chapter 5

Experimental Methodology

Chapter 5 presents a general description of the experimental work of this research. It is considered as a reference of the experimental parts of Chapters 6, 7 and 8. Section 5.1 highlights the strategy of research which was followed in this thesis. Section 5.2 includes a description of experiments set-up, materials and chemicals used in the experimental work. Section 5.3 presents simplified description of the operation process of the SMEBR system. Experimental procedures and analytical methods of different physicochemical and biochemical parameters were described in section 5.4.

5.1 Strategy of Research

As the submerged membrane electro-bioreactor system (SMEBR) has been designed for the first time in this work and in order to verify the feasibility of the system for wastewater treatment, it was decided to operate the SMEBR on continuous operation mode to obtain results close to the normal operation conditions in a wastewater treatment plants. Both water quantity and quality were monitored to assess the performance of the SMEBR system under various operating conditions.

In order to study the fouling degree accurately, the process was operated at constant transmembrane pressure mode. The same strategy has been followed by other investigators (Meng et al., 2006). This means that the permeate flux may decrease with time due to the fouling phenomenon. Moreover, no back washing of the membrane module was performed during the operation.

Water quality analysis was based on the change of physicochemical parameters (pH, temperature), COD, ammonia nitrogen (NH_3–N), nitrate nitrogen (NO_3–N), nitrite nitrogen (NO_2–N) and orthophosphate (PO_4-P). The rate and extent of membrane fouling were quantified by measuring permeate flux at constant suction pressure. Changes in the sludge properties within the SMEBR system were based on the following measurements:

- The MLSS and MLVSS concentrations;
- Sludge specific resistance to filtration (SRF);
- The change in zeta potential of flocs.

Base on the measurements of electrical parameters, the changes of the following parameters were calculated:

- Changes in current density;
- Electrodes consumption;
- Energy consumption.

Figure 5.1 shows a flow chart of the research strategy that was followed in this thesis. The experimental work of this study was divided into three phases. In Phase I (preliminary phase), a comprehensive investigation of the impact of applying direct current (DC) fields on the characteristics of wastewater was studied. The objective of Phase I was to investigate the proper voltage gradient and an operating mode of DC that could be applied to get the best operating conditions for the SMEBR system, where selected electrical parameters would not impede the biological treatment. To simulate a

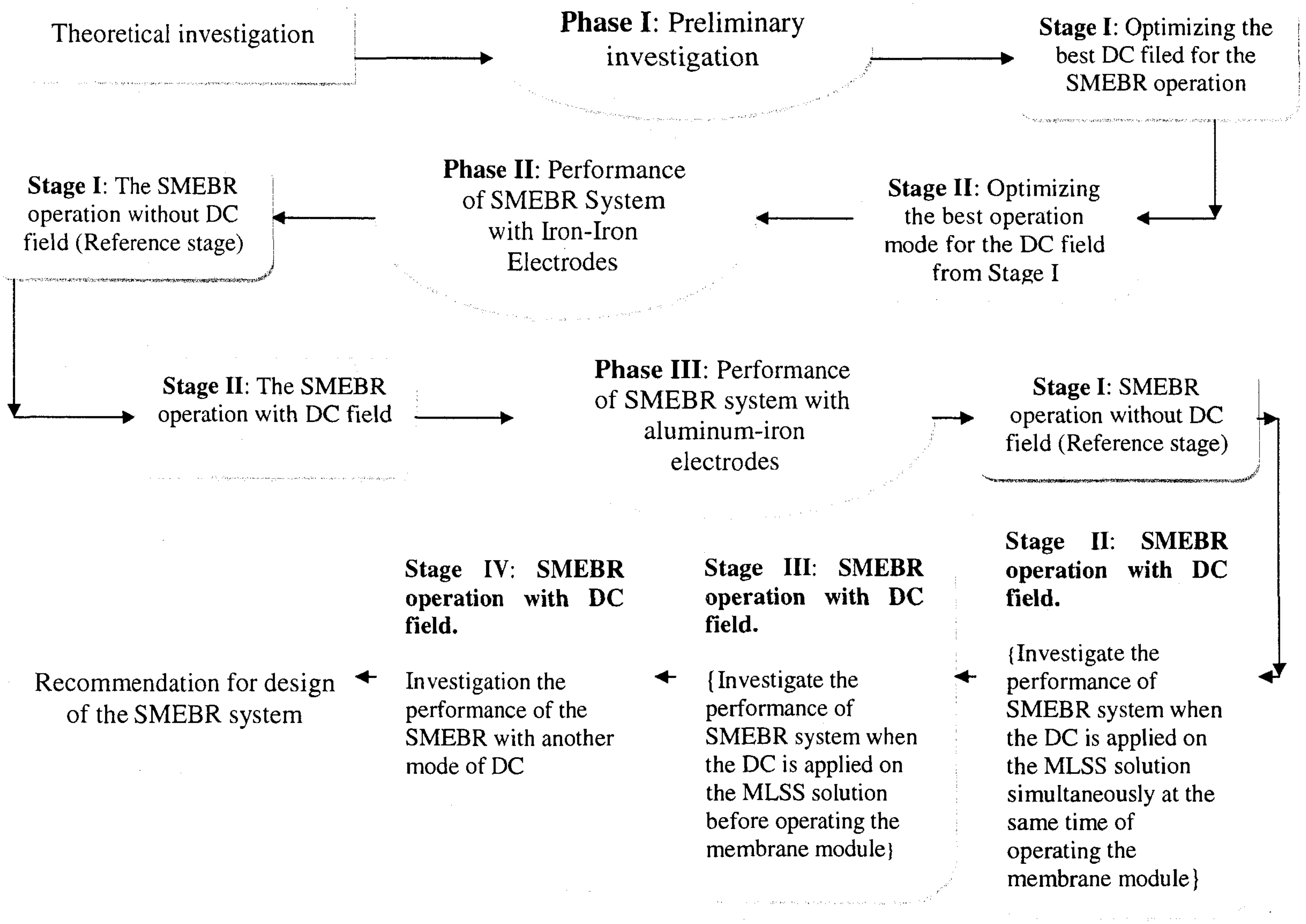


Figure 5.1 Experimental work strategy of research

real case, a small electro-bioreactor was used in Phase I. The output results of the Phase I were presented in Chapter 6. Based on the obtained results from Phase I, the best electrical parameters were selected to operate the SMEBR (submerged membrane electro-bioreactor) system in Phases II and III.

In Phase II, the SMEBR system was under investigation using cylindrical iron mesh as electrodes. The Phase II was performed in sequential two stages: the Stage I was considered as a reference stage in which the system was operated without applying DC field, while the Stage II presented the operation of the SMEBR system with DC power supply. Detailed description of the experimental conditions of Phase II and the output results were presented in Chapter 7.

In Phase III, the perforated cylindrical aluminum sheet was used as anode while the cathode was built with iron mesh (the same one used in the Phase II). The Phase III was performed in sequential four stages. The Stage I was as a reference stage in which the system was operated without applying DC field. In the Stages II and III, the SMEBR system was operated under the same operating conditions. The main difference between the Stage II and the Stage III was in the way of starting the operation of the SMEBR system. In the Stage IV, a different operating mode of supplying DC was investigated. Detailed description of the experimental conditions of the Phase III and the output results were presented in Chapter 8.

5.1.1 Definition of Membrane Washing

Strategy of washing the membrane module was followed through Phases II and III to recover the membrane permeability. The membrane module was washed physically during each stage of the experimental Phases II and III by taking the membrane outside the electro-bioreactor when the permeate flux significantly declined and washed with distillated water for few minutes to remove the attached sludge cake particles over the membrane surface. Chemical cleaning of the membrane module was done at the beginning of each stage. The membrane was washed with tap water for 20 minutes, and then immersed in tank containing distilled water and backwashed with distilled water for 2 hours to remove the small particles entrapped in the membrane pores; then, it was immersed in 5% NaOCl solution for 8 hours. Afterwards, it rewashed by tap water and distilled water. By using this strategy, most of the membrane permeability can be recovered. Meng et al. (2006) obtained more than 95% of the original membrane permeability when the membrane module was immersed in 0.3 % NaClO solution for 24 h.

5.2 Experimental Setup

5.2.1 Experimental Setup of the Phase I

The experimental set-up of the Phase I is shown in Figure 5.2. The setup consisted of a batch conical electro-bioreactor of 14 cm inner diameter at the top and 11.2 cm at the bottom and 16.5 cm height.

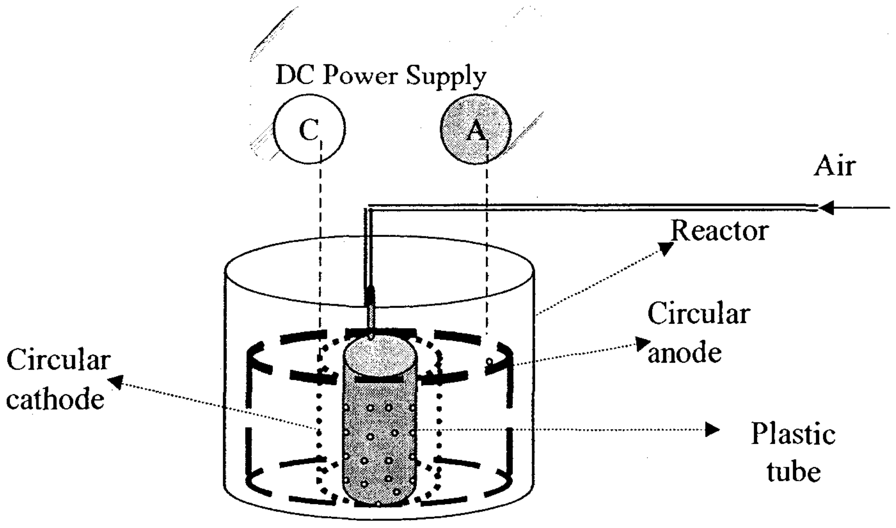


Figure 5.2 Experimental setup of the Phase I

Perforated cylindrical iron meshes were used as electrodes. To simulate the case in the SMEBR system, a perforated plastic tube of 10 mL volume was fixed at the center of the electro-bioreactor. It was used for two purposes: a) to simulate the position of the membrane module which would be designed at the center of the electro-bioreactor in the SMEBR system, b) to supply air through the pores to simulate the air stream around the membrane module in the SMEBR system.

The anode was fixed closed to the internal wall of the electro-bioreactor, while the cathode was fixed around the plastic tube. The distance between the electrodes was 5 cm.

The above configurations presented the actual design of the SMEBR system without using membrane module in a smaller scale.

5.2.2 Experimental Setup of the Phases II and III

Figure 5.3 represents a schematic diagram of a laboratory scale set-up which was used in this research in the Phases II and III. The experimental set up consisted of the

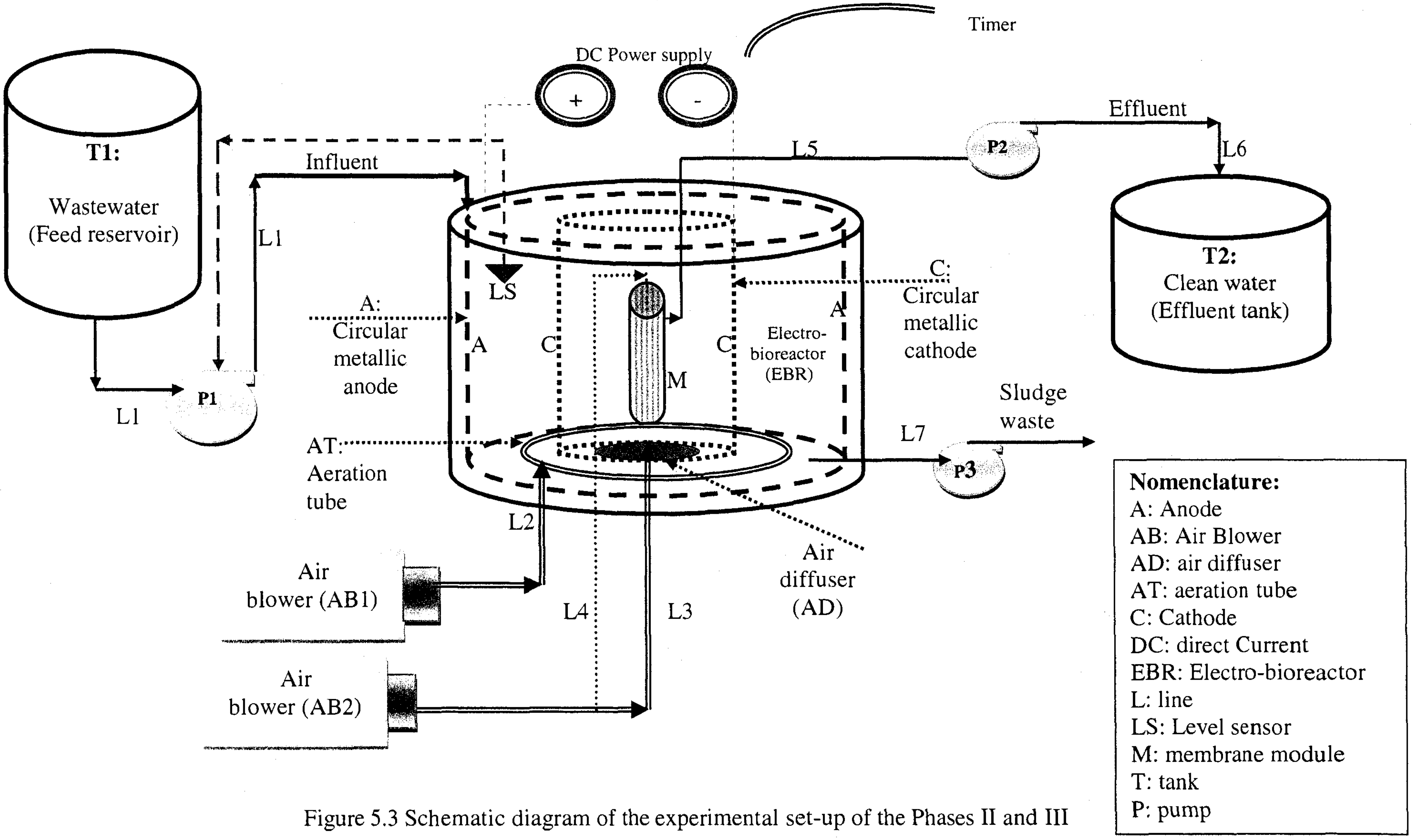


Figure 5.3 Schematic diagram of the experimental set-up of the Phases II and III

following major units: electro-bioreactor, membrane module, wastewater supply system, aeration system, and DC supply system.

5.2.2.1 Electro-Bioreactor

The electro-bioreactor (EBR) is the main unit in the SMEBR system in which different treatment processes taking place. The electro-bioreactor consisted of the following components:

- **Plastic Tank**

A plastic cylindrical tank was used in this research wastewater treatment. The tank had a total volume of 20 L, height of 460 mm inside diameter at the top of 284 mm, and at the bottom of 240 mm. The working volume of the tank when all modules were included found to be = 13.43 L.

- **Electrodes**

Two cylindrical electrodes (anode (A) and cathode (C)) were used. The anode was made of iron mesh in the Phase II or perforated aluminum sheet in the Phase III while the cathode was made of iron mesh in both Phases II and III. The fixed distance between the electrodes was 5.5 cm in both phases. Due to differences in perforation of anodes, the iron anode had an effective surface area of 93 cm^2, while the aluminum anode had 234 cm^2 effective surface area. The cathode had 106 cm^2 effective surface area.

5.2.2.2 Membrane Module

Submerged hollow fiber membrane module (M) ZeeWeed-1(Zenon Environmental Inc., Ontario, Canada) was used in this research. The module specifications are summarized in Table 5.1.

Table 5.1 Characteristics of the membrane module used in the experimental work

Category	Characteristic
Membrane type	hollow fiber membrane (Polyethylene)
Total filtering area, [m^2]	0.047
Number of fibers	80
Length, [cm]	20
Hollow-fiber membrane diameter, [µm]	0.04
External diameter, [mm]	3.4

The membrane was fixed vertically in the centre of the electro-bioreactor and it was used to separate treated effluent from the mixed liquor in the electro-bioreactor.

As mentioned in Chapter 3, the selected design of the SMEBR system divides the electro-bioreactor into two main zones (Figure 3.3). The Zone I is extended from the wall of the electro-bioreactor to the cathode and the Zone II is extended from the cathode to the membrane module.

5.2.2.3 Supply System

- **Supply Reservoir**

Two tanks were used in the experimental work. The first tank is a feed tank (T1) which was used to store the prepared wastewater to supply the required feed for the bioreactor, and the second tank (T2) was used for collecting the effluent resulting from membrane filtration process. Both tanks were made of plastic and each tank had a total volume of 20 L.

- **Pumps**

Three (P1, P2, and P3) peristaltic pumps (Model: 13-876-2, Fisher Scientific, Canada) were used during the operation of the submerged membrane electro-bioreactor system. The first one was used as a feeding pump, the second one was used as a suction pump and the third pump was used to withdraw the MLSS solution from the electro-bioreactor for sampling purposes.

5.2.2.4 Aeration System

The system of aeration in the submerged membrane electro-bioreactor system consisted of three parts: the first part was a porous air diffuser (AD) which was installed just below the membrane module in the bottom center of the electro-bioreactor in the Zone I; the diffuser supplied air continuously with the help of air blower (AB) to maintain the required dissolved oxygen level (>5 mg/L). The supplied air also agitated the sludge and helped in reducing the sludge solids attached to the membrane surface in the Zone I.

The second component of the aeration system was a perforated air tube (AT) which was also used to supply air stream for maintaining the required dissolved oxygen level (>5 mg/L) in the Zone II. The air tube was installed in the Zone II in the middle distance between the anode and the cathode. The supplied air also agitates the sludge in the Zone II.

The third component of the aeration system was pumped through the membrane module as described by the manufacture to reduce fouling and cake formation.

5.2.2.5 DC Supply System

- **DC Power Supply**

Electrodes in the electro-bioreactor were connected to a digital external DC power supply (TES 6230, 0-30 V, 0-3 A). Two digital multi meters were used to measure the current and the applied potential.

- **Timer**

Timer model 5500 (Control Company, USA) was connected with the DC power supply to regulate the operating mode of the applied DC field.

- **Level Sensor**

Level sensor (LS) was connected with the feeding pump to control the level in the electro-bioreactor at the desired level for maintaining a constant volume in the electro-bioreactor.

5.3 Wastewater

5.3.1 Wastewater Characteristics

In this study, synthetic wastewater was used as influent to maintain the consistency of the wastewater compositions during the experimental period. The composition of synthetic wastewater is shown in Table 5.2. The synthetic substrate was mainly consisting of glucose, peptone, and yeast extract. In addition to that, other chemicals were added to the synthetic wastewater to provide the required inorganic and micronutrients, as well as nitrogen and phosphorous for the development of the biomass growth. The synthetic wastewater was prepared using tap water. About 40 L of synthetic wastewater was prepared once per week. Table 5.3 shows the compositions of the biochemical parameters resulted from the preparation of the synthetic wastewater.

Table 5.2 Composition of the synthetic wastewater

Compound	Chemical formula	Molecular weight [g/mol]	Concentration Solution [mg/L]
Glucose	$C_6H_{12}O_6$	180.0	310
Peptone	-	-	252
Yeast extract	-	-	300
Ammonium sulfate	$(NH_4)_2SO_4$	132.1	200
Potassium phosphate	KH_2PO_4	136.1	37
Magnesium sulfate	$MgSO_4.7H_2O$	246.5	40
Manganese Sulfate monohydrate	$MnSO_4.H_2O$	169.02	4.5
Iron (III) chloride hexahydrate	$FeCl_3.6H_2O$	270.29	0.4
Calcium chloride	$CaCl_2.2H_2O$	147.0	4
Potassium chloride	KCl	74.55	25
Sodium bicarbonate	$NaHCO_3$	83	25

5.3.2 Cultivation of Activated Sludge

The fill-and-draw technique described by Chang et al. (1999) was used to cultivate the activated sludge. Activated sludge mixed liquor supplied to this purpose was sampled from secondary clarifier in the municipal wastewater treatment plant, in Saint-Hyacinthe (QC, Canada). The initial properties are listed in Table 5.4.

Table 5.3 Characteristics of the prepared synthetic wastewater

Items	Range
Average COD, [mg/L]	280- 410
Ammonia-nitrogen, [mg/L]	25-55
Nitrate, [mg/L]	<0.05
Nitrite, [mg/L]	not detected
Phosphorus, [mg/L]	19-31

Table 5.4 Properties of activated sludge mixed liquor samples used to acclimatize experimental wastewater

Items	Range
MLSS, [mg/L]	3400
pH	6.78-7.78
Zeta Potential,[mV]	- 32.2
Oxidation-Reduction-Potential, ORP, [mV]	6-8
Supernatant COD, [mg/L]	85
Supernatant ammonia-nitrogen, [mg/L]	25
Supernatant nitrate, [mg/L]	<0.05
Supernatant nitrite, [mg/L]	not detected
Supernatant phosphorus, [mg/L]	47.2

Sludge was allowed to settle for 30 minutes and the supernatant was withdrawn and discarded. Then, the reactor was refilled with fresh feed solution (synthetic wastewater) and aeration was started. These fill-and-draw processes were repeated every

12 or 24 hours. Aeration and mixing were provided through a porous air diffuser. An activated sludge had been acclimated to this synthetic wastewater for two months to achieve stable conditions prior to the experimental tests.

5.4 Description of the SMEBR Operation

Referring to Figure 5.3, after preparing the synthetic wastewater as shown in Table 5.2, the wastewater was stored in feed tank (T1) and was pumped through line (L1) via peristaltic pump (P1) to the electro-bioreactor (EBR). Supplying of wastewater from the feed tank was across the anode (A) toward Zone I.

Inside the Electro-bioreactor; and throughout Zone I, two wastewater treatment processes should be done: biological and electrochemical treatment (Chapter 3). In the Zone II, membrane filtration process took place to separate liquid from solid.

Air stream was supplied to the electro-bioreactor through line (L2) via air blower (AB1) and through line (L3) via air blower (AB2). Air was used in the SMEBR system for three main reasons: i) to supply sufficient oxygen for the microorganism to achieve the biological process, ii) it was used to reduce the fouling rate at the membrane module, and iii) it was used to make agitation for the mixed liquor solution in the electro-bioreactor's zones.

The air stream from line (L2) was used to supply air to the Zone I in the electro-bioreactor through the aeration tube (AT) while the air stream from line (L3) was used to supply air to the Zone II in the electro-bioreactor through the air diffuser (AD) which was fixed directly under the membrane module (M). Air bubbles will transfer from the bottom toward the top of the reactor. The third stream of air (L4) was pumped thought the top of membrane module as described by the manufacture to help in reducing fouling on the membrane module (M).

The treated water was withdrawn thorough line (L5) via peristaltic pump (P2) and thought line (L6) to permeate tank (T2).

For sampling purposes, the mixed liquor solution was withdrawn from the electro-bioreactor's zones thorough line (L7) via peristaltic pump (P4).

The DC power supply was used to supply the required voltage for the process through connection DC Power supply with the immersed electrodes (anode (A) and cathode (C)) in the electro-bioreactor. The DC power supply was connected with timer to regulate the exposure time of DC field.

5.5 Sampling Methodologies

All the description of sampling methodology in this section is related to the Phases II and III of this research. The sampling methodology related to the Phase I was described in the section of the experimental work in Chapter 6.

To properly monitor the SMEBR system performance, samples from the influent, bioreactor's zones and the effluent were taken regularly on a daily base during the periods of operation to analyze for specific parameters. Influent and effluent samples were taken as grab samples at the same time as the MLSS solution form the electro-bioreactor's zones. As for the MLSS and MLVSS concentrations in the electro-bioreactor, their values were calculated as the average concentrations in the electro-bioreactor's zones.

The influent and the effluent were sampled daily and analyzed for total COD, ammonia nitrogen (NH_3–N), nitrate nitrogen (NO_3–N), nitrite nitrogen (NO_2–N) and orthophosphate (PO_4-P). Each sample was analyzed four times with a standard deviation 1%- 5% for COD, 3%- 6% for (NH_3–N) and (NO_3–N), and 1 % - 3% for (PO_4-P).

Biomass samples were withdrawn from the electro-bioreactor daily and analyzed for MLSS and MLVSS according to Standard Methods (APHA, 1998).

The COD concentration was analyzed using a UV-Vis spectrophotometer instrument. Ammonia nitrogen (NH_3–N), nitrate nitrogen (NO_3–N), nitrite nitrogen (NO_2–N) and orthophosphate (PO4-P) concentrations were analyzed using Hach Digestion Vials (Hach, DR 2800, USA).

The dissolved oxygen (DO) concentration was measured using a DO meter (YSI, Model 52, USA). The values of pH and temperature were measured using a pH meter model 215 (Denver Instrument, USA). Calibration of pH, and DO meters were conducted once a day before use and the room temperature (20 ± 1 ^{o}C) was set as default temperature.

Influent samples were filtered before analysis to remove any suspended solid materials. Effluent samples were analyzed without any pre-treatment. Samples from the bioreactor's zones were filtered with 0.45 mm filter paper. The deposit solids on the paper were used for the MLSS and the MLVSS measurements and the filtrate was taken for measuring organic and nutrients parameters in the supernatant.

One sample (50 mL) from the mixed liquor was taken daily from each zone in the electro-bioreactor and the supernatant was taken for zeta potential measurement after settling the mixed liquor for 30 minutes. The sample was measured ten times and the average value was taken as zeta potential with a standard deviation 2 %- 6%. To decrease the amount of sludge lost from the electro-bioreactor, the sample was returned back to the electro-bioreactor after taking the measurement.

About 100 mL were sampled form each zone of the elector-bioreactor for the specific resistance to filtration (SRF) tests. In order to minimize in the waste sludge from the electro-reactor in Phases II and III, the SRF tests were determined every 10 days during the operation process of each phase.

To measure the oxygen uptake rates (OUR) in the Phases II and III, about 250 mL were sampled form each zone and the samples were returned back immediately to the elector-bioreactor's zones after finishing the OUR measurements. The OUR was measured by using a YSI DO meter, Model 52 and a DO probe inserted into the sample bottle, which was tightly sealed to prevent oxygen transfer from the outside. The decrease in DO concentration with respect to time was recorded and the slope of the concentration versus time plot gave the oxygen uptake rate.

The value of the OUR was used to calculate the specific oxygen uptake rate (SOUR) from equation (4.32). The OUR tests were determined every 2 days during the operation process of each phase.

5.6 Analytical Methods

As mentioned in section 5.1, different physiochemical and biochemical parameters were analyzed in this research to assess the performance of the SMEBR system. Table 5.5 summarizes the measured parameters and the methodology that has been followed up to analyze or measure each parameter. Detailed description of analyzing and measuring each parameter were described in Appendix A.

Table 5.5 Measured parameters and analytical methodologies

Parameter	Methods
COD	Digestion vials and then UV-Vis Spectrophotometer instrument
Phosphorous as orthophosphate (PO_4-P)	Hach method (Hach, DR 2800, USA, Method 8178)
Ammonia nitrogen (NH_3–N)	Hach digestion vials (Hach, DR 2800, USA, Method 10031)
Nitrate nitrogen (NO_3–N)	Hach method (Hach, DR 2800, USA, Method 8192)
Nitrite nitrogen (NO_2–N)	Hach digestion vials (Hach, DR 2800, USA, Method 839).
MLSS, MLVSS	According to Standard Methods APHA (1998)
Specific resistance to filtration (SRF)	Vacuum filtration apparatus (Buchner funnel test)
Zeta potential	Zeta meter analyzer (Zeta meter 3.0 $^+$, USA)
Dissolved oxygen (DO)	DO meter (YSI, Model 52, USA)
OUR, SOUR	DO meter (YSI, Model 52, USA), sealed bottle
pH, ORP and temperature	Denver instrument, pH meter model 215, USA

Chapter 6

Phase I: Preliminary Investigations

6.1 Summary

This chapter presents Phase I of the experimental work which highlights the effect of electrocoagulation phenomenon on activated sludge mixed liquor by applying direct current (DC) fields. The main objective of this phase was to generate information on the changes of the physiochemical properties (pH, oxidation-reduction potential (ORP), specific resistance to filtration (SRF), temperature and the concentration of the mixed liquor suspended solids) and biochemical proprieties (COD, nutrients) of the mixed liquor activated sludge when it is exposed to different DC fields.

The experimental work of this phase was divided into two stages. In the Stage I, 200 ml of MLSS samples exposed to voltage gradient of 0, 1, 2, 4, and 6 V/cm were evaluated. This experiment was carried out for 15 and 30 minutes of DC exposure time with and without air effect. Based on the results from the Stage I, a voltage of 1 V/cm was found to be the best and it was selected for the Stage II in which 1000 mL MLSS sample was used in the same batch electro-bioreactor during 6 h of operating time to optimize the best mode of operation in terms of DC interrupting supply.

The results from the Phase I showed that the applying DC into mixed liquor suspended culture did have significant change in pH and ORP at both cathode and anode in batch experiments and the effect was more significant at high voltage levels (4 and 6 V/cm). An injection of air stream reduced the pH effect at anode. The COD was monitored to assess potential inhibitory/stimulating conditions of electrical field on COD removal in an aerobic suspended culture. It was found that low voltage gradient (1V/cm) did not have a significant impact on COD reduction; the COD removal efficiency was 15 % and 18 % for 15 minutes and 30 minutes of DC exposure time respectively. Exposure the MLSS solution to moderate voltage of 2 V/cm increased the COD removal efficiency to 25 % and 36 % for 15 minutes and 30 minutes of DC exposure time respectively. The aeration showed little effect on the COD removal efficiency during the proposed time. However, when the MLSS solution exposed to high level of DC fields (i.e. 6 V/cm), the COD removal efficiency increased to 41 % and 76 % for 15 minutes and 30 minutes of DC exposure time respectively. Moreover, the results showed that DC fields can enhance the phosphorus removal up to 98.5 % while DC fields did not show positive impact on the ammonia-nitrogen removal.

The results showed also that applying DC field improved the size of the flocs in the mixed liquor solution and the size increased with increase of voltage. This was reflected directly on the filterability process of the solution by decreasing the specific resistance to filtration (SRF). The results showed that the SRF decreased at high voltage levels (between 4-6 V/cm). It was speculated that flocs building up on the anode material at this level of DC may decrease the efficiency of the electrocoagulation process on long operation time.

Three different modes of operation of DC were investigated in the Stage II as 15 minutes ON / 15 minutes OFF, 30 minutes ON / 30 minutes OFF and 15 minutes ON / 30 minutes OFF. The results showed that the mode of operation of 15 minutes ON / 30 minutes OFF of DC supply was the best mode for maintaining the pH in the mixed liquor solution within the range $5 \leq \text{pH} \leq 9$ during the 6 h of electro-bioreactor operation.

6.2 Introduction

According to the literature, Electrocoagulation (EC) Process has been investigated by many researchers as wastewater treatment method to remove organic pollutants (COD), nutrients (nitrogen and phosphorus) and suspended solids (SS). For example, Kurt et al. (2008) used EC process to treat domestic wastewater using iron-iron electrodes. They reported that the removal efficiency of COD and SS were over 60% and 70% respectively.

Bayramoglu et al. (2006) reported that the EC could be an effective method for the treatment of poultry slaughterhouse wastewater. In comparison with iron, they found that aluminum electrode performed better in reducing the COD, with a removal efficiency as 93% in 25 minutes at low initial pH such as 3 and current density of 150 A/m^2.

Yu et al. (2005) applied EC technology to reduce the residual of organic matter and phosphorous contained in secondary effluent. They combined bipolar iron electrodes with biofiltration system in their study. The combination system achieved 76.6-83.7% removal efficiency for COD and 70.7-93% for phosphorous.

In another study, Yu et al. (2006) reported that the use of an intermittently aerating bioreactor combined with electrocoagulation enhanced phosphorus removal in sewage treatment plants.

In order to run the SMEBR system in best operating conditions in terms of DC supply, it is important to optimize the electrical parameters and studying the effects of applying DC on activated sludge mixed liquor suspended culture.

Because the SMEBR system has been designed with working volume of 13.42 L, it was difficult to perform the experiments of the Phase I in the designed system, because that would consume large amount of the mixed liquor solution. Therefore, the experiments of the Phase I were achieved on a simulated small scale electro-bioreactor without using membrane module. The output results of this experimental phase served as inputs to the operation of the SMEBR system in the next experimental phases.

Applying direct electrical current (DC) filed into the mixed liquor suspended culture affects its physiochemical parameters as described in Chapter 4. Accordingly, measuring the changes of these parameters is of great importance to give indication of the impact of the applied DC on these parameters. In the Phase I of this research, the following physiochemical parameters were under investigation:

- The pH and the ORP in the mixed liquor culture after introducing a DC;
- Temperature of the mixed liquor culture after introducing a DC;
- Sludge specific resistance to filtration (SRF);
- MLSS, and MLVSS concentrations.

On the other hand, the impact of applying DC fields on the biochemical parameters (COD, nutrients) removal is also important to see the degree of contribution of removing these parameters by using EC process as integrated wastewater treatment method in the designed SMEBR system.

One of the objectives of the Phase I of this research was to investigate the expected contribution of using EC technology as an integrated wastewater treatment method in the designed SMEBR to reduce the concentration of COD and nutrients. Another objective of the experimental phase I was to select the best operation conditions in terms of the electrical parameters required to operate the SMEBR system in the Phases II and III of this research.

Therefore, this phase aimed to identify the best electrolysis condition in terms of the appropriate current density so as not to impede the biological treatment, and to determine the best exposure time of DC when electrolysis should be applied intermittently to the SMEBR system.

6.2.1 Theory of Electrocoagulation by Iron Electrodes

Section 4.3.2.1 of this thesis has already presented the theoretical background for electro-coagulation using iron.

6.3 Experimental Work

6.3.1 Experimental Set-up and Methodology

The experimental set-up of the Phase I is shown in Figure 5.2. The experimental procedure of the Phase I was divided into two stages (Figure 5.1). In the Stage I, batch experiments were done on mixed liquor suspended activated sludge culture. Stage II simulated the SMEBR system in which the batch experiments took 6 hrs of hydraulic retention time (HRT) with changing the operating mode of DC. The operating conditions for the two stages are shown in Table 6.1. Activated sludge mixed liquor supplied to the experiments was sampled from secondary clarifier in municipal wastewater treatment plant the city of Saint-Hyacinthe, Quebec, Canada. The initial properties of samples are listed in Table 5.4.

6.3.1.1 Stage I

In the Stage I, 200 mL of mixed liquor activated sludge were exposed to different DC fields (0, 1, 2, 4, and 6 V/cm) for 15 minutes of exposure time to DC.

Table 6.1 Experimental conditions of the Phase I

Items	Stage I	Stage II
DC [V/cm]	0,1,2,4,6	The best DC from the Stage I
DC exposure time [minute]	15 minutes, 30 minutes	Based on mode of operation
Operation mode OFF/ON [minutes]	All the experiments were run at continuous DC supply	Mode #1 15/15 Mode #2 30/30 Mode #3 15/30
DO in bioreactor [mg/L]	- Without air effect - With air effect (3-5 mg/L)	3-5
Temperature [^{o}C]	Ambient temperature (19-21)	Ambient temperature (19-21)

The same procedure was repeated for 30 minutes of DC exposure time. At the end of each test, two samples were taken, one closed directly to the anode and the other closed directly to the cathode (around 2 mm). The values of pH, ORP, and temperature were measured for each sample. Then the remaining sample in the electro-bioreactor was used to measure the specific resistance to filtration (SRF). The experimental set-up for measuring SRF is shown in Appendix A (Figure A.1). The filtrate was taken to measure the overall concentrations of COD, ammonia nitrogen (NH_3–N) and orthophosphate (PO_4-P) in supernatant.

To study the effect of aeration, the above procedure was repeated by blowing air to the electro-bioreactor throughout the plastic tube.

6.3.1.2 Stage II

In the Stage II, the electro-bioreactor with 1000 mL MLSS sample was exposed to the best operating condition of DC fields obtained from the Stage I. The purpose of this stage was to simulate possible conditions in the SMEBR system for hydraulic retention time operation and aeration effect.

The output of this stage provided the suitable mode of operation in SMEBR system in terms of DC power supply. The value of pH (such range between 6 and 9) was selected as a key parameter to optimize the best mode of operation.

6.3.2 Analytical Methods

During the experiments, it was noted that the activated sludge tended to create biological film on the surface of electrodes especially at high voltage. Therefore, MLSS and MLVSS measurements would not provide a realistic impact of applying DC fields. It was decided to use biochemical indicators (COD, NH_3-N and PO_4-P) as indication of the overall efficiency.

Samples of filtrate from each filterability test were filtered again through a 0.45 µm-pore-size membrane filter (Isopore, Millipore) prior to water quality measurement. The concentrations of COD, ammonia nitrogen (NH_3–N) and orthophosphate (PO_4-P) were determined using the analytical methods described in Chapter 5 and Appendix A.

The dissolved oxygen (DO) concentration was measured using the DO meter (YSI, Model 52, USA). The values of pH, ORP and temperature were measured using a pH meter model 215 (Denver Instrument, USA).

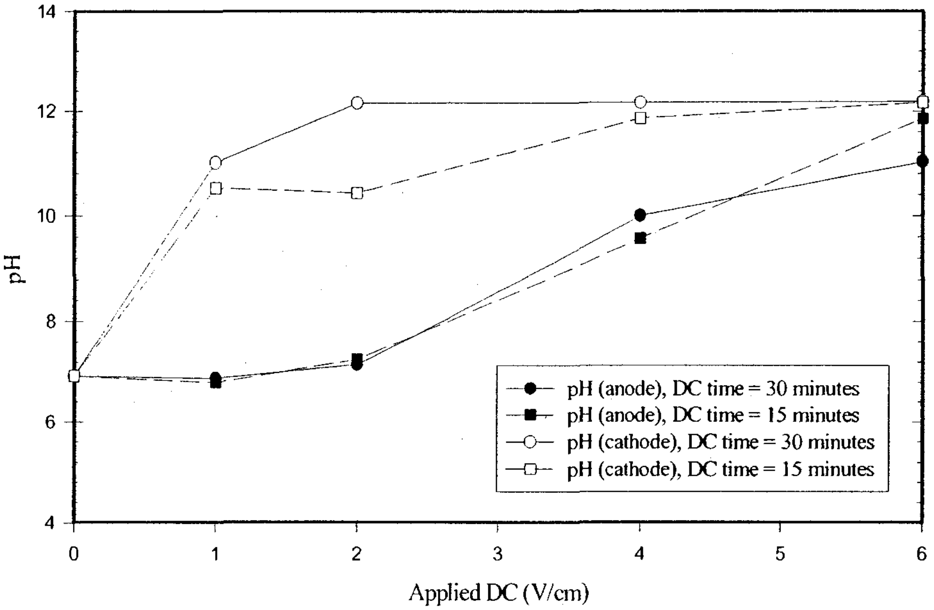
The specific resistance to filtration (SRF) was determined by the same procedure described in Appendix A.

6.4 Results and Discussion

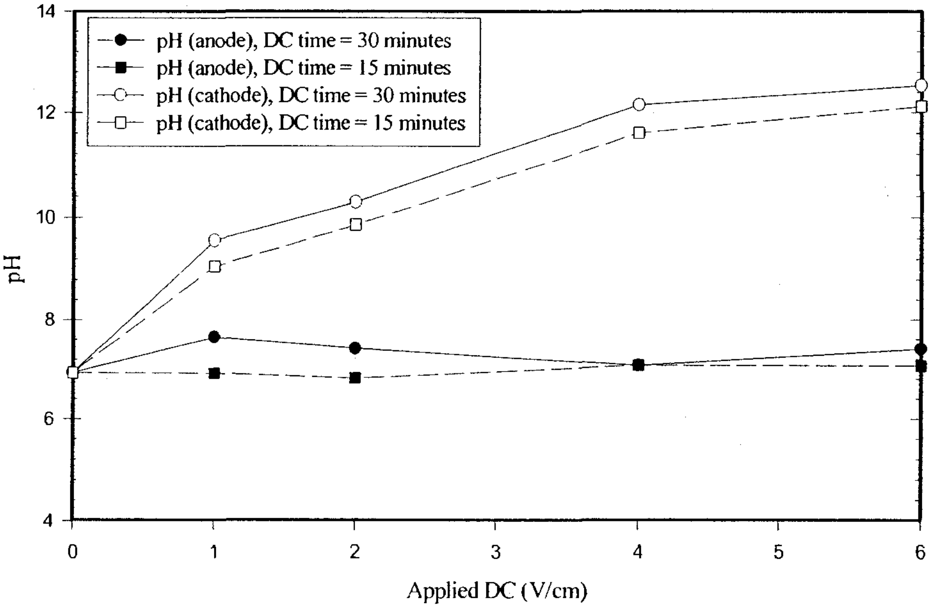
6.4.1 Results of the Stage I

6.4.1.1 Changes of pH, ORP and Temperature

Figures 6.1 and 6.2 show respectively, the effects of applying voltage gradient on pH and ORP of the solution closed to the electrodes. The effects of exposure time to DC (electrocoagulation time) and aeration are shown also in the same figures.

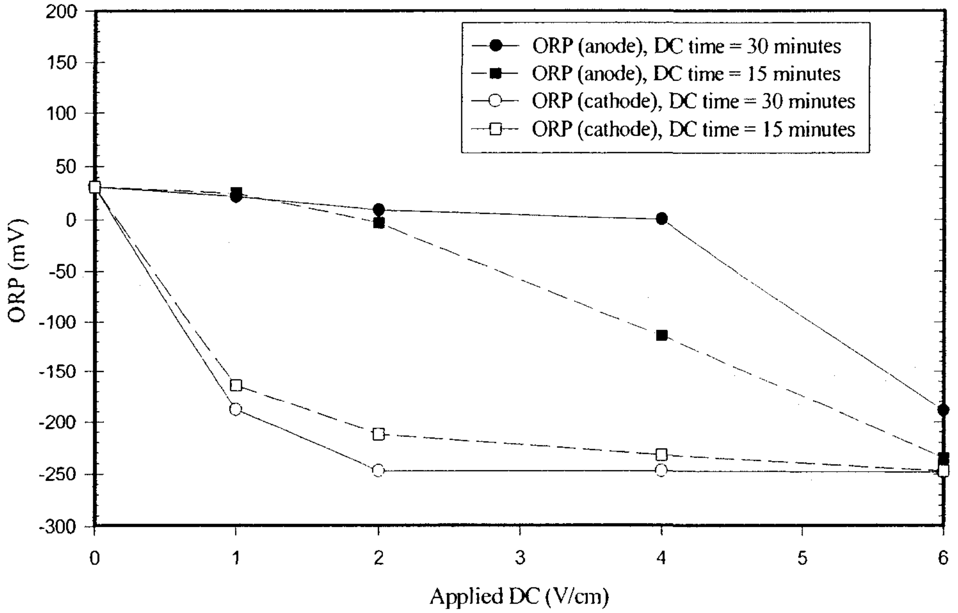


(a) Without air effect

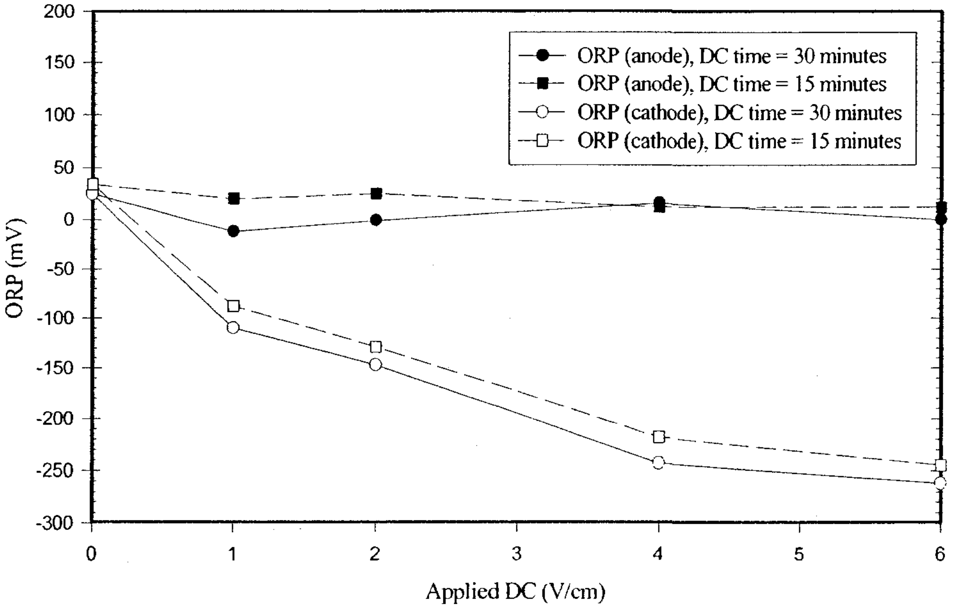


(b) With air effect

Figure 6.1 Changes of pH at electrodes with DC fields: (a) without air effect; (b) with air effect



(a) Without air effect



(b) With air effect

Figure 6.2 Changes of ORP at electrodes with DC fields: (a) without air effect; (b) with air effect

Apparently, Figure 6.1 shows that the pH at the cathode increases with increasing in the applied DC fields due to OH^- ions releasing associated by hydrogen gas evaluation, which could be understood from the rodex reaction which takes place at the cathode (Equation 4.17). On the other side, the pH at the anode did not decrease as it was expected according to Equation 4.19 due the production of hydrogen ions (H^+). This means that the cathode activity was more dominant in this type of treatment. The same result was reported in the study conducted by Kurt et al. (2008) on the treatment of domestic wastewater by EC using iron-iron electrodes.

Furthermore, Figure 6.1 shows that the pH increased also at the anode with increasing in the applied DC fields when the electrochemical reactions were without air effect. This could be attributed to the motion of the particles in the solution from the cathode side toward the anode side by electrophoresis forces. These particles when they came in contact with the acidic particles at the anode, they reduced the degree of acidity and increased the pH around anode. At higher level of the applied DC fields through the solution, the electrophoresis forces increases and the particles transferred faster toward the anode to the point at which the pH at the anode closed to the pH at the cathode at DC = 6 V/cm. This phenomenon might be enhanced by formation a white froth around the cathode resulting from blubbing gases which indicated the hydrogen gas production according to Equations (4.17) and (4.18). This white froth expanded to the anode and made an increase in pH as shown in Figure 6.1. Increasing the exposure time of the mixed liquor solution to DC increased the pH at the cathode also, while the effect on the anode had less effect.

The effect of aeration is observed clearly through Figure 6.1(b). Blowing air stream through the mixed liquor decreased the pH at the cathode at low level of DC fields, but at the higher level, the effect of aeration was negligible.

The effect of aeration on the anode side was more obvious. Blowing air flow rate reduced the pH at the anode significantly. It should be mentioned here that the direction of air flow was perpendicular to the length of the cathode and it flowed through the perforated plastic tube toward to the perforated cathode and then toward the bulk solutions. This arrangement in the electro-bioreactor might explain why the pH at the anode was almost neutral after applying aeration into the MLSS solution.

The ORP data verifying the redox potential of the solution in mV has been shown in Figure 6.2. The ORP decreased with increase in the applied voltage gradient means that the treated solution became more and more reductive owing to the presence of dissolved iron ions in the solution. The same conclusion was reported by Kurt et al. (2008). A dependent relationship was observed between the ORP data presented in Figure 6.2 and the pH data presented in Figure 6.1. Increasing in the pH associated with a decrease in the ORP.

With respect to the temperature, the measured data did not record significant changes in temperature close to the cathode and the anode. The temperature was close to the ambient temperature (20 ± 1 ^{o}C) during all the experiments. It was expected that temperature would increase by introducing DC fields through the solution as it was reported by Alsawabkeh et al. (2004). However, unchanged temperatures could be attributed to the relatively short exposure time to DC.

6.4.1.2 Change of Specific Resistance to Filtration

As it was mentioned in Chapter 4, sludge specific resistance to filtration (SRF) is an index representing the filterability of mixed liquor when it is dewatered through filter medium.

The SRF can be used in this research to assess the effect of applying DC fields on mixed liquor activated sludge. In the following discussion, r_o represents the SRF of the original MLSS solution without aeration and when no DC was applied through the MLSS solution, while r is the specific resistance to filtration at a given DC field. All the measuring filtration resistances were compared with relative to the SRF of the original mixed liquor solution (r_o).

A change of (r/r_o) of mixed liquor samples with the applied DC fields is shown in Figure 6.3. Note that, at DC= 0 and when the MLSS solution aerated for 15 and 30 minutes, the specific filtration resistance increased by 4.5 % for 15 minutes and 7.4 % for 30 minutes which could be attributed to the decreased in the particle size of the flocs resulting from aeration (Sun at al., 2006). The effect of aeration on floc's particle size is illustrated in Figure 6.4.

After DC was applied, the SRF decreased by 9 % at 1 V/cm for 15 minutes of DC exposure time without air effect but the SRF decreased only 2 % with aeration which means that at lower level of DC, the aeration had more impact on microbial floc size. The SRF also decreased by 34% at 1 V/cm DC field when the DC exposure time increased to 30 minutes without air effect, but with air effect, the SRF decreased by 20% for 30 minutes of DC exposure time, which was attributed for the same reason discussed before.

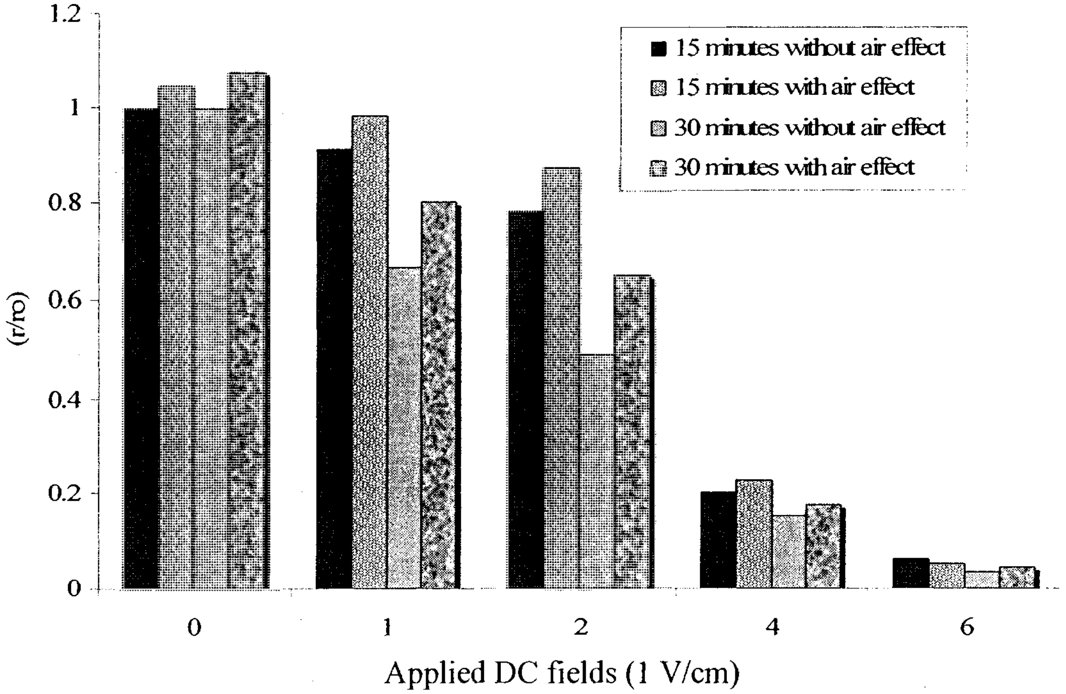


Figure 6.3 Change of the specific resistance to filtration of the MLSS solution

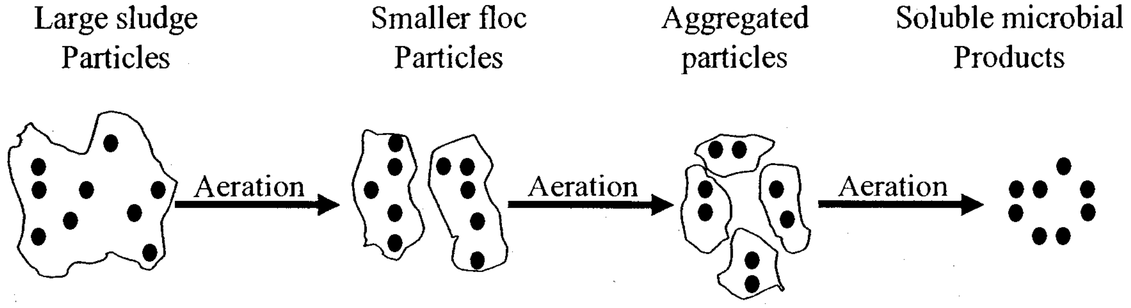


Figure 6.4 A schematic illustration of the effect of aeration on activated sludge (adapted from Sun et al., 2006)

When the applied DC filed increased to 2 V/cm, the SRF decreased by 22% for 15 minutes and 51% for 30 minutes of DC exposure time when there was no air effect. But with aeration effects the reduction in the SRF was 13% and 35% for 15 minutes and 30 minutes of DC exposure time respectively.

At higher level of DC and when the applied DC was 4 V/cm, the filterability increased sharply, (r/r_o) was between 0.13 and 0.23 corresponding to 77 % to 87% improvement in the mixed liquor filterability. Finally, the results showed that the value of (r/r_o) $\rightarrow$ 0 when the applied voltage was at 6 V/cm regardless the DC exposure time and the air effect. This implied a significant improvement in the filterability of the mixed liquor at high voltages. These results seem to be good if the objective of the process is to increase the filterability of the mixed liquor, but applying high voltage showed negative side effects on the process as a whole which are summarized by the following points:

- Increasing the applied DC fields thought the solution also produced a white froth around the cathode and this may cause negative effect on the overall performance of the SMEBR system if it is operated at high level of DC field.
- Increasing the applied DC fields to high levels (between 4-6 volts/cm) throughout the MLSS solution would increase the anode corrosion, and this was shown clearly for the samples taken from anode side in which a red and turbid color was observed (Figure 6.5).
- Increasing the applied DC fields (between 4 -6 V/cm) through the MLSS solution increased the floc size dramatically, and the floc started to build up with time on the anode. This could decrease the efficiency of the electrocoagulation process with time.

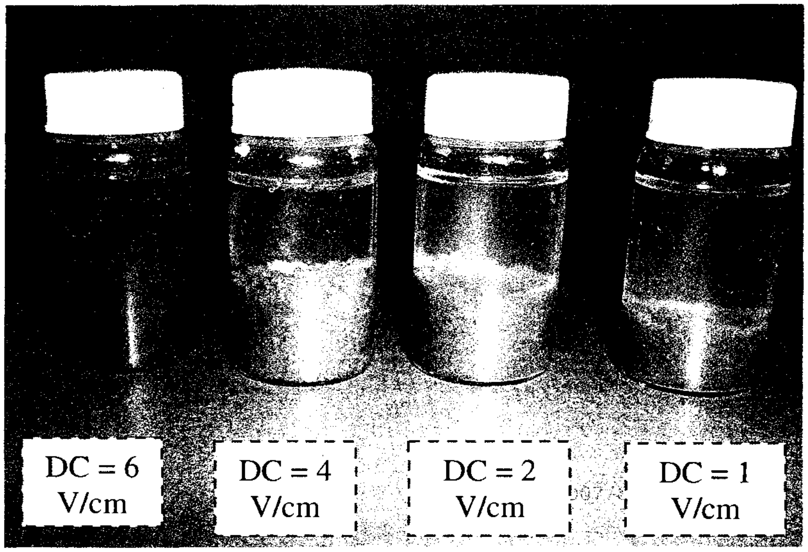


Figure 6.5 Samples closed to anode

As indicated before, the SRF as an indicator representing filterability of mixed liquor could be used to roughly evaluate the fouling rate during the membrane filtration process. Thus, it might be predicted from the above results that applying DC fields on mixed liquor solution will give a better effect on membrane fouling control in the submerged membrane electro-bioreactor system by increasing the floc sizes.

However, as it was mentioned previously, there were still some differences between filterability of mixed liquor and membrane fouling rate in the SMEBR operation. Therefore, the effect of applying DC fields on membrane fouling control will be further confirmed in the SMEBR system operation in the next phases.

6.4.1.3 Effects of EC on COD Removal

Figure 6.6 shows the percentage removal in COD concentration in the supernatant of the solution with applying DC electrical fields as it was measured as a function of DC exposure time (15 and 30 minutes) and aeration effect (2-5 mg/L). When the experiments were performed without air affect, Figure 6.6 shows that low level fields of 1V/cm did not have a significant impact on COD reduction and the COD removal efficiency was 15 % and 18 % for 15 minutes and 30 minutes respectively of DC exposure time. Exposure the MLSS solution to moderate level DC field of 2 V/cm increased the COD removal efficiency to 25 % and 36 % for 15 minutes and 30 minutes respectively. However, when the MLSS solution exposed to high level of DC fields (i.e. 6 V/cm), the COD removal efficiency increased up to 41 % and 76 % for 15 minutes and 30 minutes respectively. When air was introduced thought the electro-reactor, the same trend was observed for both periods of DC exposure time (15 and 30 minutes) but the aeration showed little effect on the COD removal efficiency during the proposed DC exposure time.

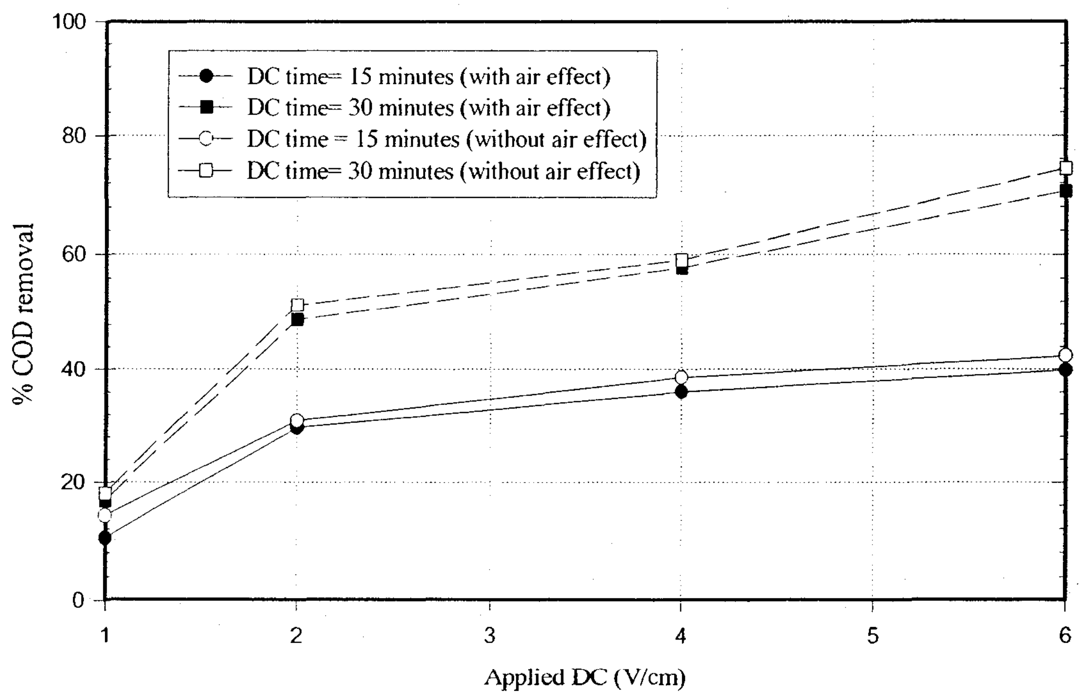


Figure 6.6 Percentage removal of the COD versus the applied DC fields

In summary, wastewater treatment by EC process involves two steps: destabilization and aggregation. The first step is usually short, whereas the second step is relatively long (Kobya et al., 2006). Destabilization and aggregation in EC process depends on two main parameters: DC exposure time and potential electrolysis (Zaroual et al., 2006). In the EC process, metal ions as destabilization agent are produced at the anode through electrochemical reactions. When the charge loading or the DC exposure time are low, the metal ion (M^{n+}) dosage is not sufficient to destabilize all colloidal and finely suspended particles, and thus the pollutant removal efficiency is not high.

The above description is in agreement with the results obtained for COD removal in the Stage I which is shown in Figure 6.6. The removal efficiency of COD in electrocoagulation process depends on the quantity of iron generated, which is related with DC exposure time and potential electrolysis as reported above. Then, when one of two parameters increases, the distribution of the coagulation agent density is more effective. This can produce the related coagulation and completes the removal of pollutants. Consequently, high removal efficiency of COD was observed at longer DC exposure time and high potential as shown in Figure 6.6. According to Murugananthan et al. (2004), at high potential, formation of Fe (III) ions is favorable. In a basic environment, simultaneous formations of ferric hydroxide/oxides are also expected. Precipitates of Fe(III) hydroxides thus formed have a coagulating character better than Fe(II) hydroxide, because $Fe(OH)_3$ is more stable than $Fe(OH)_2$ (Bagga et al., 2008), then, the removal efficiency increases. Generally, as it was mentioned in Chapter 4, the mechanism of electrocoagulation for wastewater treatment is very complex. The COD removal process may also involve electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment (Zaroual et al., 2006).

6.4.1.4 Effects of EC on Phosphorous Removal

Figure 6.7 shows the variation in the percentage of phosphorous removal from supernatant versus the applied voltage gradient. As expected, the results show that phosphorus removal efficiency increased by increasing of the applied voltage and DC exposure time. The reasonable explanation of this behavior is the same that described for COD removal in the previous section regarding of DC exposure time and applied voltages. The average concentration of total phosphorous in the original sample was 47.16 mg/L. Applying 1 V/ cm of DC results about 63-77 % uptake from the supernatant, and the percentage increased by increasing the applied voltage and it reached greater than 98 % at 6 V/cm of DC.

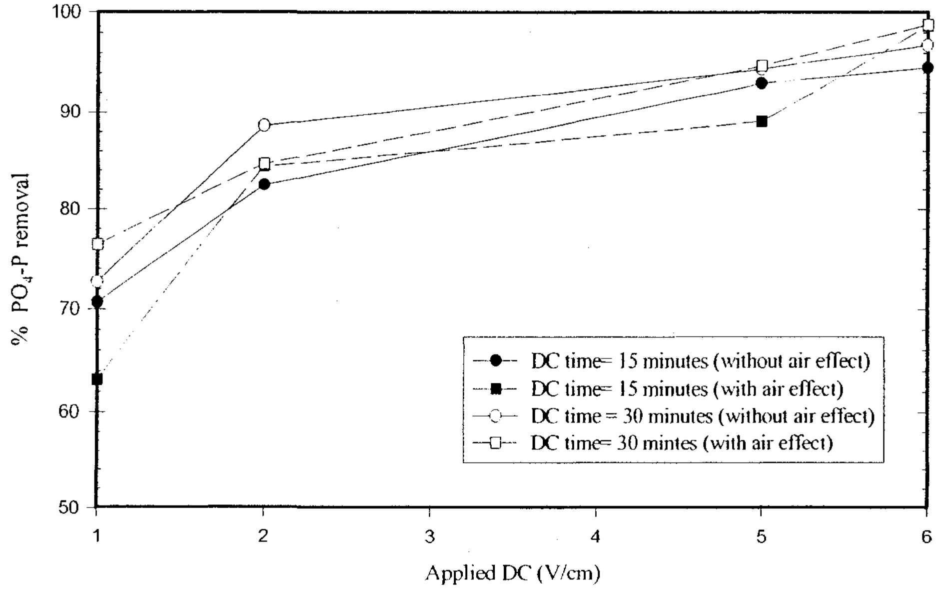


Figure 6.7 Percentage removal of the phousprous versus the applied DC fields

Introducing air through the solution showed small effect on the removal efficiency during the proposed DC exposure time. The mechanism of reducing phosphorus by EC process was explained by Yu et al. (2005). According to their study, the main reactions that may occur during the electrocoagulation are as follow:

- Reaction at anode:

$$Fe\ (s) \Longrightarrow Fe^{2+} + 2e^{-} \qquad (6.1)$$

- Reaction in the bulk solution:

$$Fe^{2+} + ½\ O_2 + ½\ H_2O \Longrightarrow Fe^{3+} + OH^{-} \qquad (6.2)$$

$$Fe^{3+}\ PO_4^{3-} \Longrightarrow FePO_4 \qquad (6.3)$$

Theoretically one Fe/ P molar ratio will be required if only the above main reactions occur (Yu. et. al., 2005). However $Fe(OH)_3$ is produced during the reactions and the actual Fe/P ratio will be different.

6.4.1.5 Effects of EC on Nitrogen Removal

The variations in the percentage reduction of ammonia nitrogen (NH_3–N) in the supernatant concentration after exposing the MLSS solutions to different DC fields are shown in Figure 6.8. The performance of NH_3–N removal was affected by the applied DC fields. Lower level of DC fields shows better removal of NH_3–N, while at high levels of DC fields, the percentage reduction decreased. This variation in the percentage reduction in NH_3–N concentration when exposed to DC field means that the nitrogen bacterium is very sensitive to DC field. The reasonable explanation of this behavior can be understood from the research reported by Lees et al. (2001) in which they suggested that accumulation of iron in activated sludge solution could give rise to the inhibitory effects on the activity of nitrifying bacteria.

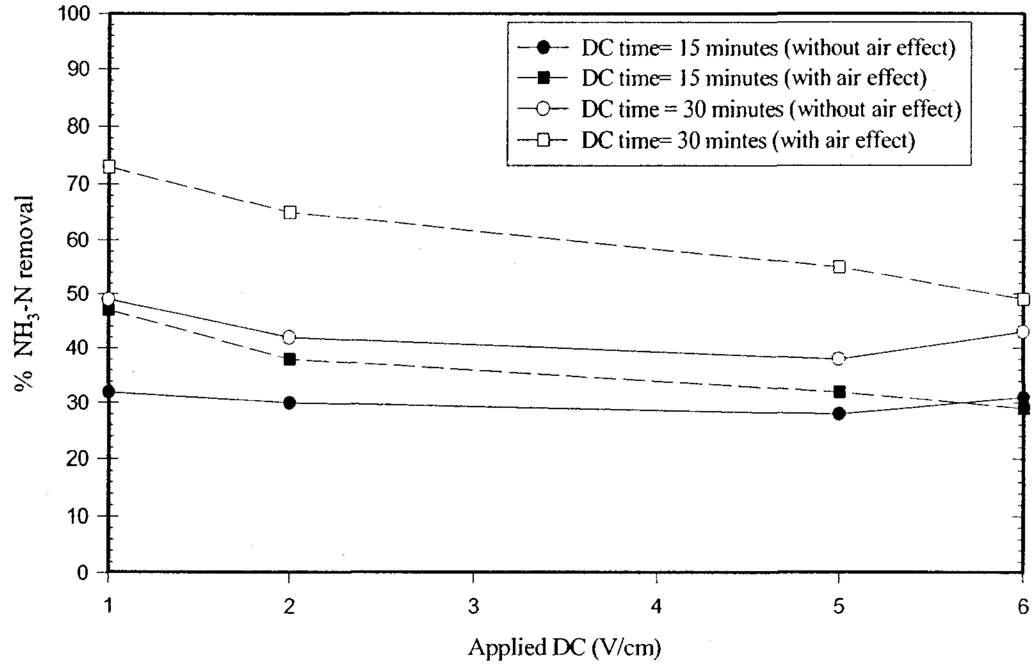


Figure 6.8 Percentage removal of ammonia-nitrogen versus the applied DC fields

6.4.1.6 Studying the Electrical Parameters

In wastewater treatment by EC technology, it is necessary to the study the variations in electrical parameters (current density, energy consumption, electrode material consumption).

Figure 6.9 shows how the current density expressed as A/m^2 varied with the applied voltages. It is apparently shown that the current density is linearly related to the applied voltage in the MLSS solution. For both the proposed DC exposure times, 15 and 30 minutes, and at lower level of the applied DC filed (i.e. < 2 V/cm), no significant difference was observed in the current density. While at higher DC fields (> 4 V/cm), the current density was relatively smaller for 30 minutes DC exposure time. This could be attributed to the changes occurred in electrical conductivity of the MLSS solution which is dependent on ionic content of the MLSS solution. A reasonable explanation for the decrease in current density when the DC exposure time increased is the increase occurred in electrical conductivity resulted from the increase in the ionic content of the MLSS solution (Alshawabkeh et al., 2004).

The experimental results did not show significant effects of the aeration on the change of the current density during the proposed DC exposure times.

The more important electrical parameters which affect economically the cost of the process of EC in wastewater treatment are the energy and electrode material consumptions. Calculation of energy consumption (E) is expressed as (Kobya et al., 2006):

$$E = \frac{U \times I \times t}{V} \tag{6.4}$$

Where E is the energy consumption (kWh/m^3 wastewater treated). U is applied voltage (V), I is the current (A), t is retention time (DC exposure time) (s) and V is the volume of the treated wastewater (m^3). On the other hand, the electrode consumption (m) having a unit of kg Fe/m^3 wastewater treated is calculated from Faraday's law in the following relation:

$$m = \frac{I \times t \times M}{Z \times F \times V} \tag{6.5}$$

Where M is the relative molar mass of the electrode concerned, Z the number of electrons in oxidation/reduction reaction, F the Faraday's constant, 96,500 (C/mol).

From the results shown in Figure 6.10, it is seen that the energy consumption per cubic meter of the treated wastewater remained approximately constant at lower level of DC fields which corresponds to lower current density as shown in Figure 6.9.

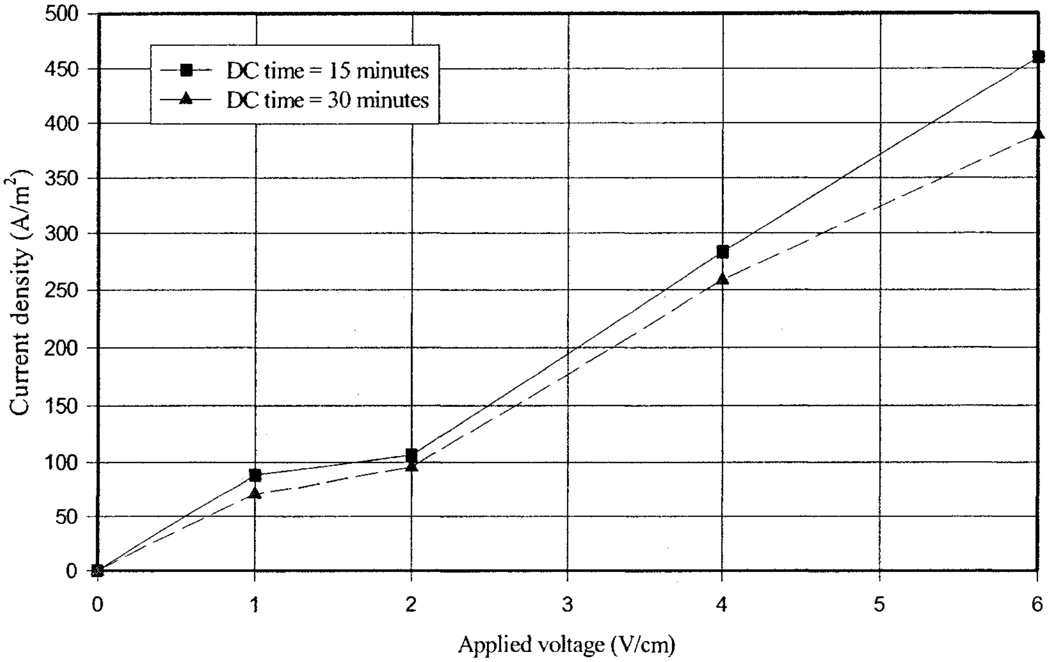


Figure 6.9 Changes of the current density with the applied voltage

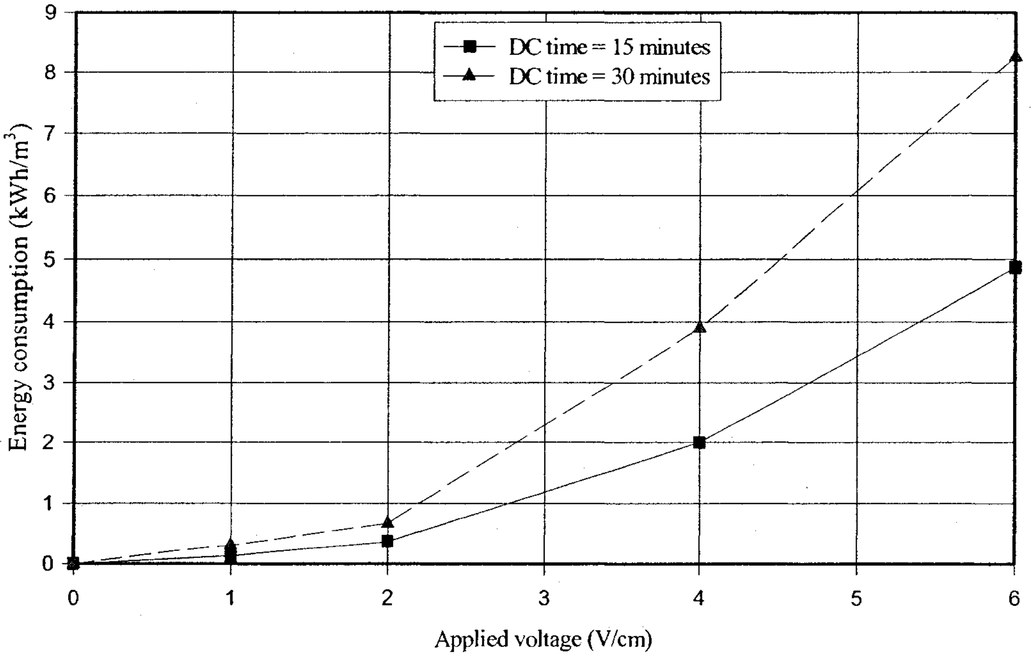


Figure 6.10 Changes of the energy consumption with the applied voltage

At higher level of the applied DC, a dramatic increase in energy consumption was observed. A similar behavior was previously observed by Holt et al. (2002).

The electrode consumption also has the same trend as the energy consumption as shown in Figure 6.11. In general, electrode consumption depends on the wastewater characteristics and operational conditions (Kobya et al., 2006), and the actual electrode consumption can be greater than the theoretical value.

It was reported that that DC exposure time is very important parameter which affects the economic applicability of EC process in wastewater treatment (Kobya et al., 2006). In the Stage I of the Phase I of this research, the effects of the DC exposure time were more obvious at high levels of current density which correspond to high levels of the applied voltages as shown in Figure 6.9.

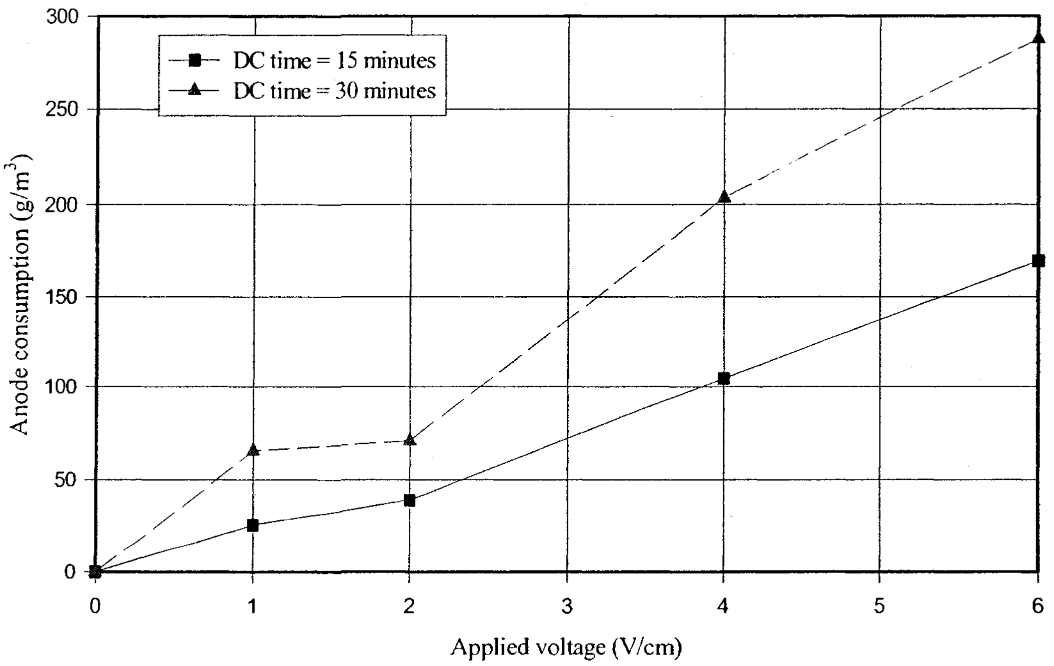


Figure 6.11 Changes of the anode consumption with the applied voltage

Figures 6.10 and 6.11 show that at high voltage levels (6 V/cm), both the energy and electrode consumptions were increased with increasing of DC exposure time. An increase in DC exposure time from 15 to 30 minutes caused an increase in energy consumption from 4.8 to 8.3 kWh/m^3, and an increase in electrode consumption from 170 to 280 g Fe/m^3 respectively.

6.4.2 Results of the Stage II

The main objective of the Stage II was to determine the best mode of operation of the DC in the submerged membrane electro-bioreactor system in the next experimental phases.

Determining the best mode to operate the SMEBR system was based on the considerations of choosing the suitable environmental conditions of the biological process so as the selected mode of supplying DC field would not impede the biological treatment process. Therefore, the value of the pH was selected as a guide parameter to optimize the best mode of operation for the SMEBR system in the next experimental phases. As reported by Alshawabkeh et al. (2004), the best range for the growth of microorganism culture is between pH = 5 and pH = 9. As shown in Figure 6.1, the pH at both electrodes increased with increasing the applied voltages gradient. However, in all the batch experiments conducted in the Stage I, the pH did not decreased below 5 at the anode. If pH=9 is chosen as the maximum allowable limit so as not to impede the biological treatment during the submerged membrane electro-bioreactor operation, the applied DC field should be less than 1.5 V/cm as shown in Figure 6.1.

To be on a safe side and to avoid all negative impacts demonstrated in the Stage I, the selected DC should be around 1 V/cm. Therefore, the DC of 1 V/cm was selected as the best DC field to operate in the submerged membrane electro-bioreactor system. Consequently, in the Stage II, the DC was fixed at 1V/cm and three different modes of operation of DC supply were investigated in different three cycles. Namely the operating modes in cycles I, II and III were: 15 minutes ON / 15 minutes OFF, 30 minutes ON / 30 minutes OFF, and 15 minutes ON / 30 minutes OFF respectively.

Figure 6.12 shows the trend in the pH values at the cathode and the anode of the operating mode of DC as 15 minutes ON / 15 minutes OFF. The pH at the cathode increased with time and exceeded pH 9 after 75 minutes of operation. The general trend of pH at the cathode was in increasing during the remaining operation. This was attributed to the relative short period between the EC time (15 minutes) and the time when the DC power supply was OFF (15 minutes).

Figure 6.13 shows the trend of the operating mode of 30 minutes ON / 30 minutes OFF. The pH at the cathode exceeded pH 9 before the first 30 minutes of DC time. Moreover, the trend of pH at the cathode was fluctuated upper the maximum limit of the target operation (pH= 9) during the operation period as it was observed for the previous operating mode (Figure 6.12) suggesting that theses modes were not suitable for the submerged membrane electro-bioreactor operation.

Therefore, the output results from Figures 6.12 and 6.13 did not satisfy the criteria to keep the pH values within the range 5<pH<9.

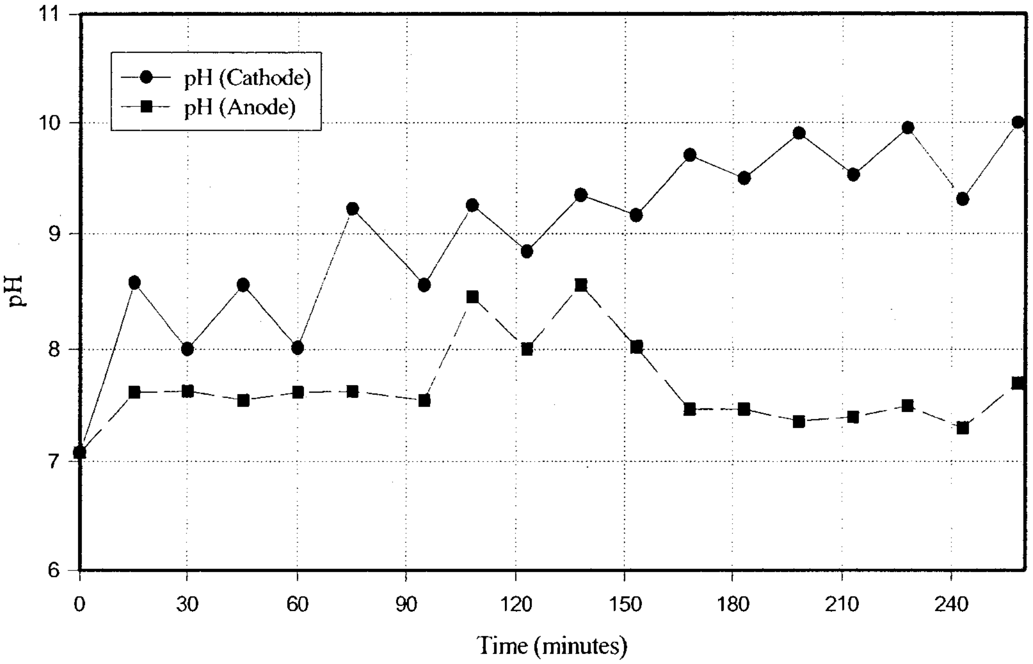


Figure 6.12 Change of the pH at electrodes during the Stage II of the Phase I
(Operating mode of 15 min. ON / 15 min. OFF)

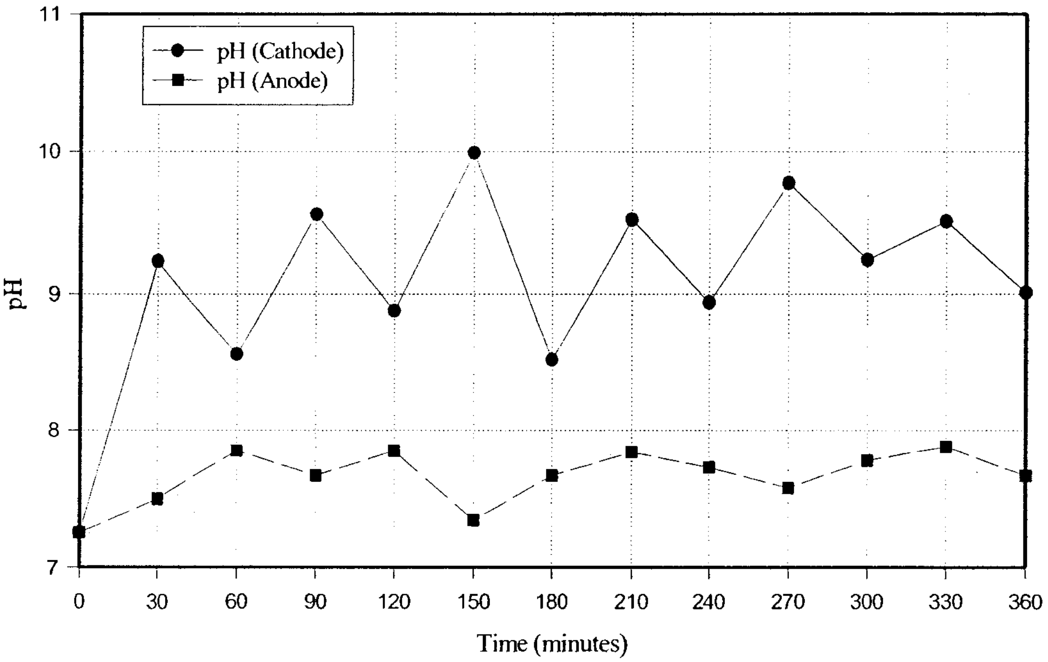


Figure 6.13 Change of the pH at electrodes during the Stage II of the Phase I
(Operating mode of 30 min. ON / 30 min. OFF)

When the operating mode was adjusted to be as 15 minutes ON / 30 minutes OFF in the third cycle, the pH value at the cathode exceeded the pH 9 after 250 minutes of operation as shown in Figure 6.14 which indicated that the operating mode presented in Figure 6.14 is the best among the investigated operating modes. This might be due to the fact that the DC time was 15 minutes while the time when the DC power supply was OFF was 30 minutes which gave much time of the pH of the mixed suspension culture to decrease with time.

The output results of the Stage II suggest that the operating mode of DC is a significant parameter in choosing the best operating time for the designed SMEBR system.

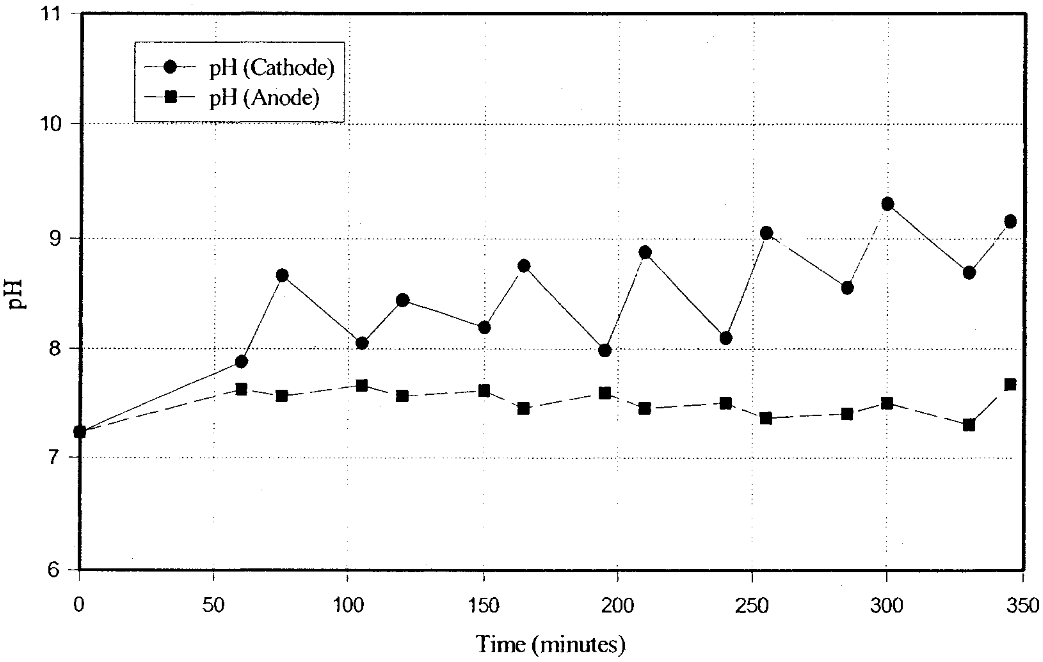


Figure 6.14 Change of the pH at electrodes during the Stage II of the Phase I (Operating mode of 15 min. ON / 30 min. OFF)

In the Stage II of this Phase, the retention time in the electro-bioreactor was 6 h which might simulate the hydraulic retention time in the designed SMEBR system. Because the operation HRT in the designed submerged membrane electro-bioreactor system might exceed 6 h, it was recommended to increase the time when the DC power supply is OFF to 45 minutes. Therefore it is recommended to operate the designed SMEBR system with 15 minutes ON / 45 OFF in during the next experimental phases.

6.5 Conclusions and Recommendations

From the experiments presented in this chapter, the following conclusions and recommendations could be drawn:

- Applying direct current (DC) electrical fields improved the floc size of the mixed liquor which was reflected directly on the filterability of the MLSS solution by decreasing the specific resistance to filtration. As the DC increases the flocs size increase and the SRF deceases.
- The results showed that the DC fields could improve the COD reduction of the mixed liquor in the reactor, but this depends on the applied DC density and the DC exposure time.
- The results showed that the DC fields could improve the phosphorus reduction of the mixed liquor in the reactor. Even a low voltage gradient is applied; phosphorus removal has shown good performance with increase in the DC exposure time.
- Although the high values of DC could increase the floc size rapidly, negative side effects were observed as building up of the floc on the anode which may reduce

the efficiency of DC with time by forming a cover layer on the anode material, also applying high levels of DC fields associated with rapid increase in the corrosion of the anode.

- Applying DC fields showed insignificant contribution of the ammonia nitrogen removal from the mixed liquor suspended sludge culture.
- As the microorganism require optimum conditions in term of pH ($5 < pH < 9$), the best operating conditions for DC which was observed from the experiments of this experimental phase was at the lower value of voltages (DC< 1V/cm). It was noted that pH at the anode did not reduced to the critical value of pH=5.
- The operating mode of 15 minutes ON / 30 minutes OFF was found to be the best operating mode to keep the pH between the anode and the cathode within the range $5 < pH < 9$ for 6 hours of experimental retention time. However, to be on the safe side, it is recommended to use the mode to be 15 ON / 45 OFF minutes during the operating of the SMEBR system since the system may operate with higher HRT.
- Energy and electrode consumptions in EC process increased by increasing the electrocogulation time and the applied voltage. In the commercial application of EC process, these two parameters should be optimized from economical point of view.

Chapter 7

Phase II: Performance of the Submerged Membrane Electro-Bioreactor (SMEBR) System with Iron-Iron Electrodes

7.1 Summary

This chapter presents the Phase II of the experimental work for this thesis. It highlights the overall performance of the submerged membrane electro-bioreactor (SMEBR) system when cylindrical tube iron mesh was used as electrodes. To compare the effect of applying DC field on the physicochemical and biochemical properties of MLSS solution in the SMEBR system, the operation period of the Phase II was divided into two stages and expanded for 53 days. Stage I lasted 26 days and operated without applying a DC field. Stage II carried on for 27 days while intermediate operation of the DC field (15 minutes ON / 45 minutes OFF) was applied to the mixed liquor solution in the electro-bioreactor. The overall performance of the SMEBR system showed that the effluent after treatment of synthetic wastewater was on average: i) 96% efficient in removing COD; ii) 90% for the removal of ammonia nitrogen (NH_3-N) in the Stage I and 70 % in the Stage II; iii) 98% for the removal of phosphorous. The effluent had no color and no odor. Furthermore, applying DC enhanced the membrane filterability up to 16.6 % without any backwashing of the membrane module.

7.2 Introduction

As mentioned in Chapter 2, membrane filtration performance in the conventional submerged membrane bioreactors can be improved by increasing the floc particles size of the MLSS solution which can traditionally be achieved by adding chemical flocculation-coagulation agents for wastewater or directly to the MLSS solution in the bioreactor. One of the coagulants materials that can be added to MLSS solution is iron salts. Using iron salts in activated sludge processes as coagulants is well known method to improve the performance of the reactor (Philips et al., 2003).

In the submerged membrane bioreactors applications, few studies were found in the literature about using iron salts to improve the membrane filtration performance as mentioned in Chapter 2.

However, in all the previous studies, iron was added as a chemical compounds into the mixed liquor solution. Although the previous studies confirmed the good performance in the membrane filtration process in the conventional submerged membrane bioreactors applications, the impact of the addition of iron was not clear on other biochemical parameters and the addition of iron as a chemical coagulant might have caused negative side effects that were not clearly discussed in the literature.

The main objective of the Phase II of the experimental work was to investigate the performance of the designed SMEBR system by using iron cylindrical tubes as electrodes materials. This is the first time where iron was added to the mixed liquor using an electrochemical phenomenon to enhance the membrane filtration. Another objective for this phase was to show the impact of applying a DC field on the overall quantity and quality of wastewater using a novel designed SMEBR system.

7.3 Theory of Electrocoagulation (EC) by Iron Anode

In order to understand the different reaction mechanisms that may occur when iron is used as the electrodes in the designed SMEBR system, the theory of electrocoagulation by iron anode needs to be highlighted. In Chapter 4 of this thesis, a brief discussion about EC process by iron was presented. Because many phenomena may occur during the EC process by iron electrodes, the theory will be discussed to some extent in this Chapter.

Many researchers reported the reaction mechanisms that occur in electrocoagulation with iron (Moreno-Casillas et al., 2007; Daneshvar et al., 2004; Larue et al., 2003; Mollah et al., 2001). Among these, the description reported by Moreno-Casillas et al. (2007) was selected in this chapter because it highlights the mechanisms of different reactions at different pH together with a description of the solution's color changes.

The following main reactions occur in the EC cell at different pH values when iron is used as the electrode material (Moreno-Casillas et al., 2007):

- For pH < 4

At the Anode:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (7.1)$$

$$Fe \rightarrow Fe^{3+} + 3e^{-} \qquad (7.2)$$

At the Cathode:

$$2H + 2e^{-} \rightarrow H_2\,(g) \uparrow \qquad (7.3)$$

As electrochemistry depends on thermodynamic and kinetic parameters, EC can be considered as an accelerated corrosion process. The rate of reaction (7.3) will depend on the removal of $[H^{+}]$ via H_2 evolution. This reaction will occur fast for low pH values (strong acids) as can be observed in the plot of corrosion rate as a function of pH (Figure

7.1). For a weak acid the rate will depend on the pKa of the acid. Fe (II) and/or Fe (III) may react with the anion associated with the acid.

- For pH 4 < pH < 7

At the Anode, reactions (7.1) and (7.2) occur and iron also undergoes hydrolysis:

$$Fe + 6H_2O \rightarrow Fe\,(H_2O)_4(OH)_2(aq) + 2H^+ + 2e^- \qquad (7.4)$$

$$Fe + 6H_2O \rightarrow Fe\,(H_2O)_3(OH)\,3(aq) + 3H^+ + 3e^- \qquad (7.5)$$

Fe (III) hydroxide begins to precipitate flocs which develop a yellowish color.

$$Fe\,(H_2O)_3(OH)_3(aq) \rightarrow Fe\,(H_2O)_3(OH)_3(s) \qquad (7.6)$$

"Rust" may also be formed.

$$2Fe\,(H_2O)_3(OH)_3 \rightarrow Fe_2O_3\,(H_2O)_6 \qquad (7.7)$$

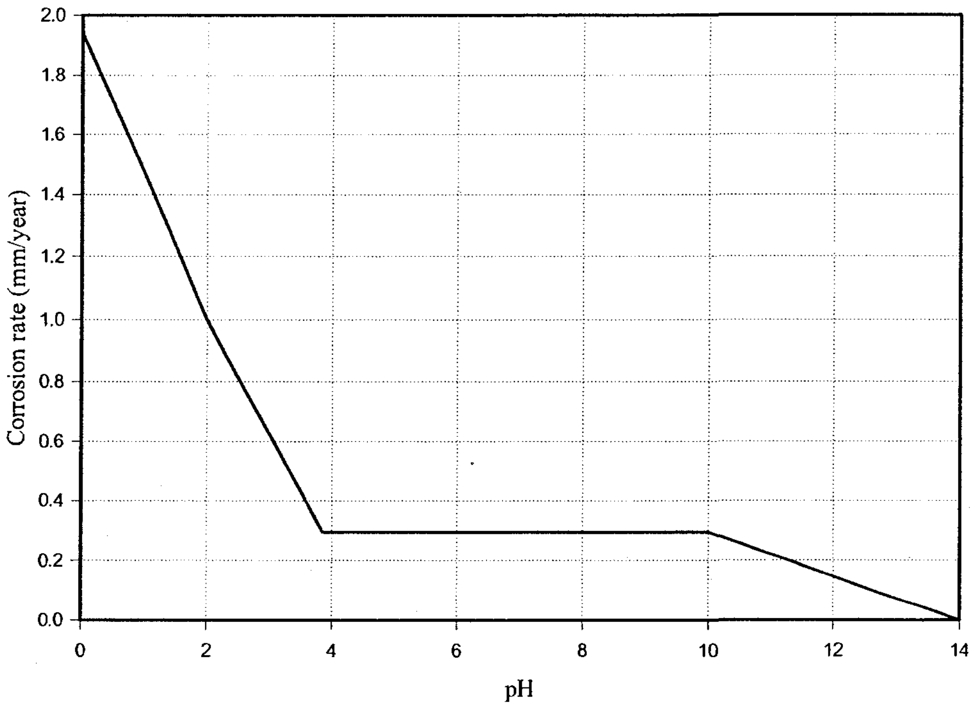


Figure 7.1 Corrosion rate of iron as a function of pH (adapted from Moreno-Casillas et al., 2007)

At the Cathode, (reaction (7.3) occurs):

$2H^+ + 2e^- \rightarrow H_2 (g) \uparrow$

More hydrogen evolution takes place but $[H^+]$ now comes from weak acids and iron hydrolysis.

- For pH $6 < pH < 9$

At the Anode, reactions (7.1) and (7.2) occur:

Precipitation of Fe (III) hydroxide (Equation 7.7) continues, and Fe (II) hydroxide precipitation also occurs represented by dark green flocs.

$Fe (H_2O)_4(OH)_2(aq) \rightarrow Fe (H_2O)_4(OH)_2(s)$ (7.8)

The pH for minimum solubility of $Fe (OH)_n$ is in the range of 7–8. EC flocs are formed due to the polymerization of iron oxy-hydroxides.

Formation of rust (dehydrated hydroxides) can be shown as the following (West, 1981):

$2Fe (OH)_3 \rightarrow Fe_2O_3 + 3H_2O$ (hematite, maghemite) (7.9)

$Fe (OH)_2 \rightarrow Foe + H_2O$ (7.10)

$2Fe (OH)_3 \rightarrow Fe (OH)_2 + Fe_3O4 + 4H_2O$ (magnetite) (7.11)

$Fe (OH)_3 \rightarrow Fe (OH) + H_2O$ (goethite, lepidocrocite) (7.12)

Hematite, maghemite, rust, magnetite, lepidocrocite and goethite have been identified as EC by-products by Parga et al. (2005) and Gomes et al. (2007).

At the Cathode, (reaction (7.3) occurs):

$2H^+ + 2e^- \rightarrow H_2 (g) \uparrow$

More hydrogen evolution takes place but $[H^+]$ now comes from iron hydrolysis and weak acids.

The overall reactions are:

$$Fe + 6H_2O \rightarrow Fe\,(H_2O)_4(OH)_2(s) + H_2\,(g)\uparrow \qquad (7.13)$$

$$Fe + 6H_2O \rightarrow Fe\,(H_2O)_3(OH)_3(s) + 1\,1/2H_2\,(g)\uparrow \qquad (7.14)$$

7.4 Experimental Set-up and Methodology

The experimental set-up for the Phase II is shown in Figure 5.3 and the operation process is described in details in Chapter 5 (section 5.4).

In Phase II of the experimental work, the SMEBR system was operated for 53 days with cylindrical tube mesh manufactured of iron as the electrodes. An activated sludge electro-bioreactor with a working volume 13.43 L was fed with synthetic wastewater as described in Table 5.2. The activated sludge had been acclimatized to this synthetic wastewater for two months in order to achieve stable conditions prior to the membrane filtration experiments. The sludge inoculation was taken from the secondary clarifier in a municipal wastewater treatment plant in the city of Saint-Hyacinthe, QC, Canada. The physical/chemical properties of the sludge samples are listed in Table 5.4. Constant wastewater level in the electro-bioreactor was maintained by level monitoring sensor, which controlled the wastewater feeding pump. The SMEBR system was operated under continuous aeration to achieve biological organic pollutants removal and nitrification process. Dissolved oxygen concentrations between 5 and 8 mg/L were maintained throughout the electro-bioreactor's zones as described in Chapter 5.

The process was closely monitored for different parameters including the physio-chemical parameters (pH, temperature, MLSS, MLVSS, specific filtration resistance (SFR) and zeta potential), as well as biochemical parameters and nutrients (COD, ammonia nitrogen (NH_3–N), nitrate nitrogen (NO_3–N), nitrite nitrogen (NO_2–N) and orthophosphate (PO_4-P)).

The operating period of Phase II was divided into two stages: the Stage I (reference stage), which was extended for 26 days without the input of DC power, and Stage II lasting 27 days with the input of DC. During the entire operating period, no sludge was extracted from the electro-bioreactor, except for the purpose of sampling analysis (conventional parameters analysis and SRF tests). On average, a volume of about 350 ml / week of sludge was removed and not returned to the electro-bioreactor, corresponding to average sludge retention time (SRT) of 200 days. Consequently, the SMEBR system was considered to operate under conditions of complete sludge retention. Table 7.1 shows the different conditions under which the process was run and monitored during the two stages.

In order to study the fouling degree accurately, the process was operated at constant transmembrane pressure mode; this means that the permeate flux may decrease with time due to the fouling phenomenon.

Table 7.1 Experimental conditions during the Phase II

Items	Stage I	Stage II
Operation time (days)	26	27
SRT (days)	≈200	≈200
DO in bioreactor (mg L^{-1})	5-8	5-8
DC (V/cm)	0	1
DC exposure time (minute)	0	15 ON/ 45 OFF
Influent temperature (°C)	19-21	19-21

Moreover, no back washing of the membrane module was performed during the operation. However, in order to enhance the recovery of the membrane permeability during the operating period, the membrane module was periodically taken out of the electro-bioreactor when the permeate flux significantly declined and washed with distilled water for few minutes to remove the attached sludge cake particles over the membrane surface. In addition, a constant rate of air flow was diffused through the membrane module to reduce fouling and cake formation.

Methodology of sampling collection and analytical methods of Phase II were described in details in Chapter 5.

7.5 Results and Discussion

The SMEBR system operated for 53 days without any serious problems. The results are discussed with respect to stages I and II according to the different operating conditions listed in Table 7.1.

7.5.1 Visual Observations

Visual observations may be considered a first assessment of the SMEBR system performance. Although the mixed liquor solutions in the electro-bioreactor showed differences in color throughout the experiment, water permeate quality had neither color nor odor. Figure 7.2 shows how the color changed of the different types of wastewater during the treatment process: influent (synthetic wastewater), the MLSS solution in the bioreactor's zones and permeate. The synthetic wastewater has light yellow color; the MLSS solution in the electro-bioreactor has gray color in the Stage I and changed from greenish yellow color to red-brown color and turbid at the end of the Stage II due to the dissolution of iron from the anode. Detailed description of these phenomena was discussed in section 7.5.3.1.

The results of the Stage II demonstrated that applying a DC field to the MLSS solution led to an increase in the pH of the treated suspensions and the increase in pH was more significant in Zone II. Moreover, the influence of applying the DC field into MLSS solution significantly affected the floc size of the MLSS solution.

Large and dense flocs appeared during the Stage II and enhanced the overall performance of liquid/solid separation processes which was reflected on the sedimentation velocity (observed visually) and increased the dewatering process by reducing the specific resistance to filtration (section 7.5.4.2).

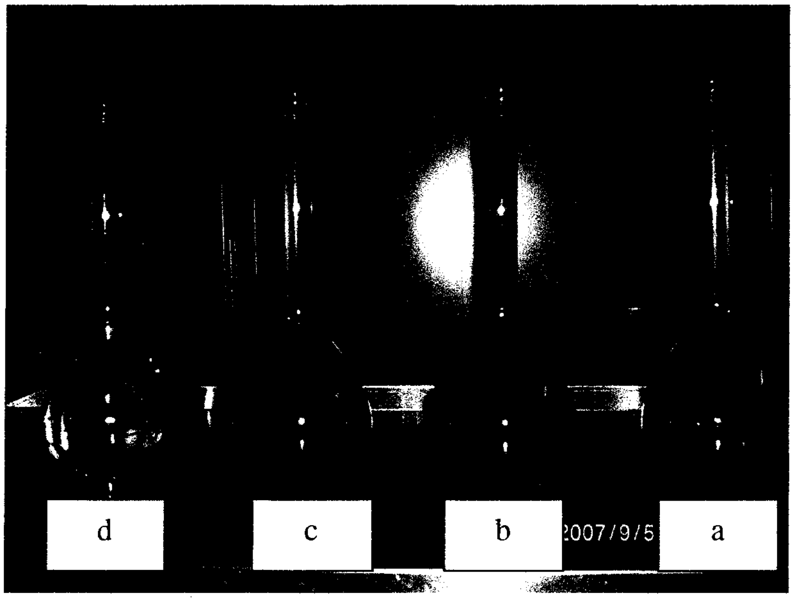


Figure 7.2 Color changes of the different types of wastewater in SMEBR system: (a) Synthetic wastewater; (b) Activated sludge from the Stage I; (c) Activated sludge from the Stage II; (d) the effluent from membrane module.

7.5.2 Impact of the SMEBR Operation on Membrane Filtration Performance

Figure 7.3 shows the ratio of permeate flux to initial water flux (J/J_i) during the operating period of the membrane filtration of sludge suspension in the SMEBR system. Since the operation mode was at constant transmembrane pressure, the permeate flux decreased with time due to the fouling phenomenon. Accordingly, the hydraulic retention time (HRT= electro-bioreactor volume/ effluent flow rate) was increased with time as shown in Figure 7.4.

The curve of Figure 7.3 is divided into two stages: from day 1 to day 26 (Stage I), and from day 26 to day 53 (Stage II). The peaks appearing in the filtration performance curve (day 6, day 12, day 35 and day 41) represented the washing events of the membrane with distilled water for few minutes outside the electro-bioreactor to remove the attached sludge cakes covering the membrane surface which increased the permeability of the membrane and enhanced the flux permeation value. In Stage I where with no DC input, the permeate flux decreased dramatically during the first operation. It is important to note that before starting Stage II, the membrane module was removed from the electro-bioreactor for physical and chemical cleaning (see section 5.1.1).

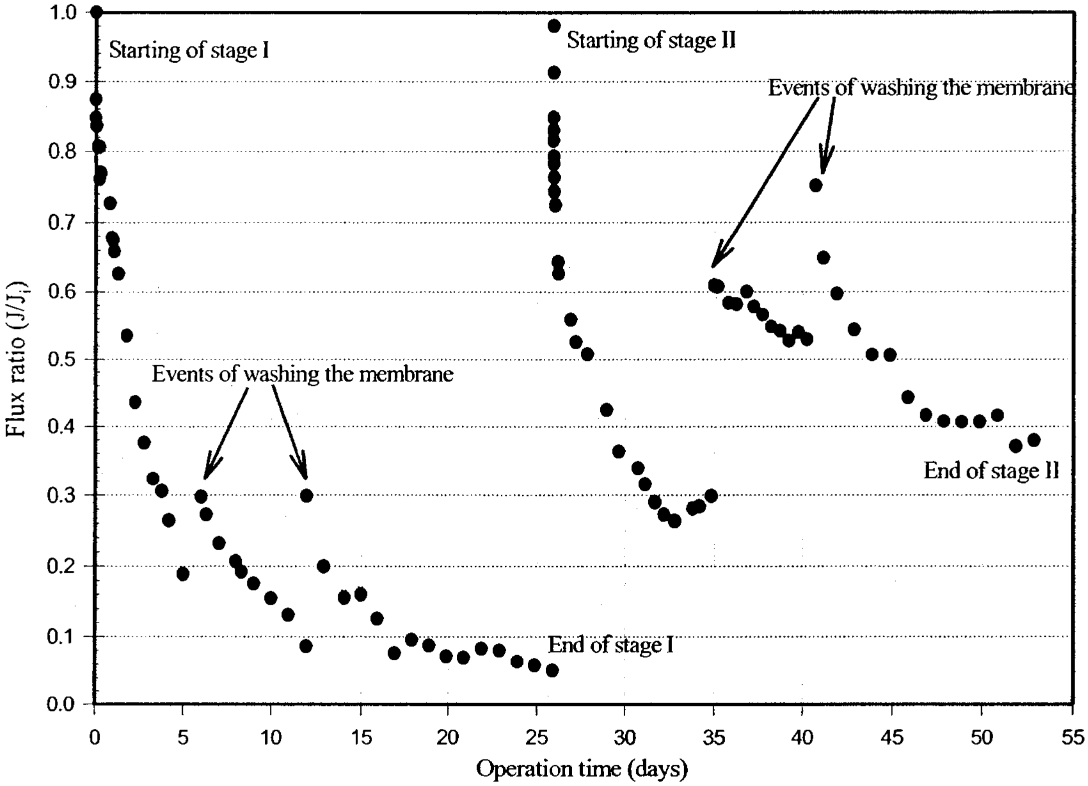


Figure 7.3 Change of permeate flux with time in SMEBR system during the Phase II

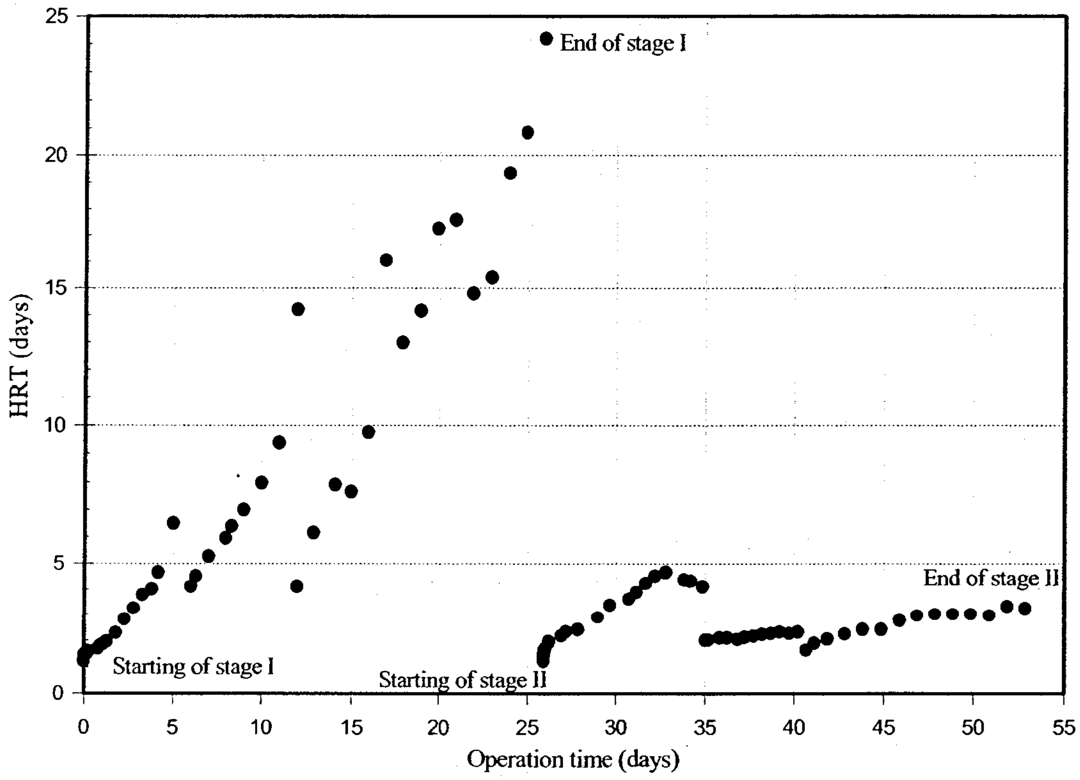


Figure 7.4 Change of HRT in SMEBR system during the Phase II

The membrane was washed with tap water for 20 minutes, and then immersed in tank containing distilled water and backwashed with distilled water for 2 hours to remove the small particles entrapped in the membrane pores; then, it was immersed in 5% NaOCl solution for 8 hours. Afterwards, it rewashed by tap water and distilled water. This procedure, in effect, restores most of the membrane's permeability. In general, the same procedure is used to recover the membrane permeability (Meng et al., 2006; Trussell et al., 2005; Mo et al., 2005).

In Stage II, a DC of 1 V/cm was applied and the mode of operation was selected based on the results obtained in Chapter 6 (i.e. 15 ON minutes / 45 minutes OFF). During the first hours of Stage II, there was no significant influence of the applied electrical field on the coagulation process, hence the flux declined rapidly as it was observed in the Stage I. However, the effect of the electro-coagulation process began to give significant evidence of coagulation on day 29 of operation (day 3rd of the Stage II), at which point the permeate flux started to decline with time. On day 32, the permeate flux was almost constant. Between day 33 and day 35, the permeate flux increased slowly reflecting the effect of applying the DC field into the MLSS solution in the SMEBR system.

In any wastewater treatment process, an important aspect to analyze is the effect of operation parameters on the process performance and to assure that the process is being operated under steady state conditions. In Phase II of this research, the change in HRT during the operation is considered another indication of the performance of the submerged membrane electro-bioreactor system to reach the steady state conditions. Figure 7.4 illustrates how the HRT increased rapidly during Stage I due to the rapid decline of permeate flux, reflecting unsteady state conditions. The HRT increased from

1.2 day at the beginning of the operation and reached 6.5 day after five days of operation in the Stage I. At the end of the operation of the Stage I, the HRT was about 24 days.

The fluctuation in the HRT diminished in Stage II as a result of a decrease in the fouling phenomenon. The HRT did not exceed 5 days during the operation period of the Stage II. This means that the submerged membrane electro-bioreactor system achieved steady state conditions when the fouling rate decreased, while taking into consideration that no back washing was achieved to reach this situation.

It is important to highlight that, only when the SMEBR system is truly operated under steady-state conditions, sound conclusions can be drawn about the effect of the HRT on the submerged membrane electro-bioreactor performance. However, the fluctuation in the HRT has direct impact on the loading rate of COD, ammonia nitrogen (NH_3–N) and orthophosphate (PO_4-P) to the electro-bioreactor. This issue was discussed in details in section 7.5.5.4.

To assess the fouling behavior in the SMEBR system during the two stages of Phase II, the concept of percentage reduction in permeate flux (*PRPF*) is used here. The PRPF is given by the following equation:

$$PRPF = \left(\frac{J_i - J}{J_i}\right) \times 100\% \qquad (7.15)$$

Where J_i is the initial permeate flux (2.72×10^{-6} $m^3/m^2.s$) and J is the permeate flux at any time. Figure 7.5 shows the percentage reduction in permeate flux (*PRPF*) during the operating period. During the first operation of Stage I, the PRPF was 81.2% after 5 days of operation. At the end of the Stage I, the *PRPF* was 94%. During the operation of Stage II, the *PRPF* was 57.8 % in 3 days (between day 26 and 29) and 68 % on day 31 (after 5 days of operation of the Stage II). This is equivalent to 16.6 %

improvement in permeate flux after applying DC field into the MLSS solution. The percentage improvement in permeate flux was calculated by the following equation (based on five days of continuous operation in each stage):

$$\% \text{ improvement in flux } = \left(\frac{\left| J - J_{Stage\ -\ I} \right|}{J_{Stage\ -\ I}} \times 100\% \right) \tag{7.16}$$

Where J and $J_{Stage\text{-}I}$ are the permeate fluxes in Stage II and Stage I respectively after five days of continuous operation. The improvement in permeate flux reflects the effect of the electro-coagulation phenomenon on membrane performance during Stage II. The maximum *PRPF* was recorded on day 33 and determined to be 73 %.

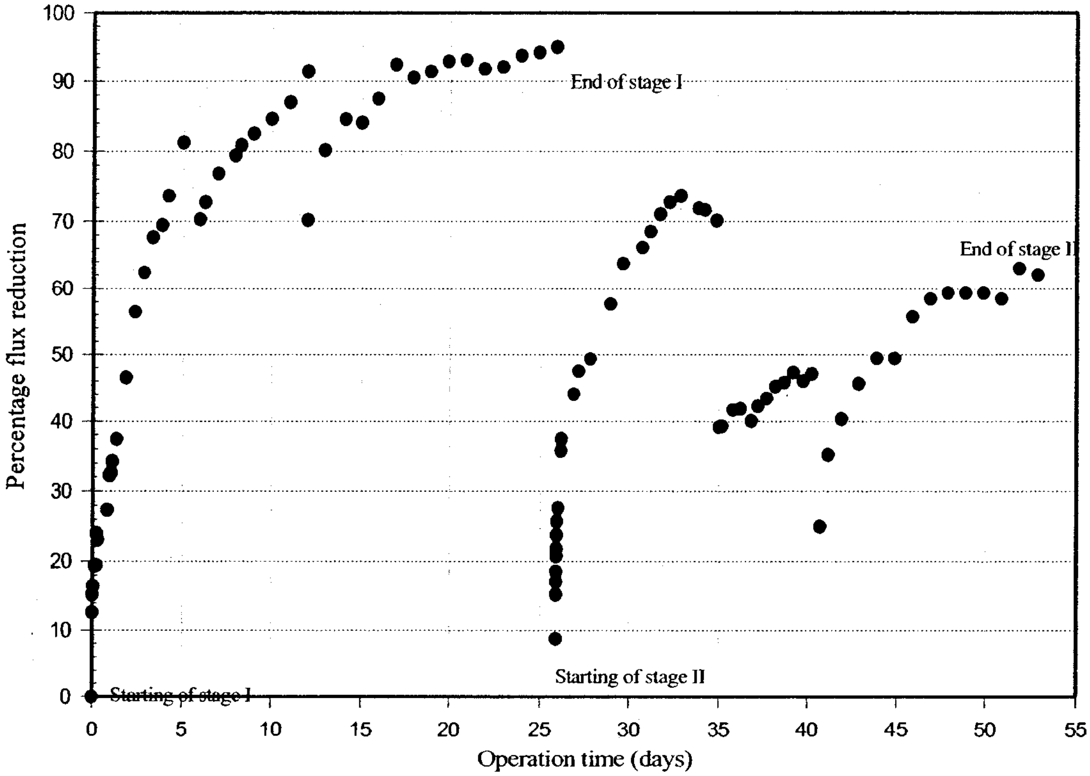


Figure 7.5 Changes in percentage reduction of permeate flux in SMEBR system during the Phase II

To get a better view about the effect of the SMEBR system on the filterability of the membrane, the membrane module was taken from the electro-bioreactor on day 35 and washed outside of the electro-bioreactor with tap water for few minutes. After reintroducing the membrane in the electro-bioreactor, the membrane had recovered 61% from its original permeability. It is clear from Figure 7.3 that the relative constant flux during the 5 days following day 35, the flux lost only 13% from its value at day 35. This means that to obtain a better filtration process in the SMEBR system, the electrocoagulation process should be achieved before immersing the membrane in the electro-bioreactor.

On day 41, the membrane module was exposed to another washing by tap water outside the electro-bioreactor. A 77 % amount of the original permeability has been recovered by this event. However, the flux decline was sharper in comparison with the previous washing. This could be attributed to the blocking of small particles within the membrane pores which could not be removed by washing the surface of the membrane alone.

In conclusion, applying DC field into the MLSS solution improved the membrane filtration in SMEBR system; however, according to the strategy of research which has been followed in this thesis, the transmembrane pressure was constant to eliminate the impact of transmembrane pressure on the results. In most applications in membrane filtrations processes, the flux is constant and the transmembrane pressure varies with time because this approach is less costly. Consequently, fouling mechanisms in constant flow applications and constant pressure applications are substantially different. Moreover, the low flux through the membrane in this research may limit particles movement to the membrane surface and pores. For this reasons, operation the SMEBR system at constant flux is addressed as future work.

7.5.3 Response of Physiochemical Properties to the SMEBR Operation

7.5.3.1 Change in pH

As mentioned in Chapter 4, DC field applied between the anode and cathode immersed in water causes water oxidation and generates an H^+ and oxygen gas at the anode (Equation 4.28); while water reduction produces OH^- and hydrogen gas at the cathode (Equation 4.29). Consequently, the acidity at the anode may increase due to (H^+) production, reducing the pH. Simultaneously, the base will increase at the cathode due to (OH^-) production and the pH will increase.

In a similar situation in the SMEBR system, applying a direct electrical current (DC) throughout the mixed liquor culture will result in a redox reaction at the electrodes. Accordingly, measuring the pH in the mixed liquor culture after introducing a DC field through the culture is an important parameter because most of the bacterial growth requires an optimum range of pH in which they can grow. This range is usually closed to neutrality with limits in minimum and maximum near 5 and 9 respectively (Gaudy and Gaudy, 1988).

The variations of pH values in the influent, the MLSS solutions in the bioreactor's zones and the membrane effluent are presented in Figure 7.6. The pH values of the influent fluctuated from 5.8 to 7.6 during the operation of the Phase II. It was noted that the pH changed with time in the feed wastewater compared to the pH of the original feed solution. This phenomenon was observed in each batch of the prepared synthetic wastewater. The variation in influent pH was attributed to the relative fluctuation in the water quality of the feed wastewater (the degradation of organic materials in the wastewater storage tank). The same phenomenon was observed by Liu et al. (2005).

During Stage I, the pH values of the MLSS solution in bioreactor's various zones were closed to each other. It was observed that the pH of the MLSS solution decreased from 7.4 to 6.6 during the first days of operation of Stage I, and it stabilized at around pH = 6.3. From Figure 7.6, it can be seen that dramatic significant change in the pH values started to appear on day 26 at the beginning of the Stage II where the pH of the MLSS solutions increased as a result of the electrokinetic phenomenon occurring in the SMEBR system in response to applying a DC field into the mixed liquor solution.

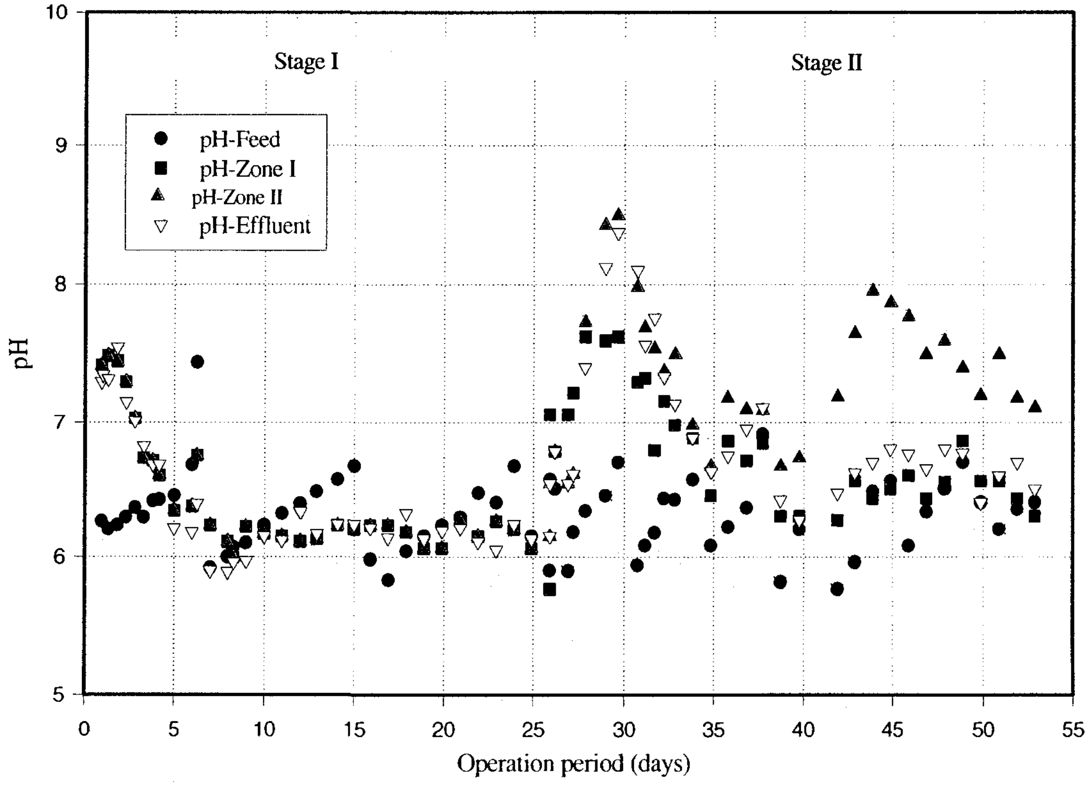


Figure 7.6 Changes in pH values in SMEBR system during the Phase II

The increase in the pH of the solution after applying DC field in wastewater was also observed by other investigators (Kurt et al., 2008; Kobya et al., 2003; Chen et al., 2000). After one day of operation during Stage II, dramatic increases in pH values was observed for the MLSS solutions and permeate from the membrane. Moreover, starting from day 26, a difference in the pH values appeared between the MLSS solution located in the Zone I and the other located in Zone II. This can be understood from the design of the SMEBR system. In Zone I where the electrokinetic phenomenon occurred (Figure 7.7), there was liberation of OH^- from the cathode according to equation 7.17. As the cathode formed the same border for the electro-bioreactor's zones, hydroxyl ion (OH^-) will move in both directions toward of the two zones in the electro-bioreactor. In Zone I, where the electro-coagulation process took place, hydroxyl ion (OH^-) were consumed as a result of its reactions with iron ions (i.e., Fe^{+2} or Fe^{+3}), which were dissolved at the anode according to the mechanism described in section 7.3.

As a result, the pH in Zone I did not significantly increase. On the other hand, the hydroxyl ion (OH^-) that moved toward Zone II contacted fewer iron ions; therefore, it accumulated in the vicinity of Zone II and increased the pH in this zone. Also, Due to the good mixing in Zone I by air, the pH of bulk solution in this zone tends to be neutralized as it is shown in Figure 7.6. The maximum pH value recorded was 8.5 on day 30 for the MLSS solution located around the cathode-membrane area (Zone II). In general, the changes in pH values during Stage II were as follows:

$$\text{pH (influent)} < \text{pH (Zone I)} < \text{pH (permeate)} < \text{pH (Zone II)}.$$

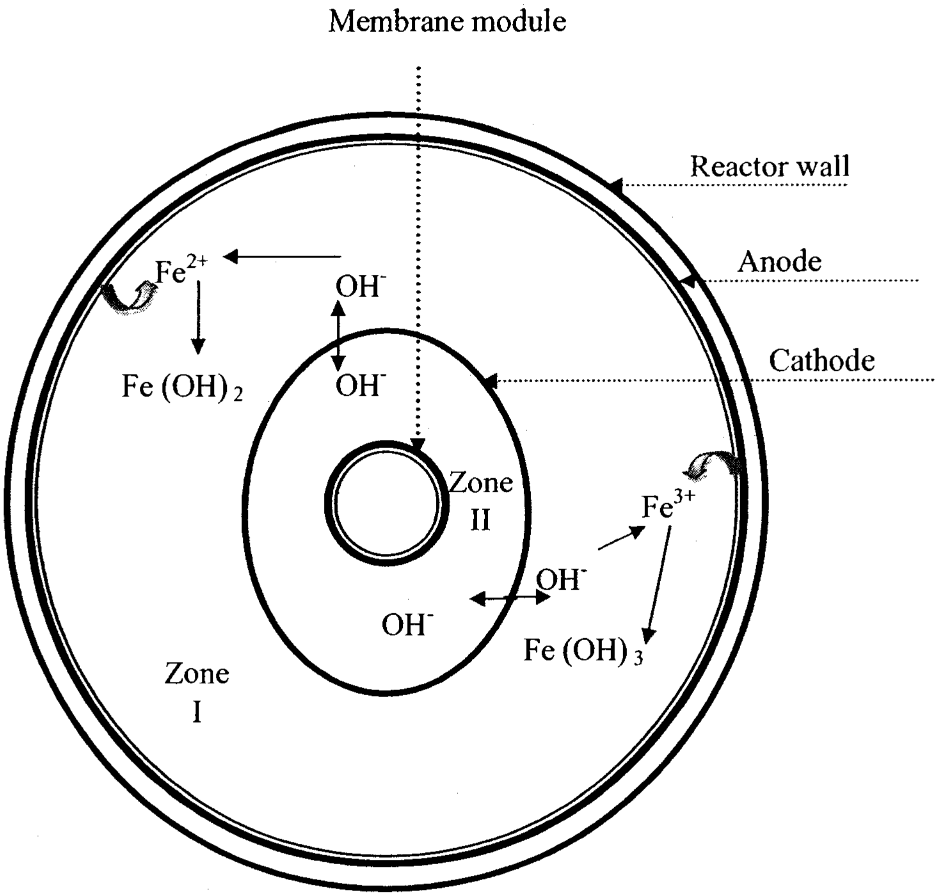


Figure 7.7 EC phenomenon in the SMEBR system (top view)

Furthermore, the change in the effluent pH in the SMEBR system during the whole operation period was between the range of 6 and 8.4. It is worth to mention here the relationship between the exposure time of DC field and the increase in the pH values in the SMEBR system. The longer exposure time produces higher values of pH. These relations were clearly demonstrated during the preliminary investigations performed in Phase I of this research (Chapter 6). On average, the pH values in the SMEBR system did not exceed pH = 7. This means that the effluent of the SMEBR system does not need further external adjustment of the pH.

The change in the pH values in the SMEBR system during Stage II was associated with color changes in the MLSS solution of the electro-bioreactor as shown in Figure 7.8. After one day of starting Stage II, the color of the MLSS solution began to change. The solution appeared greenish yellow in the first few days (day 27 to day 31) of Stage II, in which the pH in Zone I was within the range 7-8 and within the range 7.5-8.6 in Zone II. After this, the color turned yellow during days 32 to 36, where the pH in Zone I decreased from 7.6 to 6.7 and decreased in Zone II from 8.6 to 7.2.

The changes in the color during those days were completely in agreement with the description reported by Moreno-Casillas et al. (2007) as discussed in section 7.3. This phenomenon was also confirmed by Ni'am et al. (2007) who attributed the green and yellow color to Fe^{2+} and Fe^{3+} ions generated during the electrocoagulation process. They reported that Fe^{2+} is the most common ion generated in-situ during the electrolysis of iron electrode. It has relatively high solubility at acidic or neutral conditions and can be oxidized easily into Fe^{3+} by dissolved oxygen in water. Finally, the color turned red-brown and turbid (Figure 7.2), and this color was stable until the end of the Stage II.

Color Change	■	■	▨	■	■
Day of operation	1-26	26--31	32-36	36-38	38-53

Figure 7.8 Change of the MLSS solution color in the SMEBR system during the Phase II

7.5.3.2 Change in Temperature

Temperature is one of the most important factors affecting microbial growth and biological reactions (Zavala et al., 2004). Most of the microorganism has optimum range of temperature in which they can grow optimally. It was reported that bacteria would grow rapidly in an aerated environment and temperatures in the range of 20 to 40 °C (Kaleli and Islam, 1997).

Applying DC fields may increase the temperature of the culture and this may affect the growth of the microorganisms (Alshawabkeh et al., 2004).

The variations in temperatures of the influent, the MLSS solutions in the two zones in the electo-bioreactor and in the membrane effluent are presented in Figure 7.9. The temperatures of the influent and the effluent were closed to each other and fluctuated according to the ambient room temperature (20.5 ± 1 ^{o}C). In contrast to what is usually expected from EC phenomena (Ni'am et al., 2007; Alshawabkeh et al., 2004) where the temperature usually increases, the temperatures of the elector-bioreactor's zones were less than the temperature of the influent and effluent by 1 ^{o}C degree during the whole experimental period. In general, applying DC field in the SMEBR did not show significant changes in the temperatures. The changes in temperatures of the SMEBR system were in the following order:

Influent temperature > Effluent temperature > Temperature in the Zone I> Temperature in the Zone II.

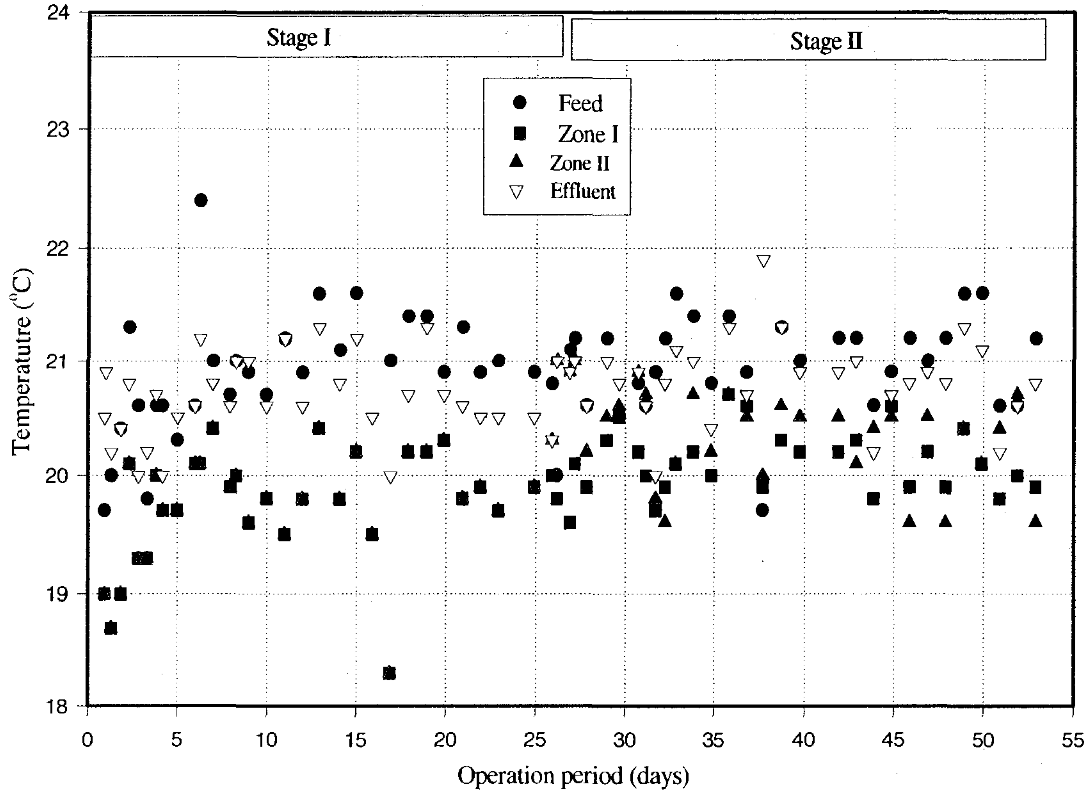


Figure 7.9 Changes in temperatures in SMEBR system during the Phase II

It is should be emphasized that the temperature has significant impact on the membrane performance because it is strongly affecting the permeate viscosity, so its impact on the membrane fouling will be significant (Mulder, 2000). Jiang et al. (2005) reported that at lower temperatures (13-14 °C) greater resistance has been observed due to sludge viscosity increase, floc size reduction, particle back transport, biodegradation of COD than higher temperature conditions (17-18 °C).

Since the influent temperature was almost constantly close to the ambient temperature (20 ± °C) during the whole operation period, its impact on the SMEBR performance could not be observed in this research. Consequently, further research is recommended in this domain especially if the designed SMEBR system might find a direct application for sewage treatment in cold regions.

7.5.4 Response of the Mixed Liquor Properties to the SMEBR Operation

7.5.4.1 Change in Sludge Concentration

Figure 7.10 shows the time-dependent variations of the MLSS and the MLVSS concentrations in the electro-bioreactor. Samples that were taken from each zone showed no significant differences in MLSS concentration in both zones and in the MLVSS concentrations as well. This was attributed to the good mixing of the mixed liquor suspension in the electro-bioreactor resulting from the aeration system in each zone. Therefore, Figure 7.10 presents the average values of the MLSS and the MLVSS measured in bioreactor's various zones. During the first eight days of Stage I, an increasing tendency in the MLSS concentration was observed. After 8 days, the sludge concentration slowly increased and reached an average of 3300 mg/L.

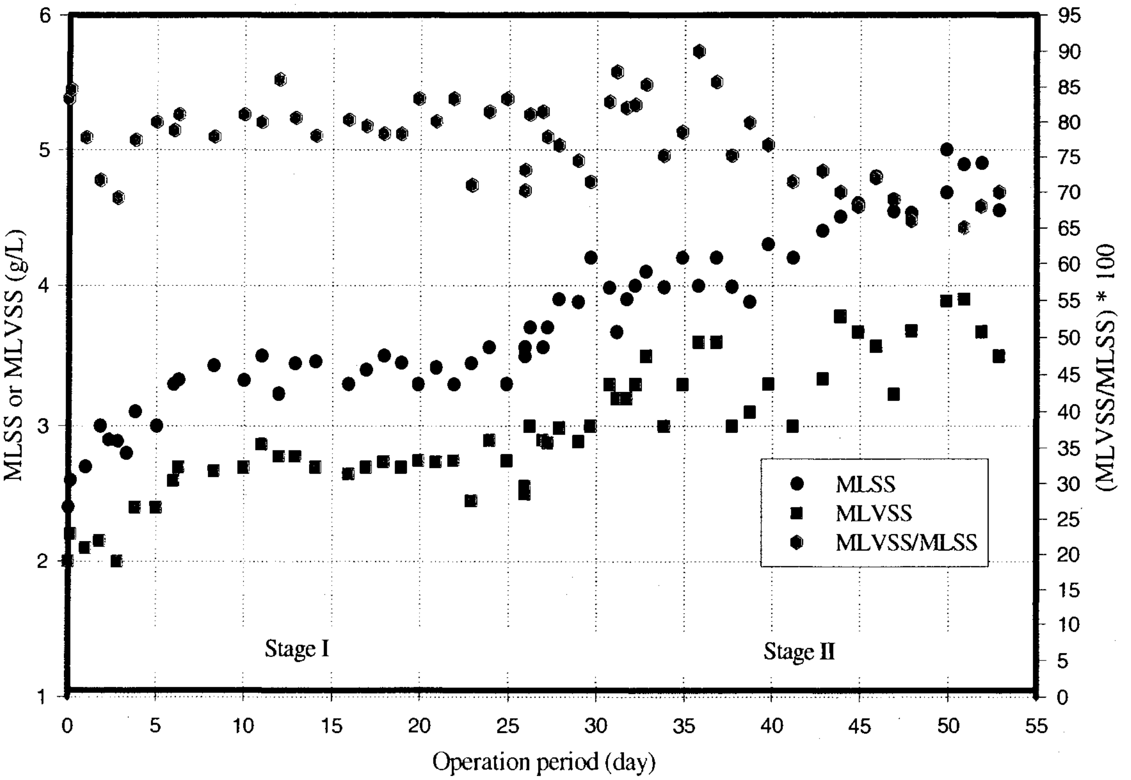


Figure 7.10 Change of the MLSS and the MLVSS concentartions in the SMEBR system during the Phase II

Since no sludge was withdrawn from the electro-bioreactor during the operation except for sampling purposes, a long SRT was achieved. This long SRT might allow the excess sludge to oxidize in the electro-bioreactor, and keep the sludge concentration constant after the eight days of Stage I (Wagner and Rosenwinkel, 2000). Another reasonable explanation for the constant sludge concentration during this period of the Phase I might be due to the long HRT (5-20 days). At relatively constant concentration of the substrate in the influent and as the HRT increased, food to microorganism ratio (F/M) decreased; therefore, the available food to the microorganism decreased and growth was limited (Section 7.5.6).

During Stage II, an increase in the MLSS concentration in the electro-bioreactor was observed a as result of electro-coagulation phenomenon. The sludge concentration increased from 3500 mg/L at the beginning of Stage II to 4500 mg/L at the end of Stage II. This was attributed to the electro-coagulation phenomenon occurring during this stage. This was confirmed by a decrease in the VSS/TSS ratio during Stage II. The ratio of VSS/TSS of sludge in the electro-bioreactor was fluctuated within the range 71% to 83 % during the Stage I, while this ratio tended to decrease to be less than 72 % after the day 42 during Stage II. This implied that there was an accumulation of inorganic matter in the electro-bioreactor.

During Stage II, it was not possible to determine the amount of the sludge that was produced from biodegradation process and that produced from the electrocoagulation process because of the complex interaction between two processes. Also, this confirms the complexity in predicting the behavior of the wastewater treated in the SMEBR system as described in Chapter 3. According to the study reported by Kurt et al. (2008) in which the EC process was used to treat domestic wastewater using iron-iron electrodes, the levels of sludge production increased between 1.5% and 9% in 5-15 minutes reaction times, and the inorganic fraction of the sludge increased gradually from 13% to 37% in 5-15 minutes as a function of current density.

7.5.4.1.1 Influence of the MLSS Concentration on Membrane Fouling

Since the SMEBR system was operated under complete SRT in two sequential stages, therefore, the role of the MLSS concentration on membrane fouling should be discussed. According to the literature, it is widely believed that the MLSS concentration is one of the predominant fouling parameters which may affect the MBR performance due to the complex interaction of mixed liquor solution in the bioreactor with the membrane module (Le-Clech et al., 2006). However, the exact influence of MLSS concentration on membrane fouling is not yet clear. Some of the recent studies reported that MLSS seems to have a mostly negative impact on MBR hydraulic performance represented by a high TMP and a low flux (Chang and Kim, 2005; Cicek et al., 1999), while others have reported a positive impact (Brookes et al., 2006; Defrance and Jaffrin, 1999), and some observed insignificant impact for small concentration changes (Hong et al., 2002; Le-Clech et al., 2003).

The above discussion about the MLSS concentration shows some inconsistencies in determining the exact effect of the MLSS concentration on MBR performance. It seems that the level of the MLSS concentration plays an important role on membrane fouling. According to Yamamoto et al. (1994), the flux decreases abruptly if the MLSS concentration exceeded 40,000 mg/L in a submerged membrane bioreactor. Le-Clech et al. (2003) investigated the effect of three different levels of MLSS concentration (4000, 8000, and 12,000 mg/L) on membrane fouling in a submerged membrane bioreactor. They found that there was no significant difference in the concentrations of 4000 to 8000 mg/L, but that a significant decrease of permeate rate was observed when the MLSS concentration increased to 12,000 mg/L.

In Phase II of this research, The MLSS concentration in the SMEBR system increased from 2100 mg/L up to 5000 mg/L during the operational period. During Stage I, the MLSS concentration was within the range 2100- 3500 mg/L. According to Figures 7.3 and 7.4, the membrane filtration performance had reached stable conditions after a few days from each event of membrane washing, suggesting that the change occurring in the MLSS solution had no significant effect on membrane fouling within the developed MLSS concentration (2300 – 3500 mg/L). During Stage II, the MLSS concentration increased from 3500 mg/L up to 5000 mg/L. Within this range, it was assumed that the MLSS concentration did not contribute significantly to membrane fouling. In other words, as there is no clear correlation between the fouling rate and the MLSS concentration in the submerged membrane bioreactor applications as it was reported from the literature, the MLSS concentration is a limited indicator of fouling propensity. Consequently, the development occurring in membrane flux during the SMEBR system is completely attributable to the changes occurring in the physical/chemical properties of the MLSS solution after applying a DC field. This hypothesis was confirmed in the analysis of the specific resistance to filtration and the zeta potential in the following subsections.

7.5.4.2 Change in the Specific Resistance to Filtration (SRF)

The specific resistance to filtration (SRF) is usually considered an indicator to characterize the fouling phenomenon in the conventional submerged membrane bioreactor applications (Yang et al., 2007). Increases in SRF result in a decline in the flux rate, and an increase in transmembrane pressure (TMP). In a conventional submerged membrane bioreactor, the membrane flux would be expected to increase with the TMP. However, higher TMP has a negative effect on membrane permeation, which can result in a more compacted cake layer and lead to a greater flux reduction (Lee and Clark, 1998). The flux decline behavior can be explained by the increase of foulants deposited onto the membrane surface at high TMP. Yang et al. (2007) reported a strong relationship between the SRF and the TMP in the filtration of sludge supernatant in a conventional submerged membrane bioreactor. Ahmed et al. (2007) also pointed out that the SRF increased as well as membrane bio-fouling due to the presence of colloidal particles.

From a physical point of view, the specific resistance to filtration (SRF) of the mixed liquor sludge is an index representing the filterability of mixed liquor when it is dewatered through a filter medium. It gives an indication of the resistance of the biomass to filtration (Ng and Hermanowicz, 2005). As mentioned in Chapter 4, the SRF is defined as resistance per unit of filter area when specific weight sludge is filtered at a given pressure. A higher SRF reflects a low filterability.

In subsequent research, the effect of applying a DC field on the performance of the SMEBR system and the specific resistance to filtration (SRF) of floc particles in the mixed liquor solution in the bioreactor's zones was measured every 10 days during the operation period as shown in Figure 7.11.

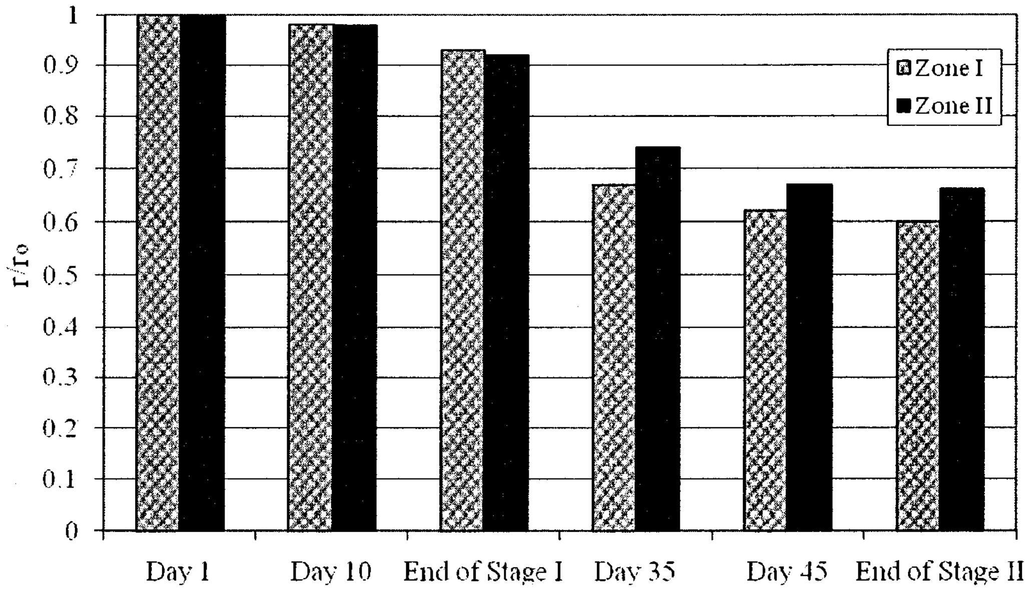


Figure 7.11 Change of spesific resistance to filtration of the MLSS solution

All the measurements were compared to the specific resistance to filtration (r_o) represented as the SRF of the MLSS solution at the beginning of the operation of the SMEBR system.

As observed from Figure 7.11, the results of SRF tests during Stage I showed a little improvement in the SRF which could be attributed to the relative increase in the particle size of the flocs resulting from an increase in sludge concentrations in the electro-bioreactor.

The above explanation is reasonable since there is a relationship between the particle size of the mixed liquor solution and its concentration (Chang et al., 2007).

During Stage II, a higher improvement in the SRF was observed on day 35 which was attributed to a significant increase in flocs sizes resulting from the electrocoagulation process occurring in Zone I. Moreover, the results of the SRF tests showed some variations in *r/ro* between the two zones. The ratio *r/ro* reduced to 0.67 in Zone I and to

0.74 in Zone II on day 35. At the end of operation of Phase II, the ratio *(r/ro)* reduced to 0.60 in Zone I and to 0.66 in Zone II. This indicated a significant improvement in reducing the SRF of the MLSS solution and agreed with the results obtained on improving the membrane flux, as shown in Figures 7.3 and 7.4.

These results suggest that a strong relationship existed between enhancing the membrane permeability in the SMEBR system and decreasing the SRF of the MLSS solution in the electro-bioreactor. According to the Carman-Kozeny equation, the specific resistance to filtration of particles is in inverse proportion to the square of particle diameter (equation 4.4). It seems that the relatively small particles that are the cause of membrane fouling had undergone flocculation due to the electro-coagulation process. Therefore, their effect is minimized on membrane fouling. Song et al. (2008) arrived at the same conclusion when they added alum as a chemical coagulant into the MLSS solution to enhance the membrane permeability in the submerged membrane bioreactor.

In fact, particle size is a key parameter in characterizing the membrane fouling phenomena (Lim and Bai, 2003; Bai and Leow, 2002). Generally, particle penetration into membrane pores can be reduced by increasing the particle size, and this will enhance particle back-transport from the membrane surface to the bulk solution (Jinsong et al., 2006, Lee et al., 2001). Applying a DC through the mixed liquor solution will increase the size particles. This principle was confirmed in the results obtained in Stage II of Phase II of this research.

7.5.4.3 Change in Zeta Potential

The propensity for particle aggregation can be determined by measuring the zeta potential of floc particles in bioreactor's various zones. Meng et al. (2006) reported a strong correlation between the zeta potential and resistance to membrane fouling, and indicated that the zeta potential is a significant membrane fouling factor. Resistance of membrane to fouling decreased from 9×10^{11} m^{-1} to 3×10^{11} m^{-1} when the zeta potential changed from -30 to -15 mV. Ofir et al. (2007) reported a strong relationship between the zeta potential and the size of particles in a colloid suspension. They found that the zeta potential increased in absolute values with increases in the particle sizes of the colloid suspension.

In Phase II of this research, one sample (50 ml) from the mixed liquor was taken daily from each zone in the electro-bioreactor and the supernatant of the sample was taken for zeta measurements after settling the mixed liquor for 30 minutes. To decrease the amount of sludge loss from the electro-bioreactor, the sample was returned to the electro-bioreactor after taking the measurement.

Figure 7.12 demonstrates the zeta potential of the MLSS solution of the two stages from both zones of the SMEBR system. During Stage I, no significant difference was observed in the two zones, and the zeta potential was approximately -30.5 mV.

In Stage II, the zeta potential of floc particles in the supernatant increased from –30.5 mV (on average) to –15.3 mV in Zone I (Day 32) and from -31 mV to -17 mV in Zone II (Day 32). However, the trend of zeta potential fluctuated with time in Stage II due to the alternate (discontinuous) operation in the DC power supply.

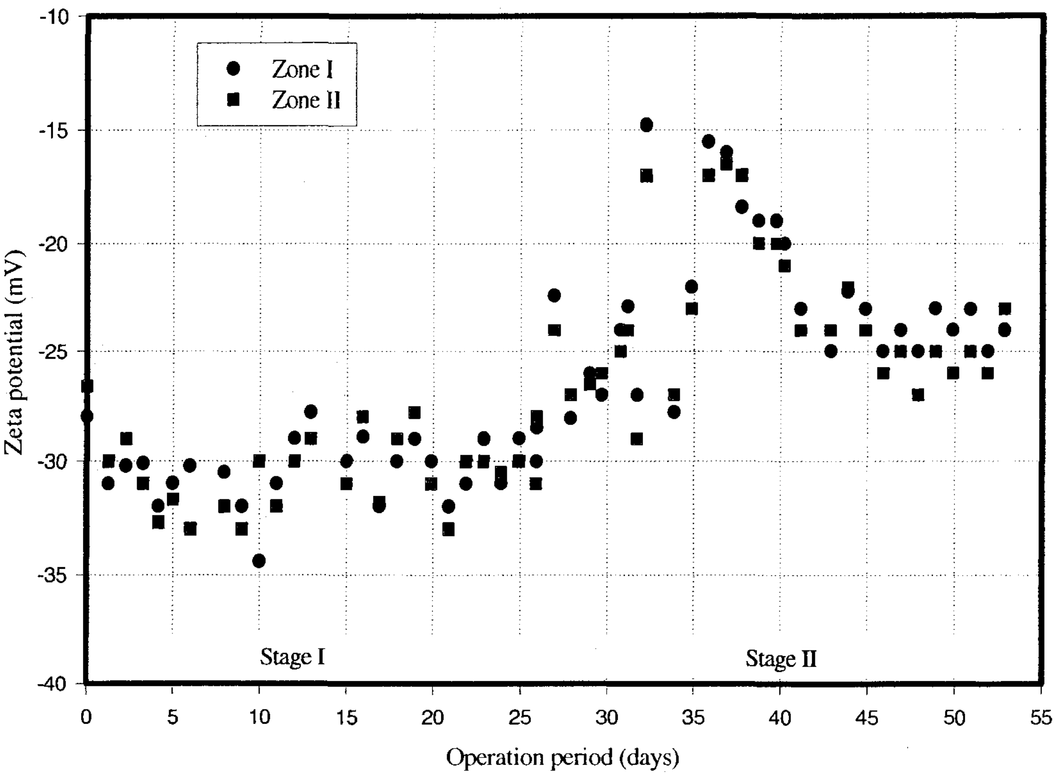


Figure 7.12 Changes in zeta potential in SMEBR system during the Phase II

The dramatic changes in the zeta potential values in Stage II were confirmed in the improvements in permeate flux as shown in Figure 7.3.

7.5.5 Response of Biochemical Properties to the SMEBR Operation

7.5.5.1 COD Removal Performance

Figure $7.13_{(a)}$ shows the variations of the COD concentrations in the influent, supernatant liquor (Zone I and Zone II) and the membrane effluent during the experimental period of Phase II. Figure $7.13_{(b)}$ shows the corresponding COD removal efficiency in the bioreactor's zones (% $R_{reactor}$) and in the whole system (% R_{system}). The efficiency of COD removal in the whole process and for the electro-bioreactor is calculated according to equations (4.10) and (4.12) respectively.

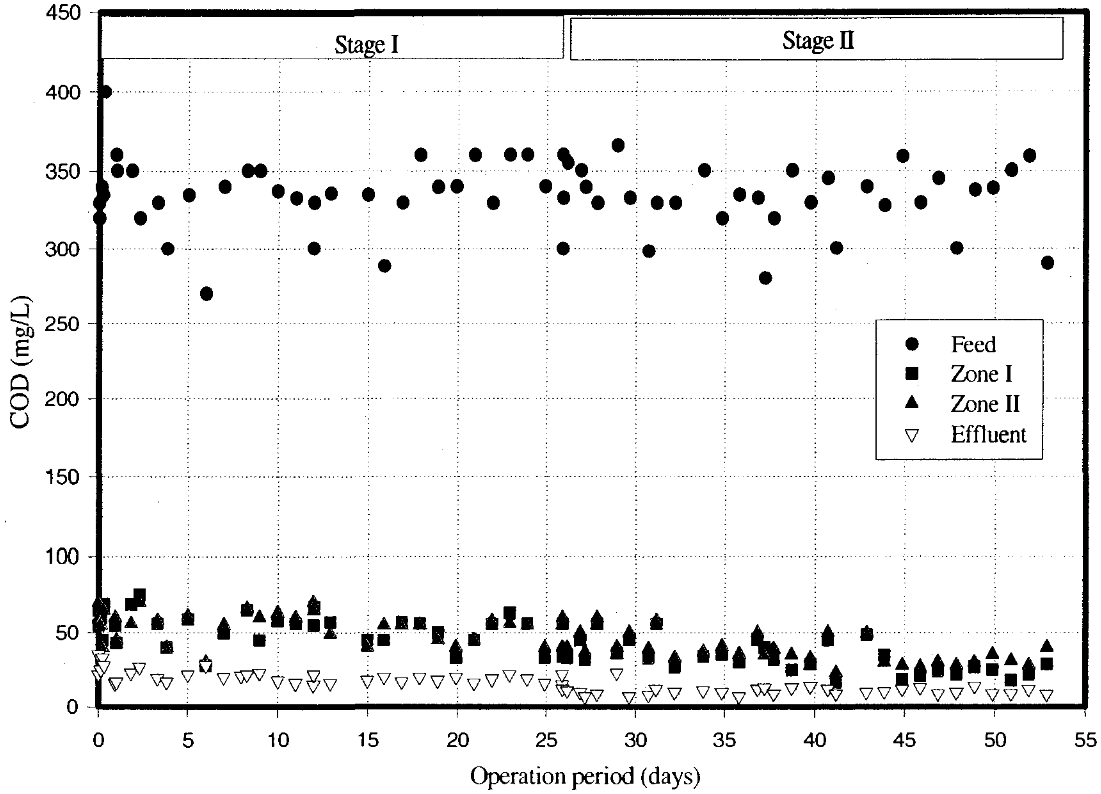


Figure 7.13$_{(a)}$ Changes in COD concentrations in SMEBR system during the Phase II

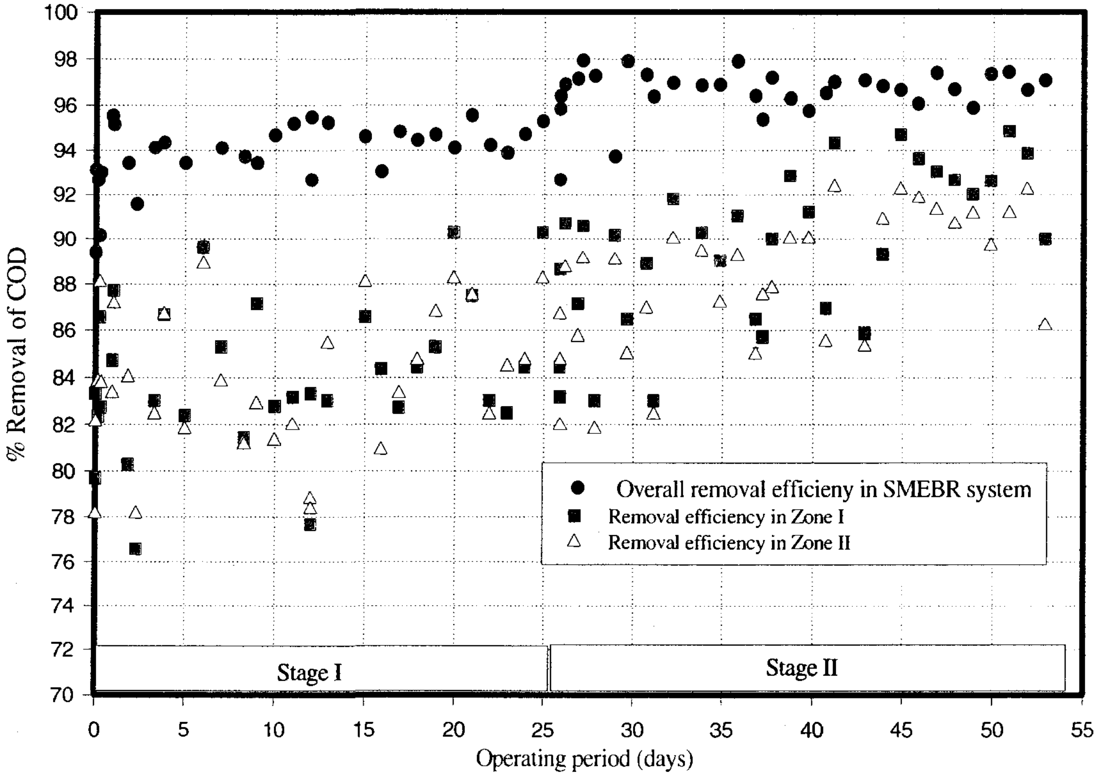


Figure 7.13 $_{(b)}$ Percentage removal of COD concentration in the SMEBR system during the Phase II

Although the influent COD fluctuated from 280 to 400 mg/L (Figure 7.13$_{(a)}$), the results show that the SMEBR system could provide a consistently high COD removal efficiency (Figure 7.13$_{(b)}$).

The COD concentration in the effluent varied between 7 and 22 mg/L, with removal efficiency between 90 to 98 %. Figure 7.13$_{(b)}$ shows that most of the fraction of COD (about 75-90%) during Stage I was degraded by the microorganisms in the bioreactor. The total COD removal efficiency for the system was maintained at a level of more than 95% because of the efficient separation by the membrane. The results demonstrated that membrane separation played an important role in providing an excellent and stable effluent quality. In fact, the membrane module plays an important role in the manipulation of the effluent concentrations with high quality in most submerged membrane bioreactor applications (Le-Clech et al., 2006, Trussell et al., 2005; Huang et al., 2001).

Figure 7.13$_{(b)}$ demonstrates a small difference in COD removal efficiency between Zone I and Zone II during Stage II; this can be attributed to the effect of electro-coagulation phenomenon that occurred in Zone I. Taking Stage I as a reference stage, Figure 7.13$_{(b)}$ illustrates that the removal efficiency of the COD in the electro-bioreactor in both zones increased from (75-90%) during Stage I to (85-95%) in Stage II. It was reported that in electrocoagulation process, the COD removal might involve electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment (Zaroual et al., 2006). This might explain the significant improvement in the COD removal in SMEBR system after applying DC in Stage II. This result is very important because as it was reported by Yamato et al. (2006) that some fractions of organic matter in the mixed liquor have higher affinities with the membrane than do other fractions and consequently cause greater irreversible fouling. It should be emphasized that the membrane fouling is caused not only by the microbial floc but also by the supernatant containing colloids and solutes (Judd, 2005; Lee et al., 2003; Defrance et al., 2000). The concentration of the colloidal and soluble polysaccharides of the liquid phase was identified as the predominant parameter causing membrane fouling (Grelier et al., 2006). Other researchers reported that for a microporous pore size membrane, the main components of the activated sludge system that contributed to membrane fouling are small size soluble and colloid components (Lee et al., 2001). Therefore, applying a DC filed in the mixed liquor can reduced the contributions load of the dissolved organic matter on membrane fouling. This result may reflect the good performance of the SMEBR system in terms of flux improvement in Stage II where the fouling rate decreased significantly.

7.5.5.2 Nitrification Performance

Nitrifying bacteria convert ammonia nitrogen (NH_3–N) to nitrate nitrogen (NO_3–N) in a nitrification reaction. Consequently, the change in ammonia concentration is often used as an indirect measurement in the changes in the nitrification process (Pollard, 2006). In Phase II of this research, the variations of ammonia nitrogen (NH_3–N) concentration in the influent, the supernatant of the electro-bioreactor's zones and in the effluent are presented in Figure $7.14_{(a)}$, The corresponding removal efficiencies of the SMEBR system is shown in Figure $7.14_{(b)}$. The influent NH_3–N varied from 25 to 36 mg/L with an average of 30 mg/L.

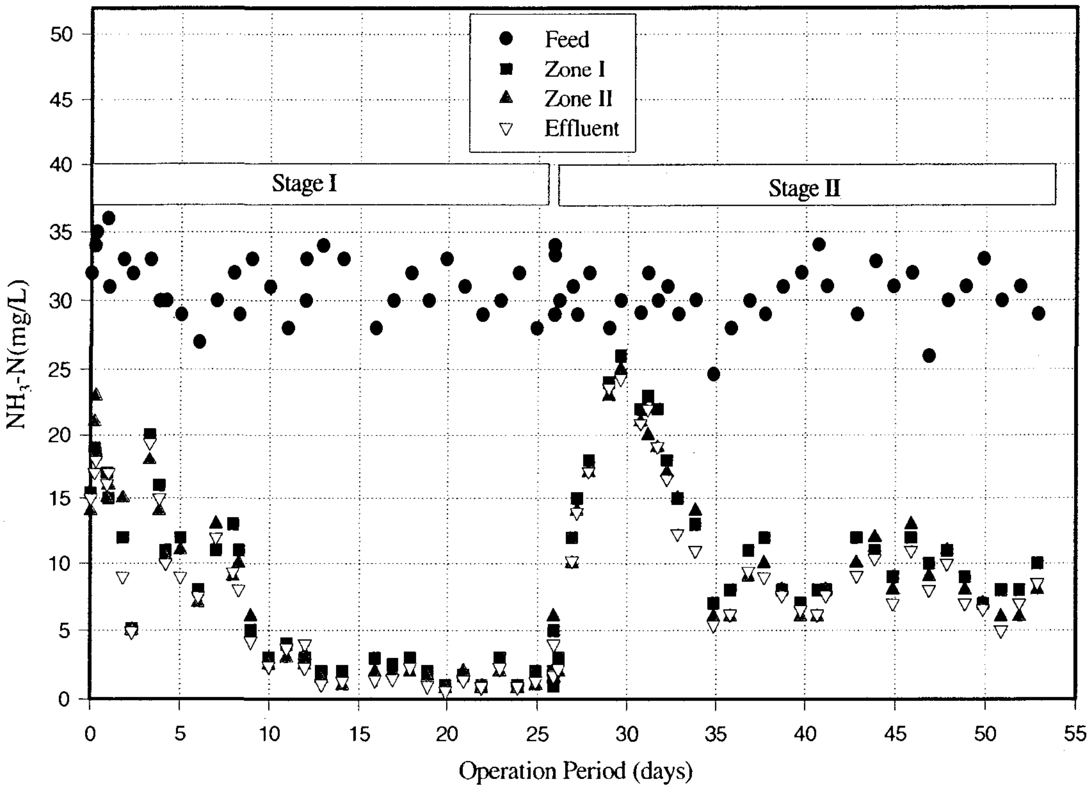


Figure 7.14(a) Changes in NH_3-N concentrations in the SMEBR system during the Phase II

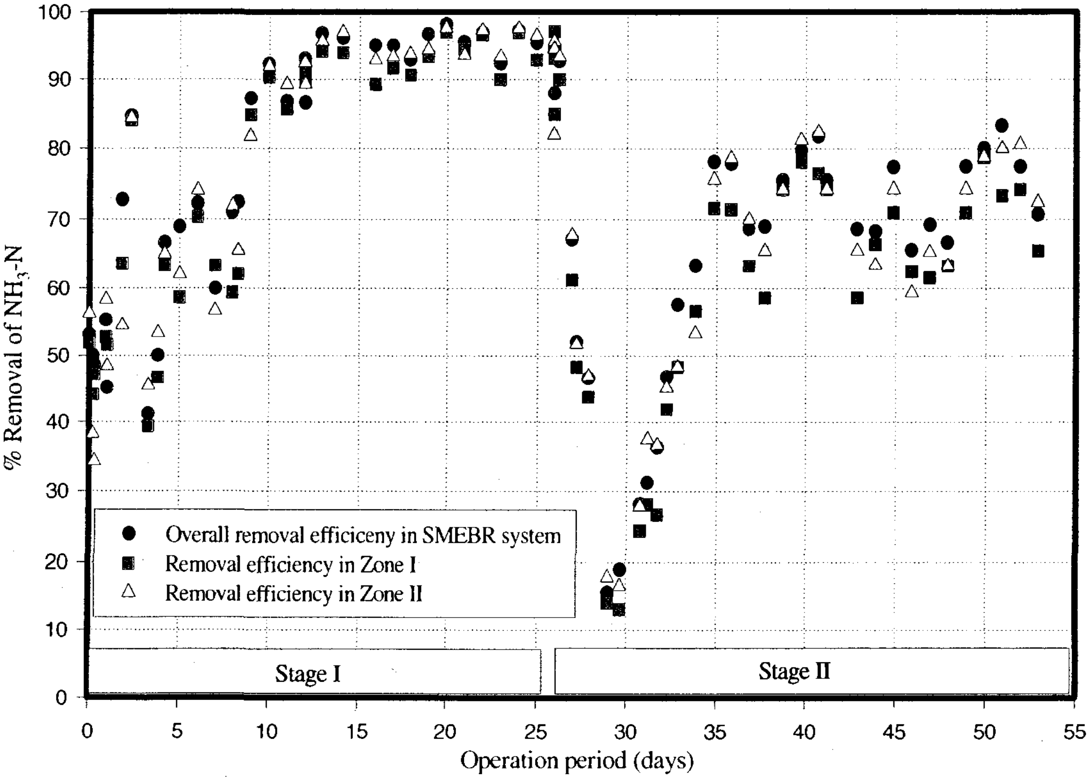


Figure 7.14 (b) Percentage removal of NH_3-N concentrations in the SMEBR system during the Phase II

The concentrations of NH_3–N in the effluent fluctuated in each stage. In Stage I (DC = 0 V/cm), the concentrations of NH_3–N in the effluent decreased from 23 mg/L during the first operation to below 0.9 mg/L at the end of Stage I.

The removal efficiency of NH_3–N began with 37 % and stabilized at around 97% at the end of Stage I. The lower percentage removal efficiency of NH_3–N during the first operation was attributed to the lower growth rate of nitrifying bacteria because these bacteria need more time to establish and reach sufficient concentrations to nitrify the ammonium (Rosenberger et al., 2002).

When Stage II started (DC = 1 V/cm, exposure time = 15 minutes ON / 45 minutes OFF), the concentrations of NH_3–N in the effluent increased from 0.9 mg/L to 3.5 mg/L during one day (day 26). On day 28, the concentration of NH_3–N in the effluent increased dramatically to 23.7 mg/L which reflected a poor oxidation of ammonia nitrogen in the elector-bioreactor which may be caused by greater sensitivity of nitrifying bacteria to the applied DC field. In other words, the rapid increase in the NH_3–N concentrations in both zones and in the effluent when the SMEBR system exposed to a DC field indicates that the nitrifying bacteria is very sensitive to an applied DC field. This suggests that accumulation of iron in the electro-bioreactor could give rise to the severe inhibitory effect on the activity of nitrifying bacteria (Lees et al., 2001; Clark and Stephenson, 1998).

The effect of applying a DC on the metabolism of bacteria was area of research for many investigators (Alshawabkeh et al., 2004; Li et al., 2001; Jackman et al., 1999; Sakakibara and Kuroda, 1993; Mizuno and Hori, 1988). For example, Li et al. (2001) investigated the inhibition of the metabolism of nitrifying bacteria by applying direct electric currents. They used stainless steel electrodes material in their study. At different operating conditions, they found that the metabolism of nitrifying bacteria was inhibited when the applied current was above 2.5 A/m^2. In this study, the average applied current density was between 37.6 and 57.7 A/m^2 (see section 7.5.6) which is greater than 2.5 A/m^2, then, it might significantly reduce the metabolism of nitrifying bacteria.

Consequently, to understand the effects of iron itself on the bacteria culture in activated sludge treatments, we have to refer to a study conducted by Carter and McKinney (1973). They suggested that although iron forms precipitates rapidly that are no longer available to microorganisms in soluble form, the iron precipitate coats particles such as bacteria. If too much iron is added, the iron precipitate forms a barrier that would tend to block the transfer of nutrients into the microorganism.

In another study by Geradi (1986), he reported that soluble metal ions complex with anionic functional groups of extracellular polymers suppressed the respiration and metabolism of bacteria. Once inside the cell, they can block the enzyme systems (Carter and McKinney, 1973), interfering in this way with the metabolism of microorganisms. Furthermore, an adsorption of metal ions onto extracellular ligands is maximized when the MLSS solution's pH is between 6.0 and 8.0 (Geradi, 1986); this corresponds to the pH range inside the electro-bioreactor of the SMEBR system during Stage II of Phase II. The above discussion might explain the rapid decrease in ammonia oxidation performance after applying the DC field in the MLSS solution. However, the concentration of NH_3–N in the effluent decreased again with operating time until it reached 2.1 mg/L at the end of Stage II where the NH_3–N removal efficiency was above 93%. According to a study reported by Maillacheruvu and Alshawabkeh (2000) on the effect of DC fields greater than 1.5 V/cm and up to 6 V/cm on the behavior of an unacclimated mixed anaerobic culture. The results established that the bacteria's activity was reduced within the DC fields limits, but the cultures were able to recover their activity within 24 h. During the operation period, no obvious NH_3–N concentration difference between the elector-bioreactor supernatant in the two zones and the membrane effluent were observed, which implied that NH_3–N removal was mainly accomplished by the electro-bioreactor. This might be due to the fact that the NH_3-N molecule was too small to be cut off by the membrane module (Huang et al., 2001).

To further confirm the impact of the SMEBR operation on the nitrification process, another indicator, the nitrate nitrogen (NO_3-N) concentration in the effluent is presented with the concentration of NH_3–N in Figure 7.15. The nitrification rate in the reference stage (the Stage I) was observed during the starting stages. Although the nitrification rate was insignificant during the first five days (39%-70%) as shown in Figure 7.14 (b), the oxidation of ammonia to nitrate increased up to greater than 97 % at the end of the Stage I. When DC was applied in the SMEBR system, the nitrification rate decreased in the Stage II and it fluctuated around 70 % (Figure 7.14 (b)).

Nitrite nitrogen (NO_2-N) was not detected during the whole operation period of the SMEBR system suggesting that the nitrification was the major process in the SMEBR system.

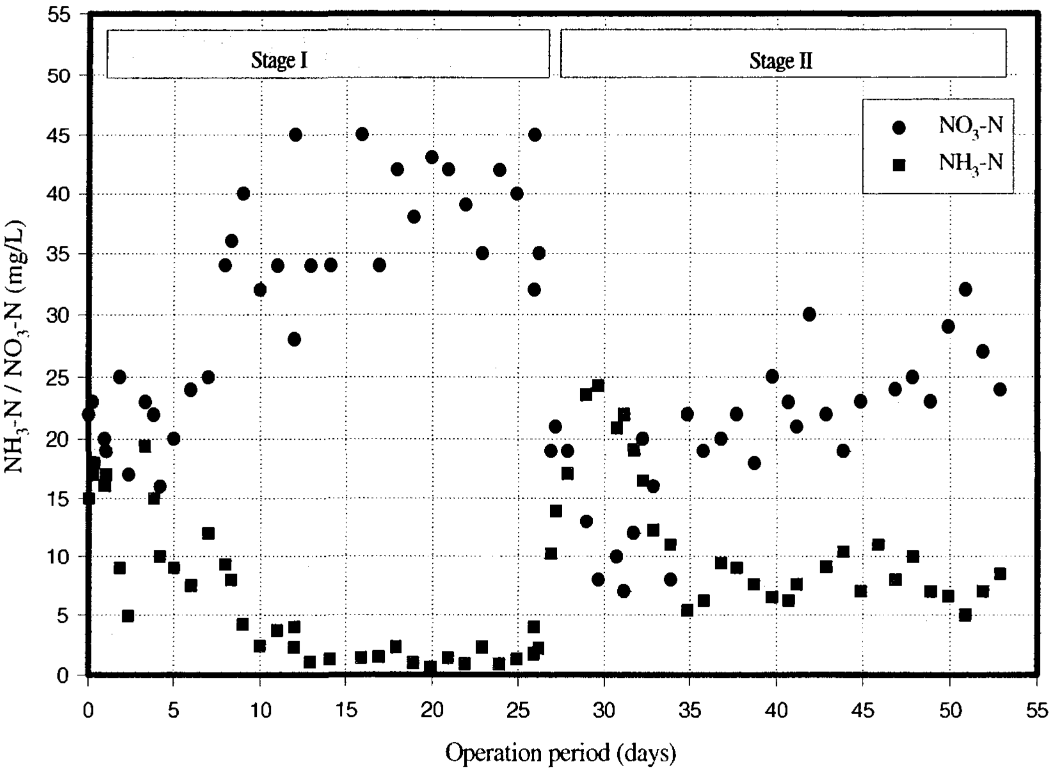


Figure 7.15 Changes in NH_3-N and NO_3-N concentrations in the effluent SMEBR system during the Phase II

7.5.5.3 Phosphorous Removal Performance

Reducing the phosphorous concentration in the effluent streams is a main target in the environmental engineering sciences because excess phosphorus concentrations in the effluents of municipal or industrial plants discharged in the environment is the main cause of the eutrophication phenomenon (Sommariva et al., 1997).

As mentioned in Chapter 1 of this thesis, one of the main objectives of designing the SMEBR system was to enhance phosphorous removal in wastewater treatment plants. The principal phosphorus compounds in wastewater are generally orthophosphate (PO_4-P) forms together with smaller amounts of organic phosphate (İrdemez et al., 2006).

With reference to the result of Phase II of this research, the variations of orthophosphate (PO_4-P) concentration in the influent, the supernatant in the bioreactor's zones and the membrane effluent are presented in Figure $7.16_{(a)}$.

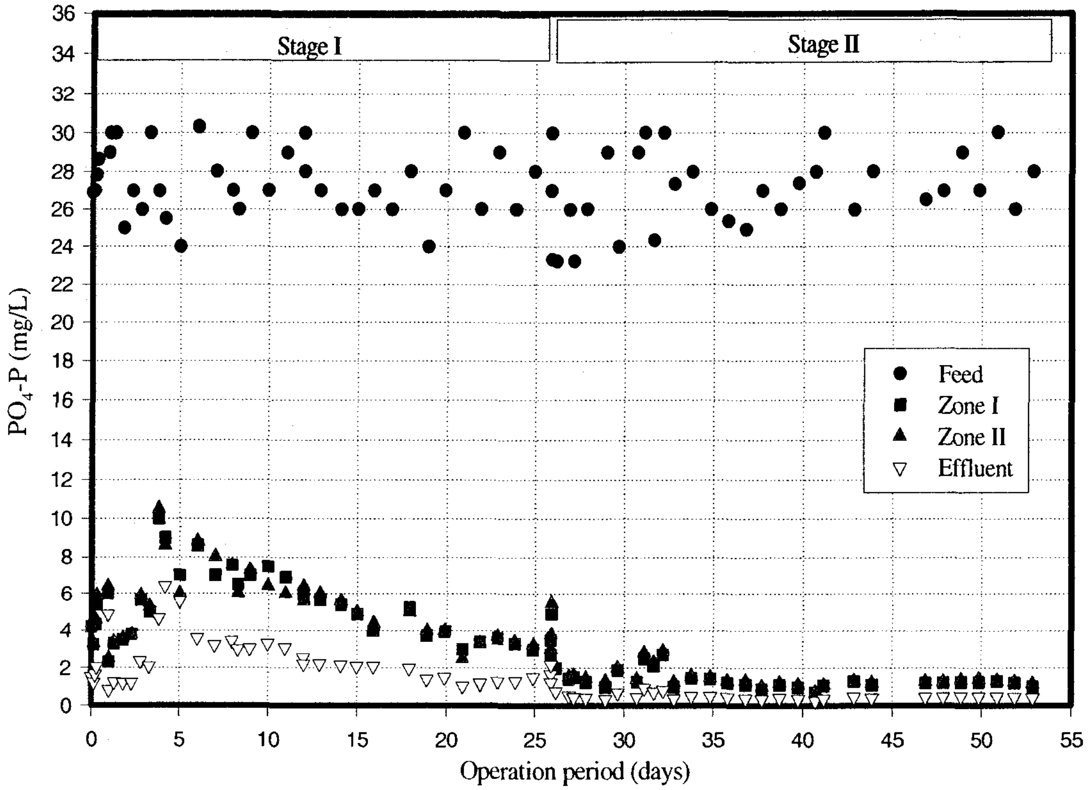


Figure 7.16 (a) Changes in PO_4-P concentrations in the SMEBR system during the Phase II

Figure 7.16$_{(b)}$ presents the corresponding removal efficiency of PO_4-P in both zones of the electro-bioreactor and for the overall SMEBR system. The influent phosphorus as orthophosphate (PO_4-P) varied from 23 to 30.5 mg/l with an average of 26.5 mg/L. the concentrations of PO_4-P in the effluent fluctuated between 0.82 and 8.14 mg/L in the first stage and reached less than 0.45 mg/l at the end of Stage II with an average of below 0.5 mg/L. The lower uptake in phosphorus concentration during the first period of operation of the Stage I was expected due to the low concentration of the MLSS solution in the electro-bioreactor. Further increase in MLSS concentration in the electro-bioreactor enhanced the phosphorus uptake in Stage I.

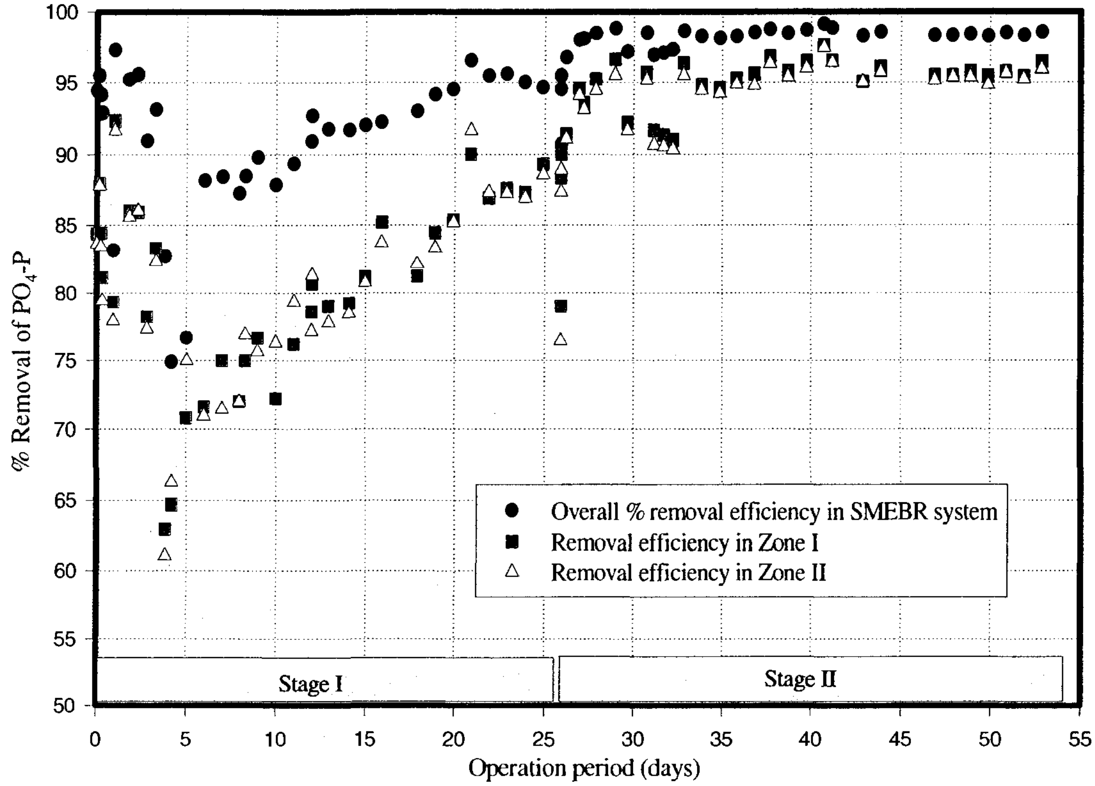


Figure 7.16 (b) Percentage removal of PO_4-P concentration in the SMEBR system during the Phase II

Although the phosphorus uptake was lower at the initial period of Stage I (percentage removal between 87% and 93%), Figure $7.16_{(b)}$ shows that the SMEBR system had excellent PO_4-P removal performance and was made obvious in Stage II after applying the DC which then was over 98 % on average.

During the operational period of Phase II, a small difference in the concentration of PO_4-P was observed between the electro-bioreactor supernatants and the membrane effluent; it might be that the membrane module served as an adsorbent material for PO_4-P. Also, the experimental results demonstrated that during Stage I, with no application of DC, both concentrations of PO_4-P in the electro-bioreactor supernatants were similar to each other; however, after the DC application, some differences were observed between the concentrations of PO_4-P in the bioreactor's zones. The concentration of PO_4-P in Zone I was less than 2-3 % of the concentration of PO_4-P in Zone II. This was attributed to the coagulation phenomenon that occurred in Zone I. Since the dissolved iron concentration was expected to be higher in Zone I as a result of applying a DC field, the electrocoagulation process produced $FePO_4$ flocs in Zone I, and the phosphorous molecule will get a greater chance to react with the dissolved iron to form $FePO_4$. Alternatively, the phosphorous might adsorb into the floc formation and settle. However, such chances are less available for phosphorous molecules in Zone II. In general, the changes in PO_4-P concentrations during Stage II were as following:

PO_4-P (Permeate) < PO_4-P (Zone I) < PO_4-P (Zone II) < PO_4-P (Influent)

On the other hand, the formation and stability of $FePO_4$ is affected by the pH in each zone. The effect of the pH in the SMEBR system on phosphorous removal is further confirmed in the following subsection.

The results demonstrate that the overall PO_4-P removal efficiency varied between 75 % to almost 96% before applying DC, and increased to over 98.5% after applying the DC. The lower removal efficiency at the earlier operation in the Stage I was attributed to the long SRT. When MBR systems operate with minimum sludge removal, enhanced biological phosphorous removal would be limited in MBRs applications (Song et al., 2008; Adam et al., 2002). The increase in phosphorus removal at the end of Stage I might be attributed to rapid increase in the HRT and the decreased in F/M ratio (Section 7.5.6).

7.5.5.3.1 Effect of pH on Phosphorous Removal

It was reported when chemical flocculation-coagulation agents like iron salts are added to phosphorus present in the water, $FePO_4$ forms in the low pH range (<6.5) and at higher pH range (>6.5) iron increasingly convert to oxides and hydroxides (İrdemez et al., 2006). Jiang and Graham (1998) reported that the addition of Fe^{3+} salts to wastewater containing phosphorus forms a stable precipitates such $FePO_4(s)$ at a pH between 5 and 7. Consequently, the removal efficiency of phosphorous in the SMEBR system may have been affected by the changes of the pH values during the operation period.

In Phase II of this research, iron was supplied electrochemically to the mixed liquor solution which created metallic hydroxide flocs within the wastewater by electro-dissolution of the anode according to the theory described in section 7.3. In Figure 7.17, the removal efficiency of phosphorus was plotted against the pH in Zone I and Zone II during Stage I (where there was no application for DC field). While the pH varied between 6 and 7.45, the phosphors removal varied between 61% and 92%.

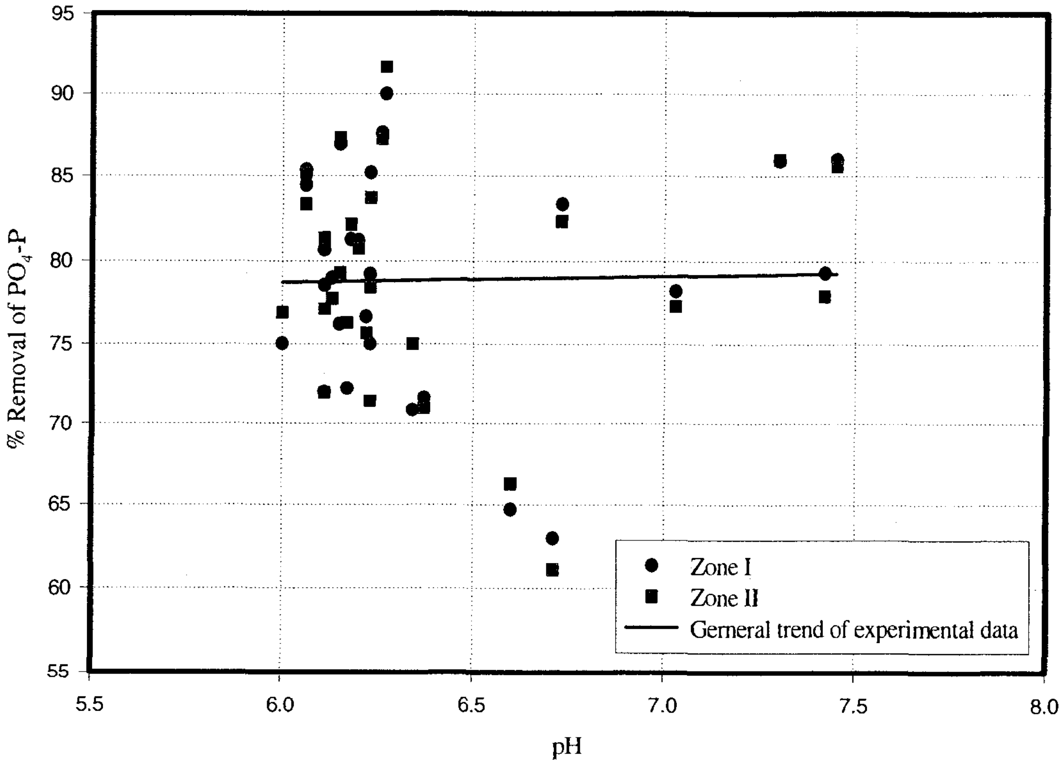


Figure 7.17 Effect of pH on phosphorous removal in the SMEBR system during the Stage I-Phase II

Because the DC power supply was turned off during the Stage I, no iron was supplied to the mixed liquor solution and the change in phosphorous concentration was attributed to the biological process in the electro-bioreactor. It is clearly shown from Figure 7.17 that the general trend of phosphorus removal was held constant during this stage.

During Stage II, the removal efficiency of phosphorous increased reflecting the impact of applying a DC field into the mixed liquor solution. As shown in Figure 7.18, the pH increased in both bioreactor's zones as a result of OH^- ions accumulation and the increase in the pH was more significant in the Zone II due to reasons discussed in section 7.5.3.1.

In spite of the increase in phosphorus removal during Stage II in comparison with Stage I, Figure 7.18 illustrates that the general trend of phosphorus removal decreases with increasing pH values in both zones of the electro-bioreactor. In order to understand this behavior, the mechanism of reducing phosphorous by electro-coagulation process should be highlighted.

According to the study reported by Yu et al. (2005) on phosphorus removal by electrocaogulation, the main reactions that can occur during the electro-coagulation process are as following:

Reaction at the anode:

$$Fe\,(s) \Longrightarrow Fe^{2+} + 2e^- \qquad (7.17)$$

Reaction in the bulk solution:

$$Fe^{2+} + \tfrac{1}{2}\,O_2 + \tfrac{1}{2}\,H_2O \Longrightarrow Fe^{3+} + OH^- \qquad (7.18)$$

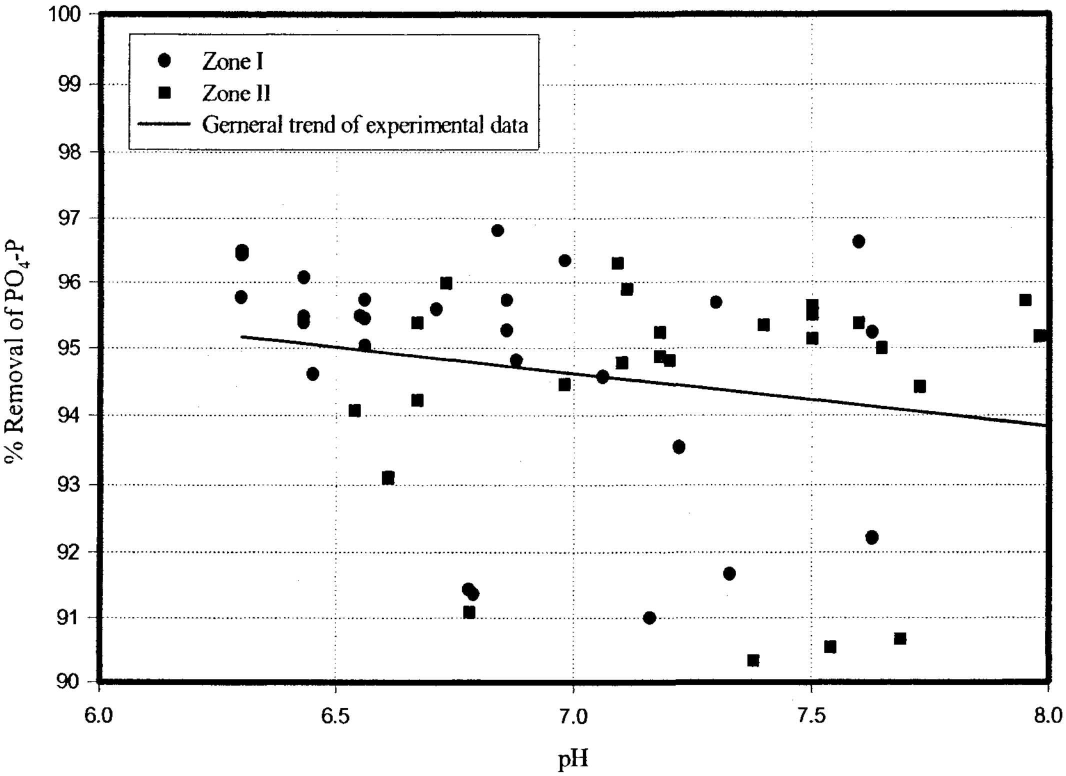


Figure 7.18 Effect of pH on phosphorous removal in the SMEBR system during the Stage II-Phase II

Fe^{3+} reacts rapidly with phosphorus according to the following equation:

$$Fe^{3+} + PO_4^{3-} \Longrightarrow FePO_4 \quad (7.19)$$

Theoretically one to one Fe/ P molar ratio will be required if only the above reactions occur (Yu. et. al., 2005). However, Fe^{3+} reacts rapidly not only with phosphate, but also with hydroxyl ions to form $Fe(OH)_3$ during the reactions; as a result, the actual Fe/P ratio will be different. Therefore, the molar ratio of added Fe^{3+} to P can generally be greater than 1:1 to achieve efficient phosphorus removal. This can be another advantage of the SMEBR system in which the supplied dosage of iron ions can be regulated by controlling the exposure time to a DC field.

7.5.6 Impact of the Volumetric Loading on the SMEBR Performance

Changing in volumetric loading affects the performance of wastewater treatment plants. For example, changing in the organic loading rate (OLR) has significant relation with feed concentration and hydraulic retention time (HRT). In general, short HRT can induce large OLR. Thus, HRT is a very important operating parameter in MBR systems, which correlated not only to the treatment efficiency of the MBR systems (Meng et al., 2007), but to the characteristics of biomass in an activated sludge system (Cho et al., 2005; Yoon et al., 2004).

Because the SMEBR system was operated on the basis of constant pressure and varying flux, which forced a fluctuation in HRT during the experimental stages (Figure 7.4), COD, NH_3-N and PO_4-P volumetric loading to the system changed continuously (dropping between cleaning events and suddenly increasing after cleaning events) as shown in Figures 7.19, 7.20 and 7.21. These trends might have impact on the removal efficiencies and distorting the microbiological picture within the electro-bioreactor.

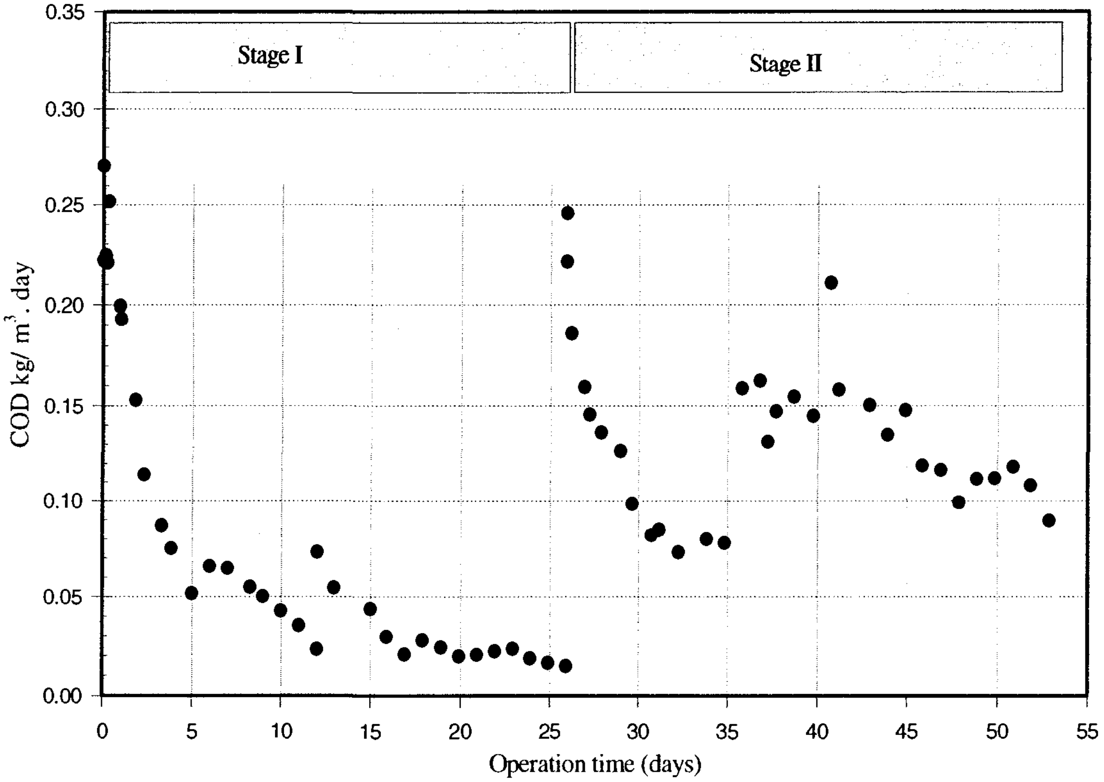


Figure 7.19 Changes of organic loading in the SMEBR system during the Phase II

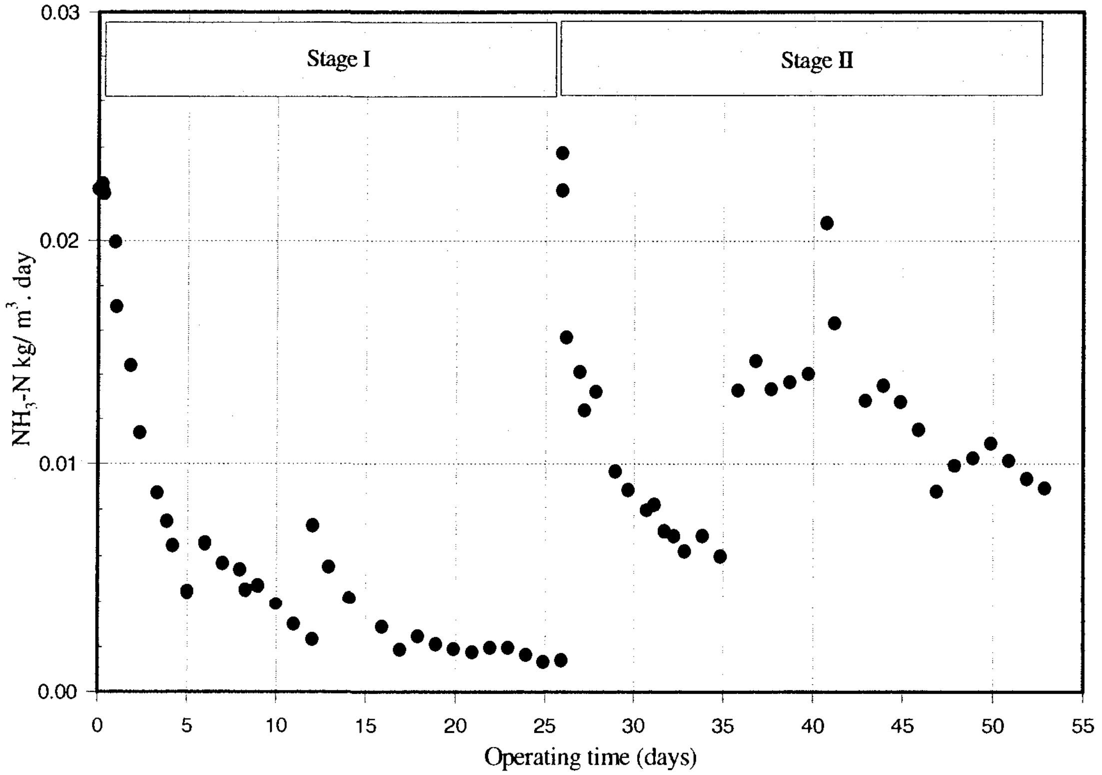


Figure 7.20 Changes of NH_3-N loading in the SMEBR system during the Phase II

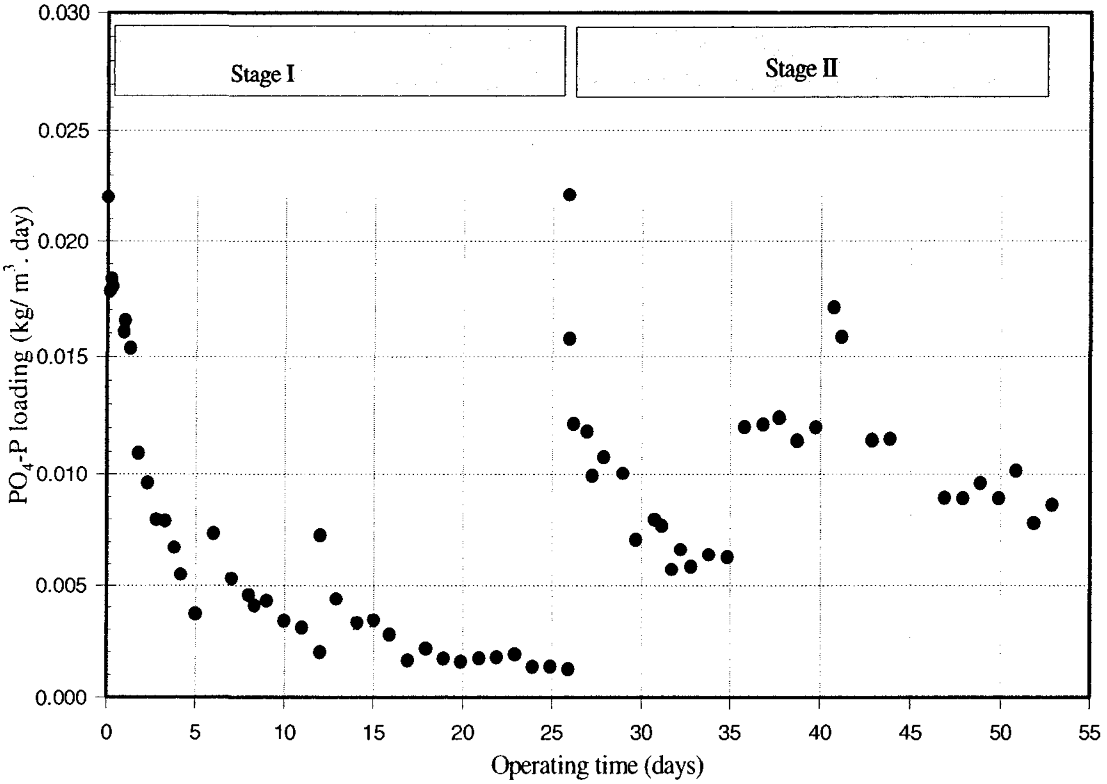


Figure 7.21 Changes of PO_4-P loading in the SMEBR system during the Phase II

It is clearly shown from the above figures that the loading rate is strongly affected by the fluctuation in the HRT. On the other side, the fluctuation in the HRT affects the food to microorganism's ratio. Figure 7.22 shows the development of F/M ratio in SMEBR system during the operation period. The *F/M* ratio is defined as:

$$F/M = (\frac{S}{HRT \times X}) \tag{7.20}$$

where S is the influent COD concentration (kg/m^3), HRT is the hydraulic retention time of the elector-bioreactor (day) and X is the MLSS concentration (kg/m^3).

Figure 7.22 shows that F/M ratio decreased rapidly from 0.11 to 0.007 in Stage I which could be attributed to the rapid increase in hydraulic retention time during this stage.

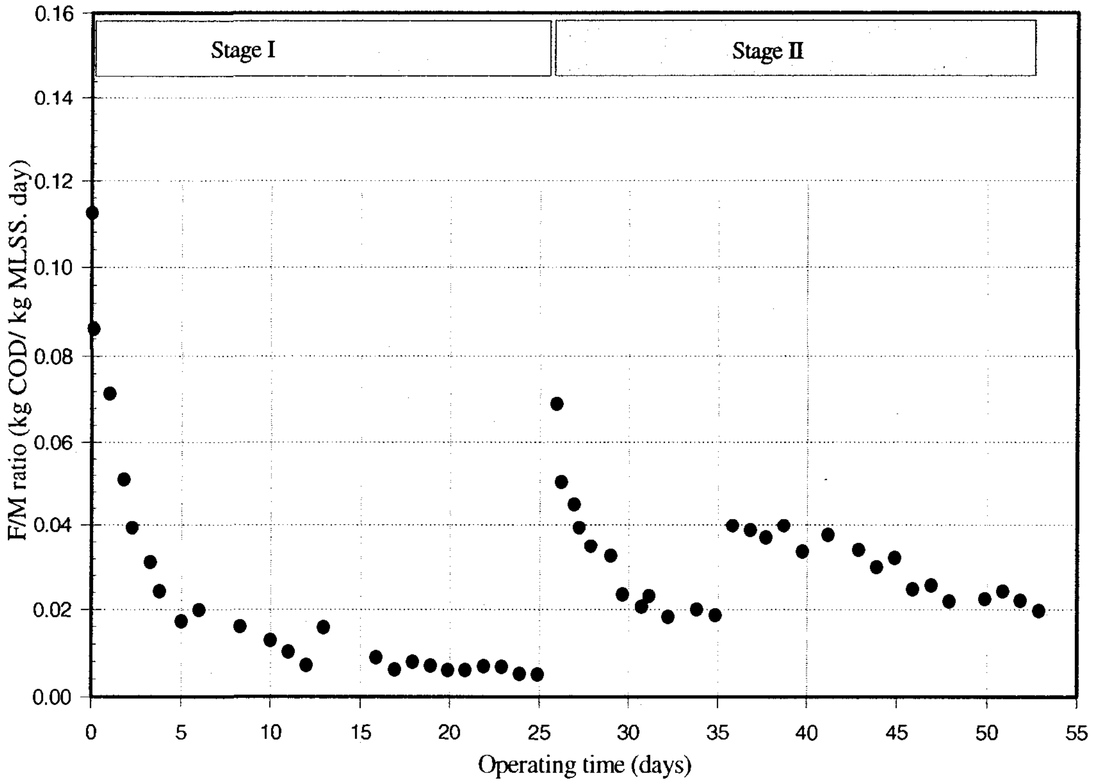


Figure 7.22 Development of the F/M ratio in the SMEBR system during the Phase II

The F/M ratio increased to 0.069 at the beginning of Stage II, and decreased to 0.019 on day 35, then it increased to 0.04 on the same day due to the washing of the membrane which increased the flux permeate and decreased the hydraulic retention time. At the end operation of stage II, the F/M ratio stabilized around 0.02.

According to the literature, different values were obtained for F/M ratio. For example, Yamamoto et al. (1989) obtained 0.1 kg COD/ kg MLSS day^{-1} for synthetic waste water. Muller et al. (1995), who worked with domestic waste water, observed only 0.021 kg COD kg^{-1} MLSS day^{-1}. This phenomenon of various F/M ratios may be due to different feed compositions and microbial populations. It is possible that there are shifts in the population which are induced by changes in the operating conditions (Rosenberger et al., 2002). In this study, a long HRT might lead to relatively low F/M values.

For further analyzing the impact of volumetric loading on the overall performance of the SMEBR system, the overall removals of organics, ammonia nitrogen and ortho-phosphorous were plotted versus the variations in loading as shown in Figures 7.23, 7.24 and 7.25 respectively.

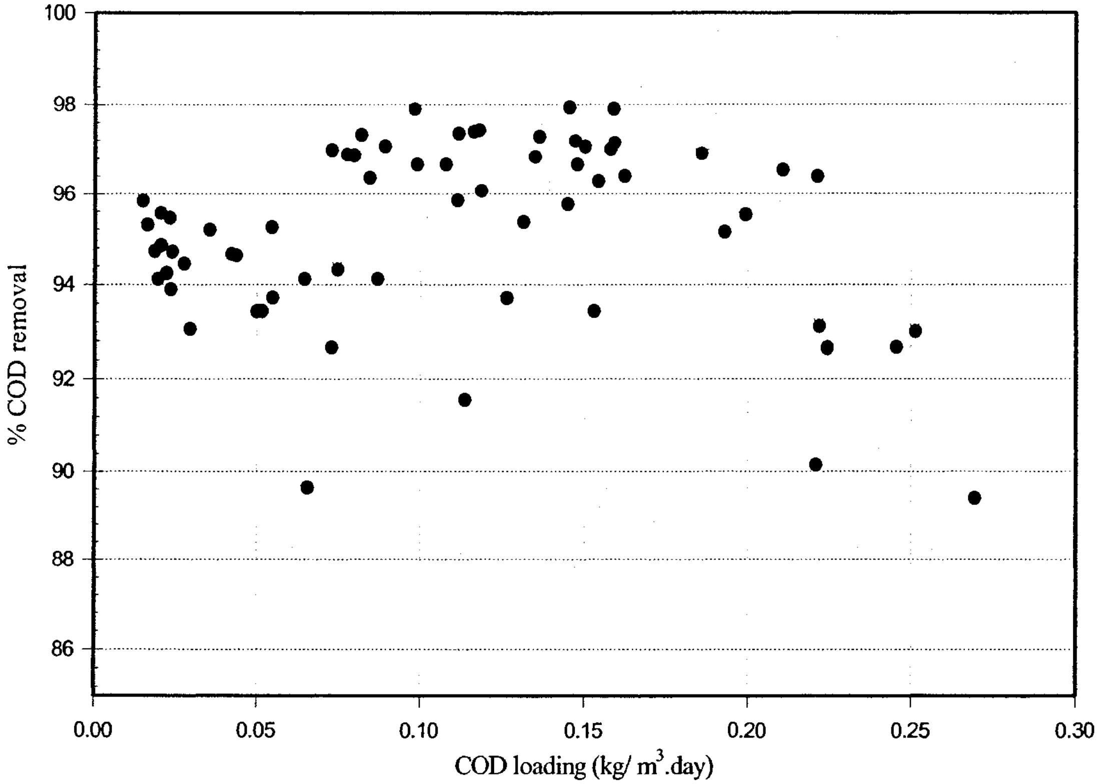


Figure 7.23 Overall COD removal versus organic loading in the SMEBR system during the Phase II

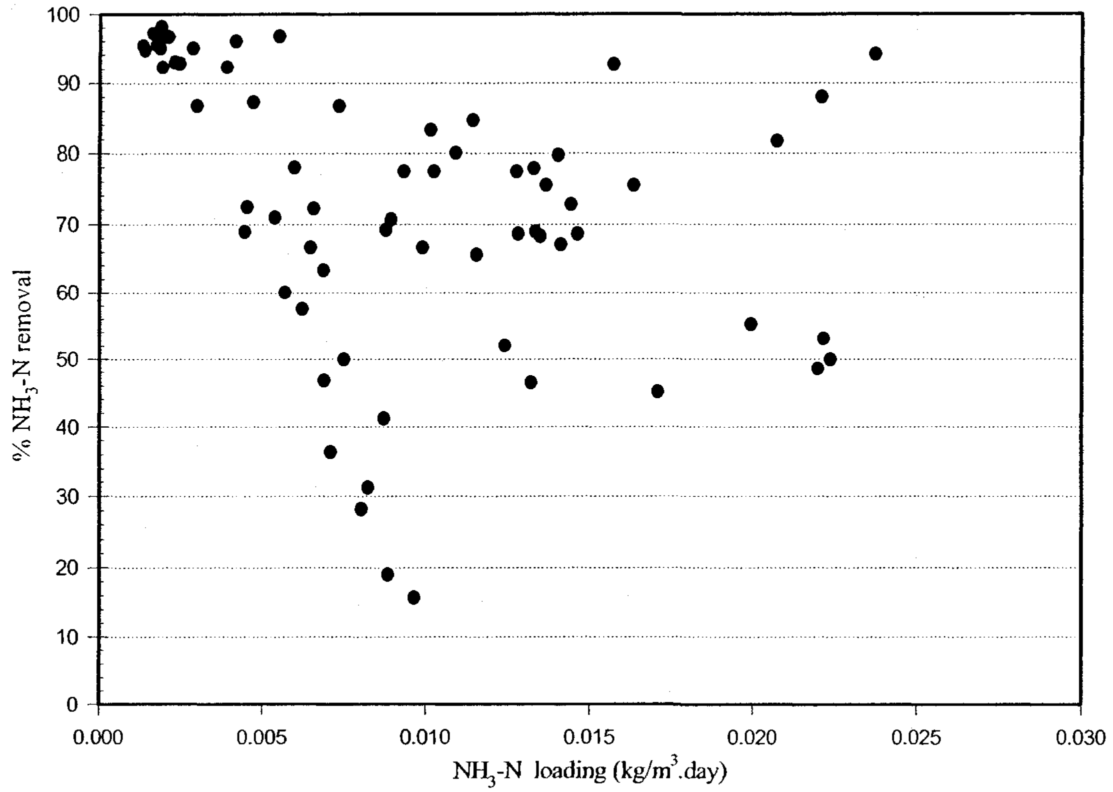


Figure 7.24 Overall NH_3-N removal versus ammonia-nitrogen loading in SMEBR system during the Phase II

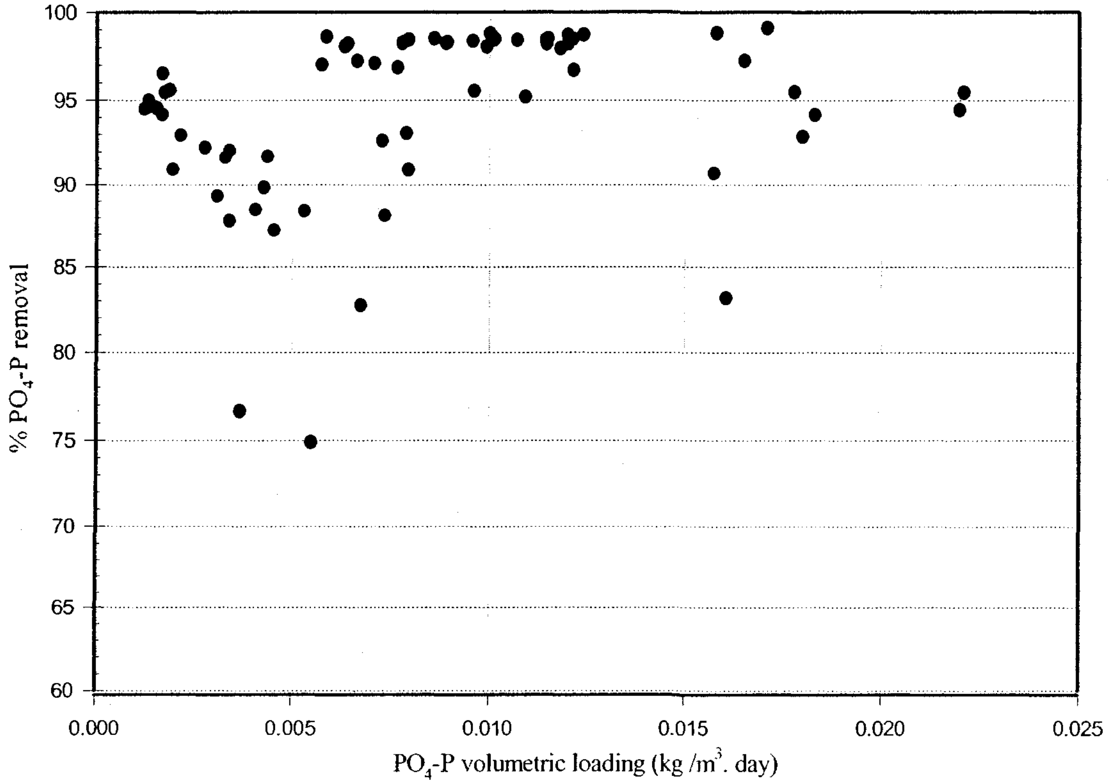


Figure 7.25 Overall PO_4-P removal versus ortho-phosphrous loading in SMEBR system during the Phase II

The above Figures (7.23 – 7.25) do not show any systematic trends, which would be concluded that the overall performance of SMEBR is independent on loading value. To get more vision about the effect of the HRT variations, the overall removal efficiencies in the SMEBR system were plotted against the change in the HRT in each stage as shown in Figures 7.26, 7.27 and 7.28.

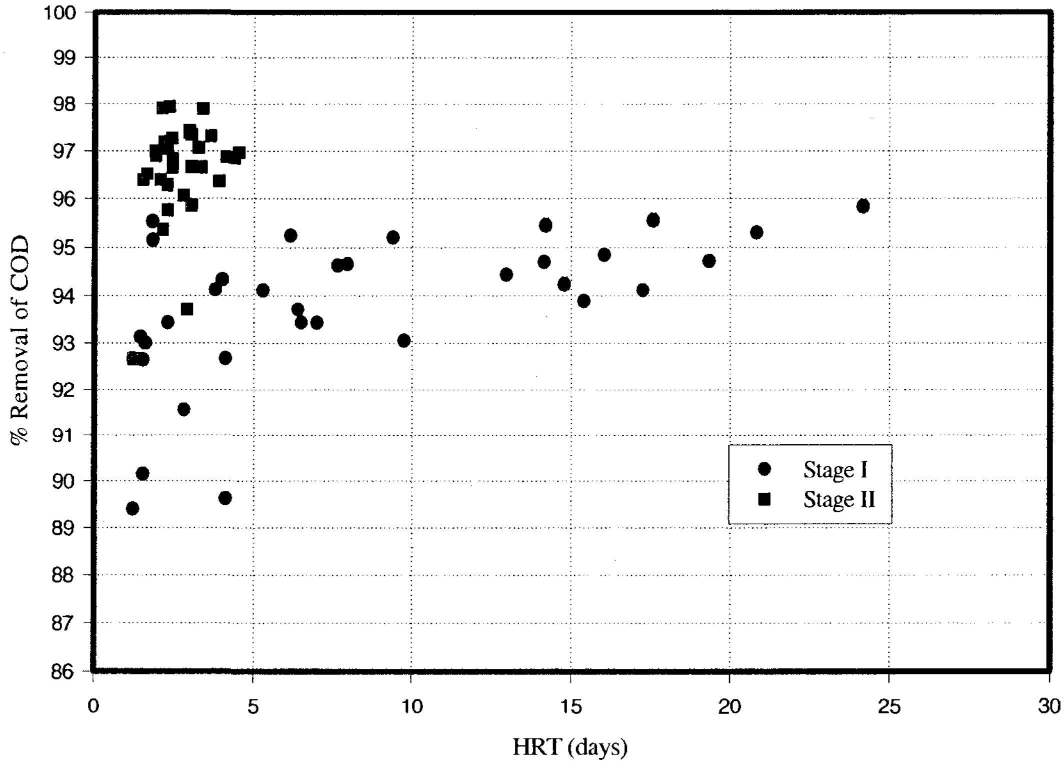


Figure 7.26 Overall COD removal versus HRT in the SMEBR system during the Phase II

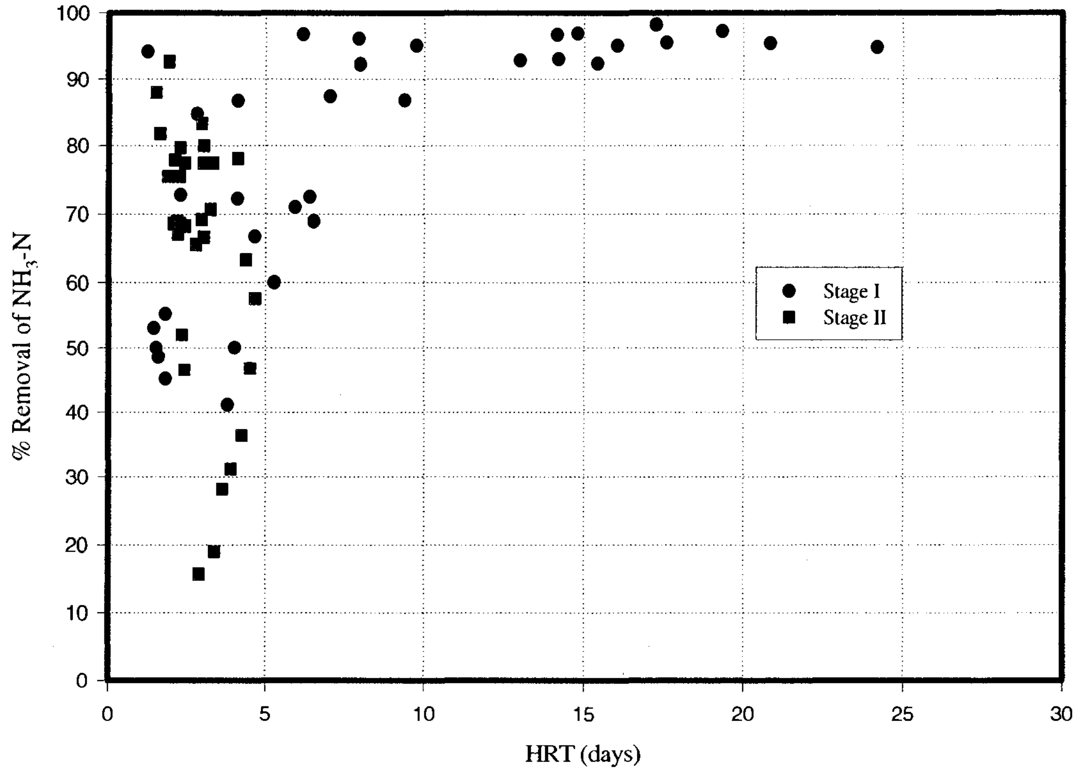


Figure 7.27 Overall NH_3-N removal versus HRT in the SMEBR system during the Phase II

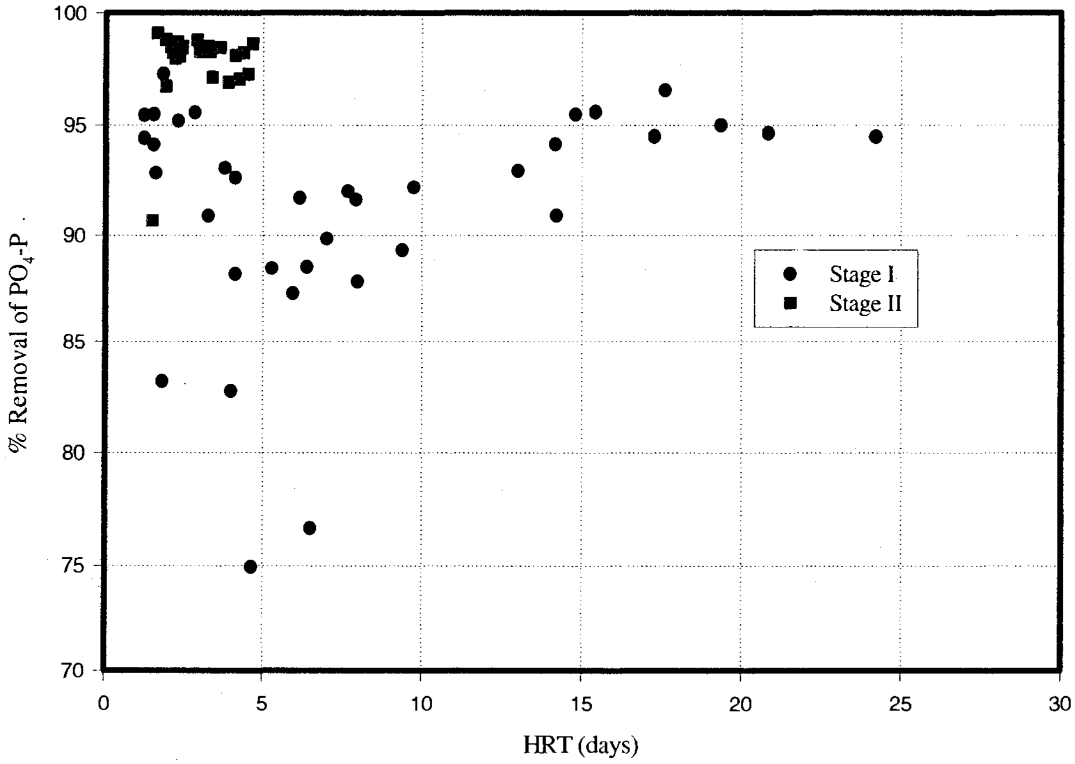


Figure 7.28 Overall PO_4-P removal versus HRT in the SMEBR system during Phase II

Figures 7.26, 7.27 and 7.28 show that the removal efficiencies of COD, NH_3-N and PO_4-P are affected by the fluctuation of the HRT during Stage I (where no DC was applied). However, these figures demonstrated that in Stage I, when the HRT was less than 5 days, the removal efficiency was less dependent on the HRT. This is in agreement with the study conducted by Tay et al. (2003) about the effects of hydraulic retention time on system performance of a submerged membrane bioreactor with a prolonged sludge retention time, which simulate the conditions of SRT in this research. They reported that for six runs at a lab scale (with HRTs of: six days, three days (two runs), one day, 12 hours, and 6 hours), the SMBR was capable of achieving over 90% COD removal, almost independently of HRT. In comparison of this research with Tay's et al. (2003) study, it seems that the performance can be affected rather by high HRTs (5 days in this research).

During the Stage II, the removal efficiencies of COD, and PO_4-P were less dependent on the variation in the HRT. The reasonable explanation for that might be due to two reasons: i) applied DC field improved the permeate flow rate and reduced the impact of fluctuation in HRT; the HRT did not exceed 5 days during Stage II (Figure 7.4), ii) due to electrocoagulation process itself, which occurred within the electro-bioreactor; this phenomenon made a continuous production of flocs, and able to deal with the sudden increase in the volumetric loading of COD and PO_4-P. This means that the designed SMEBR system can deal with sudden shocks in volumetric loading, which is considered as another advantage of the designed SMEBR system.

Moreover, Figure 7.27 demonstrated that the removal efficiency of the NH_3-N in Stage II was independent on HRT. The removal efficiency of the NH_3-N was within the range of 13 % to 93%. Consequently, decreasing in removal occurred in Stage II could be rather related to the sensitivity to DC field as explained in section 7.5.5.2.

7.5.7 Change in Electrical Parameters

The efficiency of implementing EC process in wastewater treatment depends on the physical/chemical proprieties of the wastewater treatment (Kobya et al., 2006). Among of these parameters, the conductivity of the solution plays important role in EC efficiency. In Phase II of this research, the direct DC field was constant during the period of operation of the SMEBR system during stage II (Voltage gradient = 1 V/cm), while the current density throughout the MLSS solution changed with time as a result of changes in wastewater properties. Figure 7.29 shows how the current density fluctuated during the contribution of a power supply. The current density was 60.5 A/m^2 at the beginning of Stage II (on day 26); after the next few days, it was fluctuated around 53 A/m^2. After that period, the current density started to decrease with time.

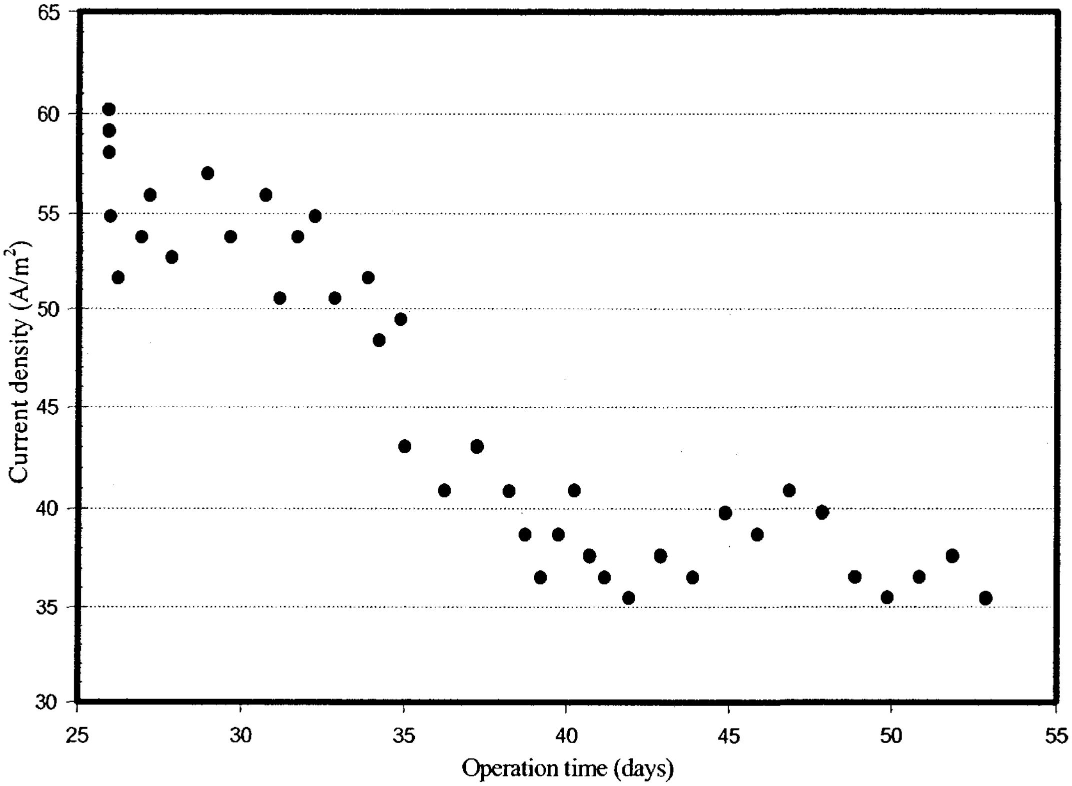


Figure 7.29 Changes of the current density in the SMEBR system during the Stage II of the Phase II

This could be attributed to the faster corrosion of the anode material. Since the anode was made of very soft iron, it acted as a sacrificial electrode. Consequently, the effective surface area available for electro-coagulation process was reduced with time. Also the reduction of the anode surface area might have affected the distribution of the current field throughout the MLSS solution in the electro-bioreactor. However, the average value of the current between the starting of Stage II and the day 35 was 0.5 A (Figure 7.29), which corresponds to a current density of 57.7 A/m^2. From day 35 to the end of the Stage II, the average current value was 0.36 A, which corresponds to a current density of 37.6 A/m^2.

7.5.8 Discussion on Other Impacts of the SMEBR System

7.5.8.1 Microbial Activity

Iron, as a nutrient in the activated sludge culture, is considered an essential element for the growth of microorganisms. It forms an important component of many of the enzymes involved in the metabolic pathways of bacteria (Philips et al., 2003, Jackson-Moss and Duncan, 1990).

However, if iron is present in more than trace amounts, it is generally considered to have properties of a toxic metal (De Freitas and Meneghini, 2001). It also may affect the floc characteristics of the activated sludge (Li, 2005). Iron salts may interact with other compounds in biological process as nitrate and nitrite and decrease or even inhibit the activity of nitrification/denitrification process (Philips et al., 2003) as it was observed in section 7.5.5.2.

In Phase II of this research, iron was supplied to the mixed liquor solution electrochemically by applying a DC field; this also may have adversely affected the microbial activity (Maillacheruvu and Alshawabkeh, 2000). Therefore, the specific oxygen uptake rate (SOUR) of the activated sludge was determined in each zone in order to know the effect of applying a DC field on microbial activity. The SOUR was considered to be equivalent to the overall metabolic activity of the sludge community. The SOUR was calculated from equation (4.32).

As shown in Figure 7.30, each time, after applying DC field in the mixed liquor, the SOUR decreased and microbial activity was weakened. However, the microorganisms were able to recover gradually their activity with time. Moreover, the results demonstrated that the weakness of the microbial activity was greater in Zone I of the electro-bioreactor; this was expected as the DC field was applied in Zone I, so the observed impact was more extensive in this zone.

Although the microbial activity was temporarily affected by the operation of the SMEBR system, it could be concluded that the change of microbial activity would not affect the treatment efficiency in terms of COD and phosphorus removal. While the effect of DC was more obvious on the microorganism bacteria, which are responsible for the nitrification process, this case was observed when the ammonia concentration was increased in the electro-bioreactor after applying DC field. However, not only can an applied DC field decrease the microbial activity, but also the long SRT can be seen to have a negative impact on the activity of the microorganism (Lim et al., 2007; Khor et al., 2006).

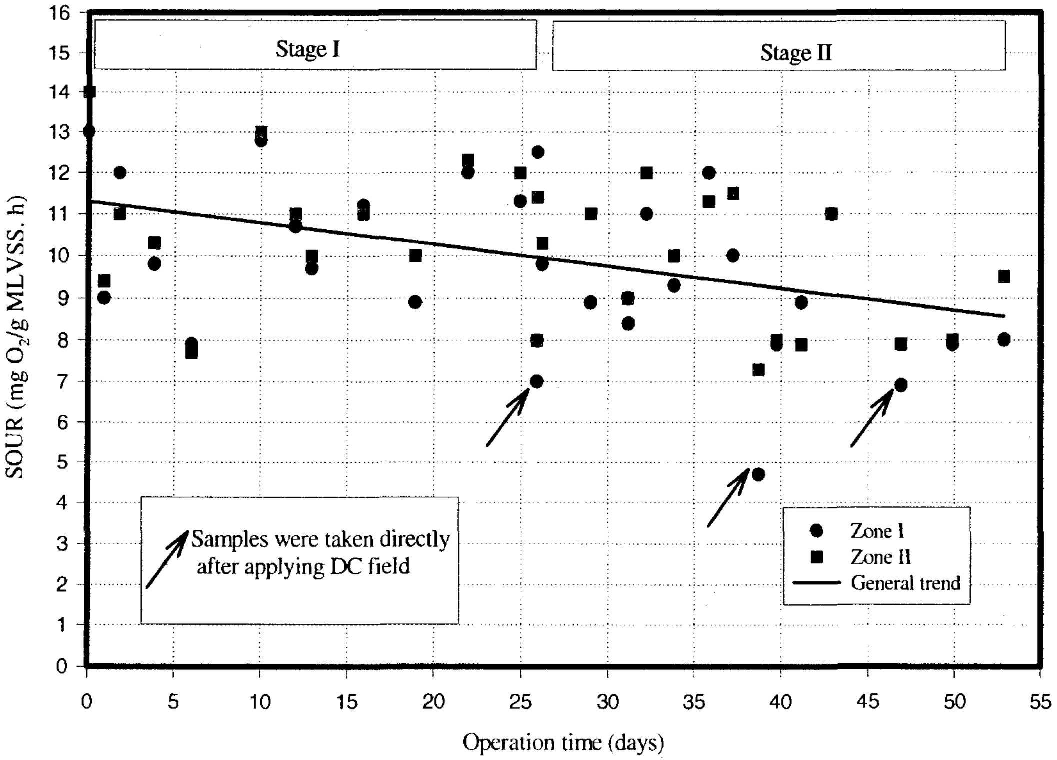


Figure 7.30 Changes of SOUR with operating time during the Phase II

7.5.8.2 Impact of the SMEBR Operation on Electrodes

Applying a direct current (DC) field in a mixed liquor suspended solids with iron electrodes resulted in the following observation, which can reduce the overall efficiency of the SMEBR system:

- Due to the soft iron material used as an anode, iron was corroded as a sacrificial electrode; subsequently, the mixed liquor solution color changed with time as described in sections 7.5.1 and 7.5.3.1. This situation might require further treatment. Studies on other material for the anode are recommended.
- The phenomenon of electrocoagulation in the designed SMEBR system may lead to the formation of a ferrous oxide layer on the cathode with time. This phenomenon may require a systematic washing of electrodes to keep the SMEBR operation efficiency at the desired level.

7.6 Conclusions

In the Phase II of this research, the impact of using cylindrical tube iron mesh on the performance of the designed SMEBR was investigated in terms of membrane permeability, organic removal, and nutrient removal. The following conclusions were drawn:

- The effluent, after the SMEBR treatment of synthetic wastewater, demonstrated, on average: i) 96% removal efficiency for COD; ii) 70% removal for NH_3-N; and iii) 98% removal for phosphorous. The effluent had no color and no odor. Furthermore, the applied DC enhanced the membrane filterability on average by 16.6 % without any backwashing of the membrane module.

- Iron anode worked as a sacrificial electrode and the mixed liquor solution color changed with time (greenish first, and then turned yellow and turbid). It was recommended to carry out the next phase with aluminum anode.

Chapter 8

Phase III: Performance of the Submerged Membrane Electro-Bioreactor (SMEBR) System with Aluminum-Iron Electrodes

8.1 Summary

This chapter presents Phase III of the experimental work of this thesis. It highlights the overall performance of the SMEBR system when a perforated cylindrical aluminum sheet was used as the anode while the cathode was made of a perforated cylindrical iron mesh (the same one used during Phase II). The operational period of this phase was divided into four sequential stages and extended for 66 days.

i) The Stage I lasted 33 days without the input of DC (reference stage).

ii) The objective of the Stage II, which extended for 7 days, was to investigate the performance of the SMEBR system when the DC is applied to the MLSS solution in conjunction with the operation of the membrane module. The mode 15 minutes ON /45 minutes OFF was used during the DC supply.

iii) The Stage III continued for 17 days after washing the membrane to recover its permeability. The mode of operation of the DC was the same as in Stage II.

iv) The Stage IV lasted for 9 days and the SMEBR system was operated with 15 ON / 105 OFF as a new mode of DC supply.

The output results from the Phase III showed that operating the SMEBR system with aluminum as an anode enhanced the membrane permeability up to 21.3 % on average for the mode of operation with15 minutes ON / 45 minutes OFF and 52.5 % for the mode of operation 15 minutes ON / 105 minutes OFF indicating that operational mode of DC supply is a key parameter in the SMEBR system. Furthermore, the results showed that a better performance of the SMEBR system can be achieved if the DC field is applied into the mixed liquor solution before immersing the membrane module into the electro-bioreactor. The electro-bioreactor needs a few minutes to establish coagulation process within the mixed liquor solution.

Furthermore, the SMEBR system did significantly improve the removal of COD and phosphorus. The overall removal efficiency for COD was greater than 96% and greater than 98% for phosphorus. In conjunction, the removal of NH_3-N was 70%.

8.2 Introduction

In the Phase II of this research (Chapter 7), the performance of the designed SMEBR system was investigated using iron as the electrodes materials. In the experimental Phase III, the performance of the SMEBR system was analyzed by replacing the iron anode with aluminum.

Throughout the literature, aluminum was added as a chemical flocculation-coagulation agent to improve the membrane filtration performance in submerged membrane bioreactor applications. The main objective of Phase III in this research was to investigate the performance of the designed SMEBR system by using perforated cylindrical aluminum sheet as anode with the central location of the membrane module.

This is the first time where aluminum was supplied to the mixed liquor activated sludge using the electrochemical phenomenon of applying a DC field into a mixed liquor suspended solution to enhance the membrane filtration. Another objective of this phase was to show the impact of DC field on the designed SMEBR performance.

8.3 Theory of Electrocoagulation by Aluminum

Section 4.3.2.2 of this thesis has already presented the theoretical background for electro-coagulation using aluminum.

8.4 Experimental Set-up and Methodology

The experimental set-up of Phase III is shown in Figure 5.3 and the operational process is described in details in Chapter 5 (section 5.4).

In Phase III of this research, the SMEBR was operated for 66 days. In this phase, a perforated cylindrical aluminum sheet was used as an anode while the cathode was produced with perforated cylindrical iron mesh (the same one was used in Phase II). The cathode was washed with tap water and immersed in diluted 1N nitric acid solution) for 8 h to remove any debris material potentially cumulated during the operation of Phase II. The cathode was then washed with tap water for 30 minutes before it was utilized in Phase III.

The activated sludge electro-bioreactor, with working volume 13.43 L, was fed with a synthetic wastewater as described in Table 5.2. The activated sludge had been acclimated to this synthetic wastewater for approximately two months to achieve stable conditions prior to the membrane filtration experiments. Inoculation of sludge was taken from a secondary clarifier in a municipal wastewater treatment plant in the city of Saint-Hyacinthe, QC, Canada. The initial characteristics of the sludge samples are listed in Table 5.4.

Constant level in the electro-bioreactor was maintained by monitoring sensor that controlled the feed pump. The SMEBR system was operated under continuous aeration to achieve organic pollutants removal and nitrification process. Dissolved oxygen concentrations were maintained between 5 and 8 mg/L in the electro-bioreactor's zones as described in Chapter 5.

The process was closely monitored for various parameters including the physical/chemical parameters: pH, temperature, MLSS, MLVSS, specific resistance to filtration (SRF), and zeta potential, as well as COD, ammonia nitrogen (NH_3–N), nitrate nitrogen (NO_3–N), nitrite nitrogen (NO_2–N) and orthophosphate (PO_4-P).

Phase III was divided into four stages: Stage I, which was considered the reference stage for comparison purposes, was extended for 33 days without input of DC. Studying the effect of DC on the physiochemical and biochemical properties on the MLSS solution could be achieved from the initial operation of the SMEBR system, but the main objective of extending this stage for 33 days was to give the ammonia nitrification bacteria a sufficient time to replicate, because nitrification bacteria require more time to establish themselves and to reach sufficient concentrations to nitrify the ammonium (Rosenberger et al., 2002). This also was confirmed by Stenstrom and Poduska's study (1980) where they reported that the growth rate of ammonia nitrifying bacteria is the single most important factor in achieving high rates of nitrification.

The impact of applying a DC field in the SMEBR performance was studied in three sequential stages starting from Stage II. The objective of Stage II was to investigate the performance of the SMEBR system when a DC is applied to the MLSS solution in conjunction with the operation of the membrane module. The duration of Stage II was 7 days and the operating mode of the DC power supply was 15 minutes ON / 45 minutes OFF.

Stage III extended for 17 days and the operational mode of the DC power supply was the same as that in the Stage II. Stage IV lasted 9 days during which time a new mode of operation in terms of applying the DC was investigated. Table 8.1 shows the different conditions under which the process was run and monitored during Phase III.

During the whole operational period, no sludge was withdrawn from the electro-bioreactor, except for the purposes of analysis of the samples (conventional parameters analysis and SRF tests). Given these conditions, the SMEBR system can be considered to operate under the complete retention of the sludge. This assumption was also assumed when the samples withdrawn from a reactor is used exclusively for sampling analysis (Grelier et al., 2006). However, on average, about 350 mL /week of sludge volume was removed and not returned to the electro-bioreactor, corresponding to average sludge retention time (SRT) of 200 days.

In order to study the fouling degree accurately, the process was operated with a constant transmembrane pressure; this meant that the permeate flux decreased with time because of the fouling phenomenon. Moreover, no back washing for the membrane module was performed during the operation.

Table 8.1 Experimental conditions during the Phase III

Items	Stage I	Stage II	Stage III	Stage IV
Operation time (days)	33	7	17	9
SRT (days)	≈200	≈200	≈200	≈200
Continuous supply of air (DO (mg/L)	5-8	5-8	5-8	5-8
DC voltage gradient (V/cm)	0	1	1	1
DC exposure time (minutes)	0	15 ON / 45 OFF	15 ON / 45 OFF	15 ON / 105 OFF
Strategy of applying DC field	No DC	Simultaneously with operating the membrane module	Before and subsequent simultaneous operation with membrane module	Before and subsequent simultaneous operation with membrane module
Influent temperature (°C)	19-21	19-21	19-21	19-21

The surface of membrane module was washed with distilled water outside the electro-bioreactor for few minutes each time the permeate flux rate declined significantly in order to recover the membrane permeability. Furthermore, a constant air flow was also injected in proximity of the membrane module to reduce fouling and cake formation.

Methodologies of sampling collection and analytical methods used in Phase III were described in details in Chapter 5.

8.5 Results and Discussion

The SMEBR system had been operating for 66 days. A failure of the level switch on the 63th day resulted in the shut-down of the process for few hours in order to replace the sensor. Another failure in the level switch on day 66 resulted in another shut-down. The output results from Phase III are discussed with respect to the four stages according to the different operating conditions mentioned in Table 8.1.

8.5.1 Impact of the SMEBR Operation on Membrane Filtration Performance

Since the SMEBR system was operated under a mode of constant transmembrane pressure, the permeate flux (J) decreased with time due to the fouling phenomenon.

Figure 8.1 shows the ratio of permeate flux to initial water flux (J/J_i) during the period of membrane filtration of sludge suspension in the SMEBR system. Alternately, Figure 8.2 illustrates the corresponding percent reduction in permeate flux ($PRPF$) calculated from the following equation:

$$PRPF = (1 - \frac{J}{J_i}) \times 100\% \qquad (8.\ 1)$$

Where J_i is the initial permeate flux and J is the permeate flux at any time during Phase III. Furthermore, the hydraulic retention time (HRT) increased with time as a result of declined flux as shown in Figure 8.3. To assess the fouling behavior in the SMEBR system during the operational period of Phase III, the curves of Figures 8.1, 8.2 and 8.3 are divided into four stages:

- The Stage I: from day 1 to day 33;
- The Stage II: from day 33 to day 40;

- The Stage III:, from day 40 to day 57; and
- The Stage IV: from day 57 to day 66.

During Stage I, with no input of DC power, the permeate flux dramatically decreased in this first operation (Figure 8.1) which was expected due to fouling phenomenon. After 5 days of operation of Stage I, the PRPF was 80%. To enhance membrane permeability, the membrane was washed with distilled water for few minutes outside of the reactor when the (*J/Ji*) ratio reached between 0.2 and 0.3. The washing events during Stage I appear on the Figure 8.1 as peaks in the filtration performance curve on days 5, 11, 19, 23 and 28.

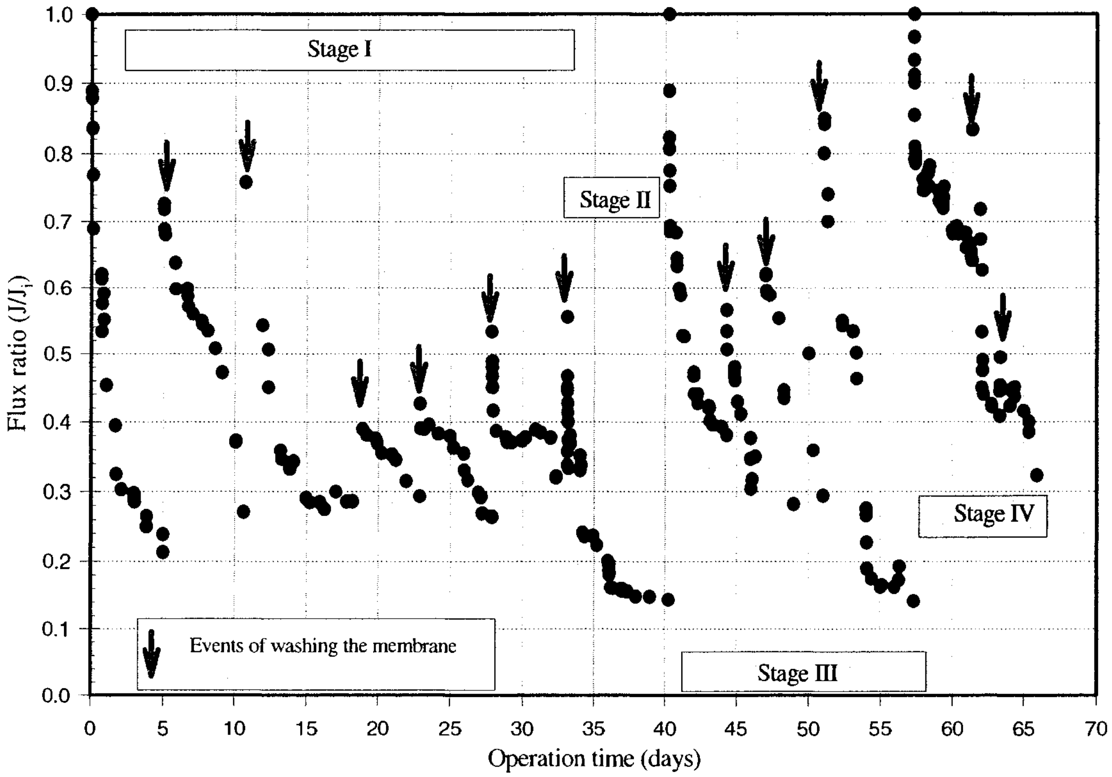


Figure 8.1 Changes of permeate flux with time in the SMEBR system during the Phase III

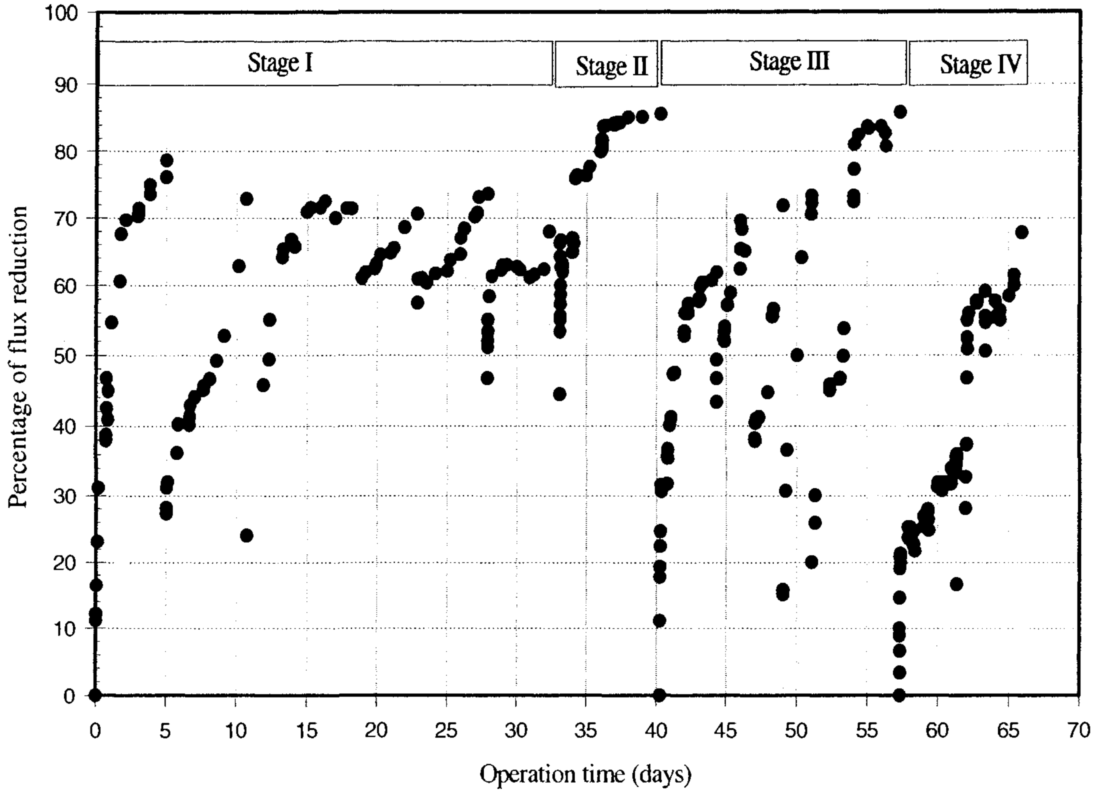


Figure 8.2 Changes of the percentage reduction in permeate flux in the SMEBR system during Phase III

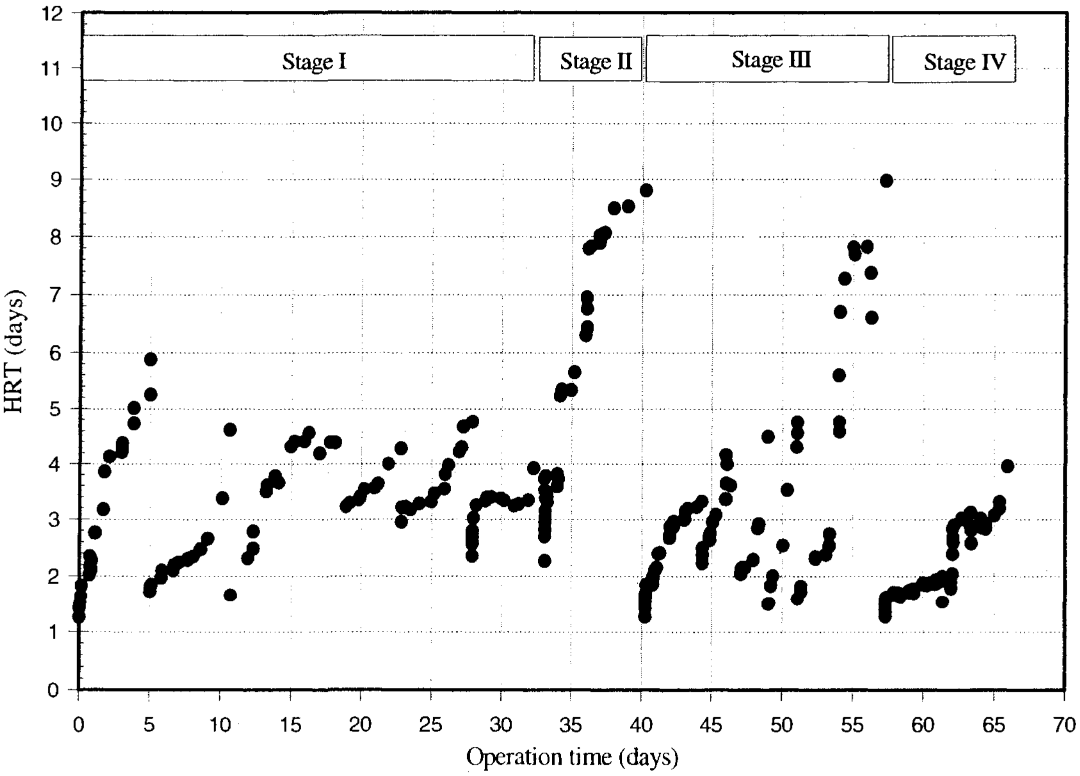


Figure 8.3 Changes of the HRT in the SMEBR system during the Phase III

The objective of Stage II in Phase III was to investigate the performance of the SMEBR system when the DC is applied to the MLSS solution in conjunction with the operation of the membrane module. At the end of Stage II, the membrane was removed for physical cleaning by distillated water for few minutes outside the electro-bioreactor, and subsequently immersed in the electro-bioreactor, at which time; the DC power supply was turned on. The action of washing enabled some recovery of the membrane permeability to certain extends. The HRT at the beginning of Stage II was 3.5 days as shown in Figure 8.2. The results obtained from Stage II did show an unexpected behavior. Immediately after applying a DC field of 1 V/cm with a mode of operation of 15 ON/ 45 OFF (selected based on the optimum results from the previous experiments of Phase I, Chapter 6), the flux declined faster than in Stage I. The PRPF was 85% after 5 days of operation and reached 87% at the end of Stage II. This behavior could be attributed to two hypothesis: i) the washing by physical cleaning before operating Stage II was not sufficient to remove all the particles that deposited within the membrane pores; ii) the electro-coagulation process did not have enough time to form aggregates in the solution, which could reflect directly on the membrane filtration process. In other words, when the membrane filtration process operates simultaneously with the DC field in the SMEBR system, the finely dispersed particles present in the electro-bioreactor have the potential to go through the membrane's pores and buildup the fouling resistance. Consequently, the optimum performance of the SMEBR system in terms of membrane filtration would be better if the SMEBR system was operating for a few minutes without immersing the membrane module in the electro-bioreactor. This result supports the conclusion derived from Stage II of Phase II, where the optimum performance of the

SMEBR system can be achieved when the effect of electro-coagulation can be generated prior to the immersion of the membrane module in the electro-bioreactor.

Theoretically, if a DC field is applied in the SMEBR system after the membrane module is immersed in the electro-bioreactor, or even simultaneously with operation membrane module, the relatively small particles that cause membrane fouling would get the opportunity to build-up within the membrane pores and cause the membrane to foul and an increase in resistance. In contrast, if a DC filed is applied before the membrane module is immersed in the electro-bioreactor, the small colloids and particles would get larger due to the electro-coagulation process. Consequently, their contribution to fouling resistance would be reduced.

Accordingly, the physical and chemical washing of membrane was done before the beginning of Stage III; the membrane module was removed from the reactor and immersed in tap water for 2 hours, and subsequently in 5% NaOCl solution for 8 hours. It was finally rinsed with tap water. This procedure enabled to reestablish most of the membrane's permeability.

To prepare the MLSS solution for coagulation, the SMEBR system was operated with the DC field but without membrane module during the first hours of the Stage III; subsequently, the membrane module was immersed in the electro-bioreactor. At this stage, the influence of the electro-coagulation process is clearly reflected in the membrane filtration process, since the permeate flux declined much lower than observed in Stages I and II. During Stage III, the ratio (*J/Ji*) stabilized at around 0.37 during the first 5 days of operation and corresponded to a 63% reduction in membrane flux.

In Stage IV, the mode of operation of the DC was modified to 15 minutes ON / 105 minutes OFF. The results from this stage showed that the *PRPF* was only 38% after 5 days of the continuous operation without any kind of backwashing of the membrane module. By comparing the first five days of operation of each stage, the SMEBR system performed best during Stage IV in term of membrane filtration when compared with any other stage, as illustrated in Figure 8.4.

Based on the results from Figure 8.4, the percentage improvement in permeate flux during the Phase III can be calculated by the following equation (based on five days of continuous operation in each stage):

$$\%\text{ improvement in flux } = \left(\frac{\left| J - J_{Stage\ -\ I} \right|}{J_{Stage\ -\ I}} \times 100\% \right) \tag{8.2}$$

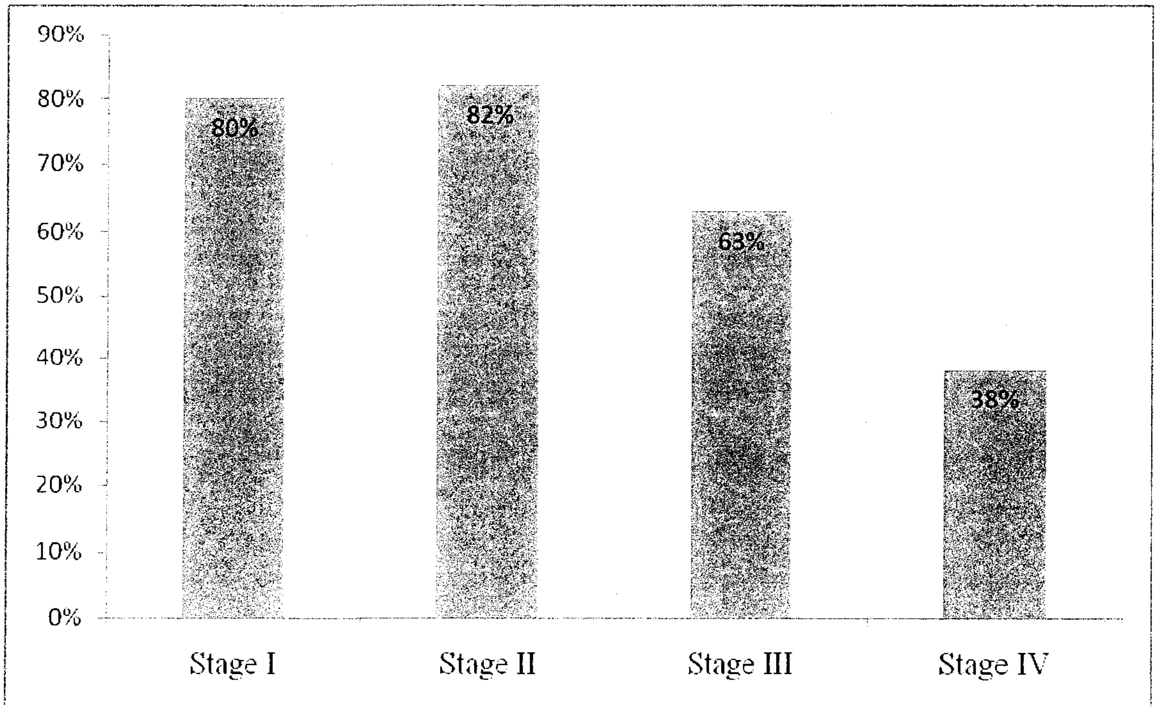


Figure 8.4 Percentage reductions in membrane flux after five days of operation of each stage during Phase III

Where J is the permeate flux in Stages II, III, and IV after five days of continuous operation, and $J_{Stage\text{-}I}$ is the permeate flux in Stage I after 5 days of continuous operation. Table 8.2 summarizes the percentage improvements in permeate flux based on Equation 8.2.

Due to a temporary problem with the switch sensor that occurred on day 63 in the electro-bioreactor, the system was temporarily stopped for a few hours of maintenance. The maintenance protocol required the removal of the electrodes assembly from the electro-bioreactor which led to a mixing between the two zones. After the switch sensor was repaired, the membrane was immersed again in the electro-bioreactor without any rinsing. This resulted in a decrease in membrane permeability compared to the earlier phases of Stage IV. At the end of the Stage IV, the *PRPF* was 68%. A permanent failure in the level switch occurred on the day 66 forced the termination of Phase III.

The change in the HRT during the operation is another indicator of the SMEBR performance. Figure 8.2 shows how the rapid HRT fluctuation in Stage I was due to the rapid decline of the permeate flux. The HRT increased from 1.2 day (at the beginning of the operation) and reached 6 days after five days of operation during Stage I.

Table 8.2 Percentage improvement in membrane flux during the Phase III based on five days of continuous operation

Item	Stage I	Stage II	Stage III	Stage IV
Percentage improvement	Reference stage	- 2 %	+ 21.3 %	+ 52.5 %

Throughout the time remaining, the HRT did not exceed 5 days, reflecting a steady performance of membrane filtration. This suggests that the resistance to pore blocking reached a stable condition

The worst performance of membrane filtration during Stage II (Figure 8.1) was associated with an increase in the HRT (Figure 8.2). The value of HRT increased from 3.5 days at the beginning Stage II to 9 days at the end.

An excellent performance of membrane filtration during Stage IV was reflected in the HRT values. At the beginning of Stage IV (day 57), the HRT was 1.3 day and increased to 2 days after five days of continuous operation (day 63.). After repairing the damaged level switch, the HRT increased from 1.5 day to 4 days by the end of Stage IV.

8.5.2 Impact of the SMEBR Operation on the Physiochemical Properties

8.5.2.1 Change in pH

As it was reported in Chapters 4, 6 and 7, measuring the pH in the mixed liquor after introducing a DC field in the activated sludge is an important parameter for the study of the impact of applying a DC on bacterial growth. Specifically, according to Gaudy and Gaudy (1988), the optimum range of bacterial growth in terms of pH is closed to neutrality with limits in minimum and maximum range near 5 and 9 respectively.

In Phase III of this research, the pH values were measured daily. The variations of the pH values in the influent, the MLSS solution in electro-bioreactor's zones and the membrane effluent are presented in Figure 8.5.

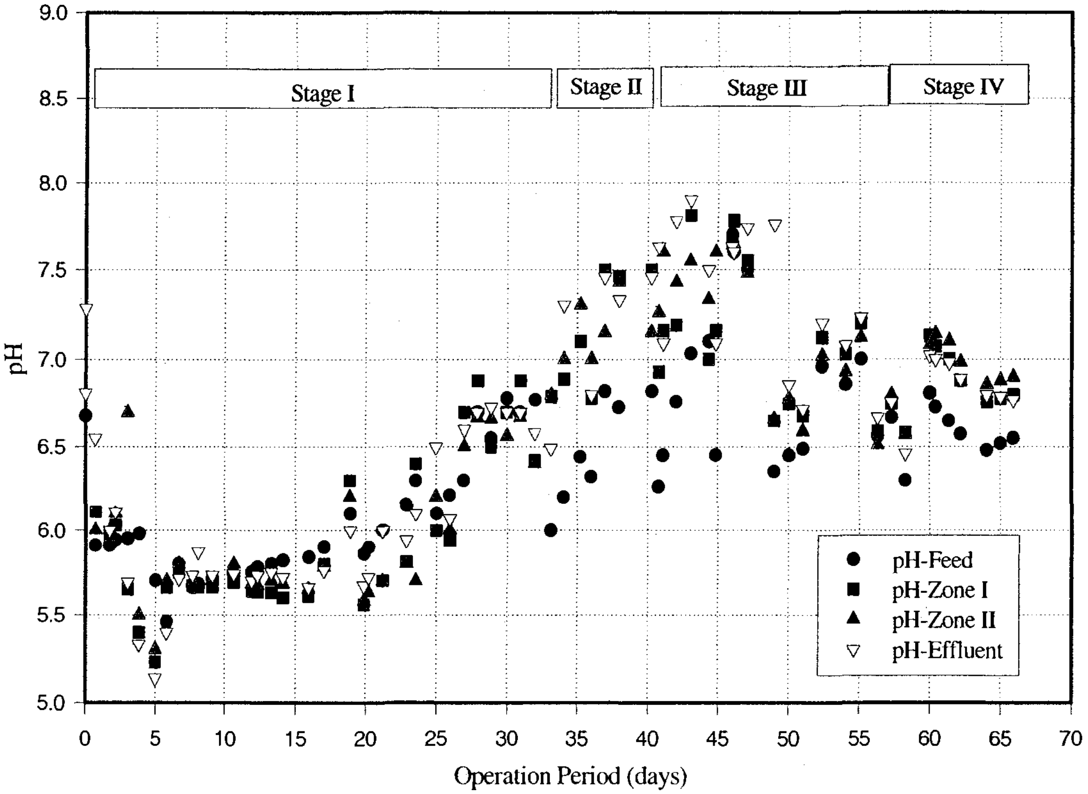


Figure 8.5 Changes in the pH values in the SMEBR system with time during the Phase III

During the first 5 days of Stage I, the pH values dropped in the SMEBR system, and were associated with a decrease of the pH in the influent from 6.7 to 5.5. It was attributed to the fluctuation in the water quality of the feed wastewater due to a slight degradation of organic materials in the wastewater storage tank. The same phenomenon was observed by Liu et al. (2005). Although this phenomenon was observed in Phase II, the dramatic change in this Phase III was sharper than in Phase II, which required increasing the amount of bicarbonate in the feed to bring the pH in the influent to the neutrality level. The drops in the pH during the first stage of operation had a negative impact on the MLSS concentrations as well as on the nitrification process (see sections 8.5.3.1 and 8.5.4.2). It was observed that the influent pH affected significantly the pH values in the SMEBR system. A relationship between the pH of the influent and the pH values in the SMEBR system during Stage I is presented in Figure 8.6.

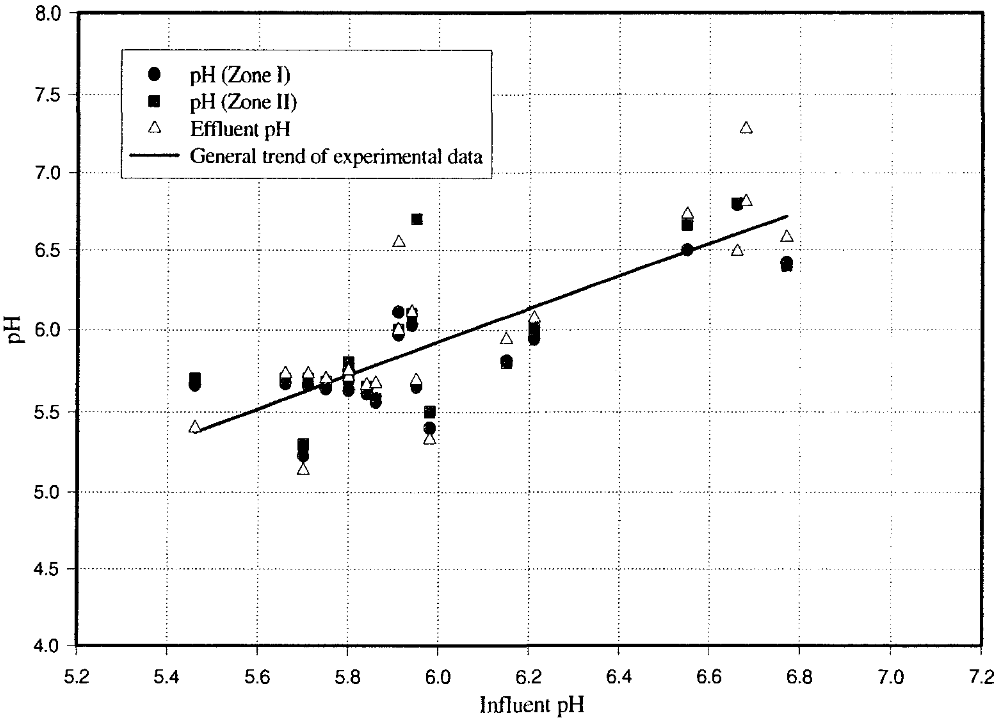


Figure 8.6 Changes in pH values in the SMEBR system with influent pH during the Stage I of Phase III

Figure 8.5 shows that changes in the pH after applying the DC field, began to appear on day 33 (at the beginning of the Stage II) when the pH of the MLSS solutions increased as a result of the electrokinetic phenomenon. The increase in the pH solution after applying DC field into wastewater was also observed by other investigators (Kobya et al., 2003; Chen et al., 2000) and it was attributed to production of hydroxyls at the cathodes associated with hydrogen evolution (Vik et al., 1984).

In Phase III of this research, after the first day of operation of Stage II, an important increases in the pH values was observed in the MLSS solutions and in the permeate from the membrane. Moreover, as of day 33, a difference in the pH values appeared between the MLSS solution located in Zone I and those located in Zone II. The pH value of the MLSS solutions increased from 6.42 at the beginning of Stage II to 6.93 in Zone I and from 6.45 to 7.35 in Zone II, while the effluent pH increased from 6.52 to 7.63.

In Stage III, the pH of the MLSS solutions and the effluent decreased to within the neutrality level. This supports the argument that the SMEBR system can act neutralize pH fluctuations.

During the application of the DC field, the changes in the pH of the effluent were within the range of 6.0 to 7.9, where the average value did not exceed a pH of 6.8. This signifies that the effluent of the SMEBR system does not need further adjustment for pH. The same result was obtained in Phase II. Moreover, the color of MLSS solution in Phase III did not change during the time of operation and was found to be the same color as the original MLSS solution; this phenomenon was not observed with the iron material as the anode applied during Phase II. Also, in Phase III, water permeate quality had neither color nor odor.

Furthermore, starting from day 33, a difference in the pH values appeared between the MLSS solution located in the Zone I and the other located in Zone II. This can be understood from the design of the SMEBR system. In Zone I where the electrokinetic phenomenon occurred, there was liberation of OH^- from the cathode according to equation 4.24. As the cathode formed the same border for the electro-bioreactor's zones, hydroxyl ion (OH^-) will move in both directions toward of the two zones in the electro-bioreactor. In Zone I, where the electro-coagulation process took place, hydroxyl ion (OH^-) were consumed as a result of its reactions with aluminum ions (Al^{+3}), which were dissolved at the anode according to the EC mechanism described in section 8.3. As a result, the pH in Zone I did not significantly increase. On the other hand, the hydroxyl ion (OH^-) that moved toward Zone II contacted fewer aluminum ions; therefore, it accumulated in the vicinity of Zone II and increased the pH in this zone.

8.5.2.1.1 Effect of Influent pH on the SMEBR Performance

It has been established that the influent pH is an important operating factor influencing the performance of electro-coagulation process (Lin and Chen, 1997) and the SMEBR system. In Phase III, the influent pH was varied between 5.4–7.0 during the operational period. The effluent pH was strongly dependent on the influent pH when the DC was turned off in Stage I (Figure 8.6). However, this dependence showed a different trend after applying the DC filed throughout Stages II, III and IV, as shown in Figures 8.7, 8.8 and 8.9 respectively.

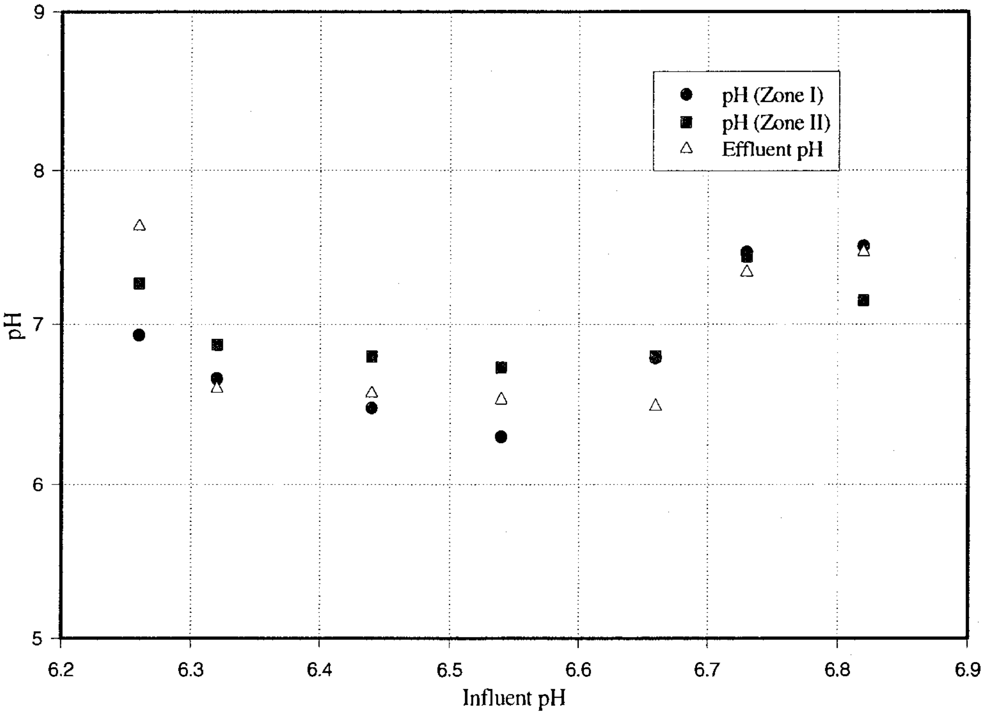


Figure 8.7 Changes in pH values in the SMEBR system with influent pH during the Stage II of the Phase III

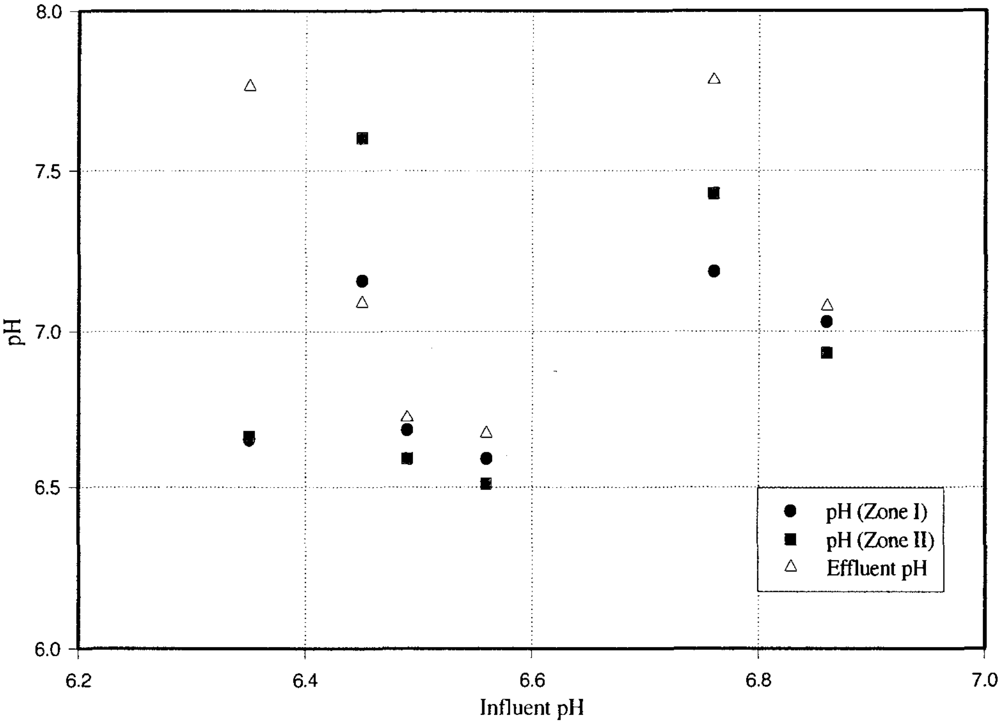


Figure 8.8 Changes in pH values in the SMEBR system with influent pH during the Stage III of the Phase III

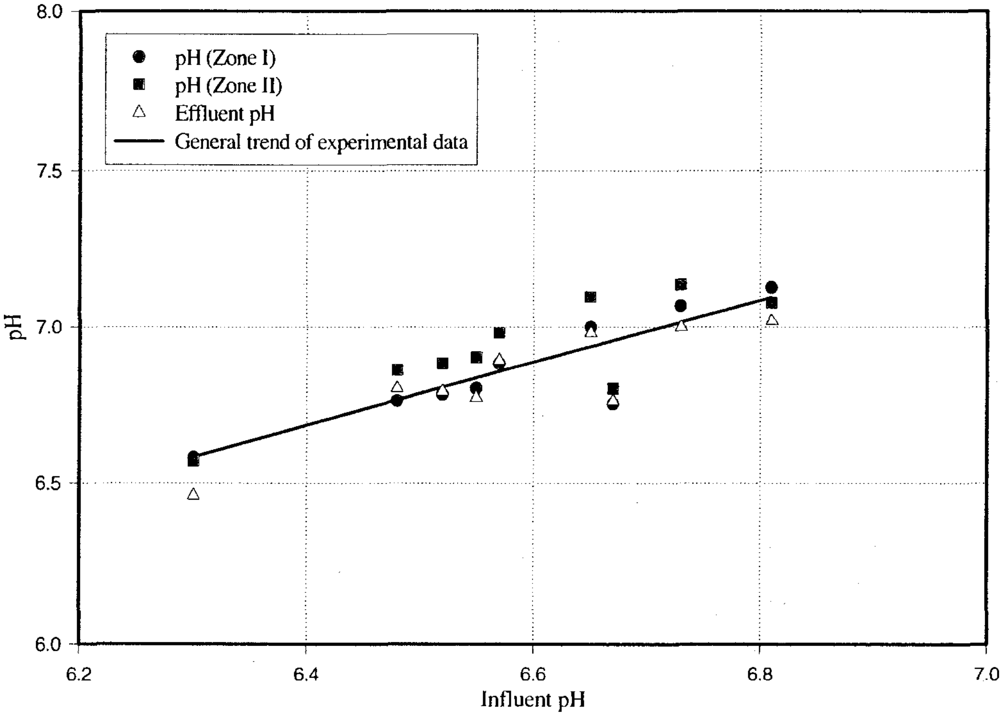


Figure 8.9 Changes in pH values in the SMEBR system with influent pH during the Stage IV of the Phase III

During Stages II and III, the change in pH values in the SMEBR system demonstrated no systematic trend with the influent pH, while in Stage IV, a liner trend was observed between the influent pH and the changes in the pH values in the SMEBR system. A reasonable explanation for this behavior may be due to the effect of the DC operating mode, which reflects the exposure time of the mixed liquor solution to the DC field. In Stages II and III, the operating mode was 15 minutes ON/ 45 minutes OFF which is equivalent to an effective operational time for electro-coagulation of 33 %; while in Stage IV, the operating mode was 15 minutes ON/ 105 minutes OFF which is equivalent to an effective operational time for electro-coagulation of 14 %. This implies that when the electro-coagulation time is high, the effects of the electrokintic processes on the MLSS solution will be greater and the SMEBR operation will be close to the EC process; however, when the electro-coagulation time is diminished, the SMEBR system operation will be similar to the conventional operation of a submerged membrane bioreactor in addition to benefitting from electrokinetic phenomenon to create coagulation. In other words, it is not necessary to operate the SMEBR system with an extended electro-coagulation time to get the best results. This indicates the importance of the exposure time to DC fields as the key parameter in the SMEBR operation and suggests that there is an optimum condition for the operational mode.

The above analysis appears to indicate that the designed of a SMEBR system can operate in two different modes. The first mode is the normal operation of the conventional submerged membrane bioreactors when the DC power supply is turned off. In this mode, biodegradation as a wastewater treatment process dominates and the pH values of the mixed liquor solution in the bioreactor as well the pH of the effluent is affected by the influent pH.

On the other hand, in the second mode where the DC power supply is turned on, the electrokinetic processes are dominant and the pH values of the SMEBR system will be less dependent on the influent pH as the electro-coagulation process acts as a pH buffer.

8.5.2.2 Changes in Temperature

The variations in temperatures of the influent, the MLSS solutions and the membrane effluent are presented in Figure 8.10. The temperature of the influent and the effluent were close to each other and fluctuated according to the room temperature ($21 \pm 2\ ^{o}C$). It might be expected from the EC phenomena that the temperature might increase, however, the temperatures in the electro-bioreactor zones were1 ^{o}C degree less than the temperatures of the influent and the effluent during the entire experimental period. It can be concluded that electrokinetic process did not change the temperatures significantly in the SMEBR in all the phases. In general, the order of change in temperatures in the SMEBR system was as following:

Influent temperature > Effluent temperature > Temperature in the Zone I >
Temperature in the Zone II

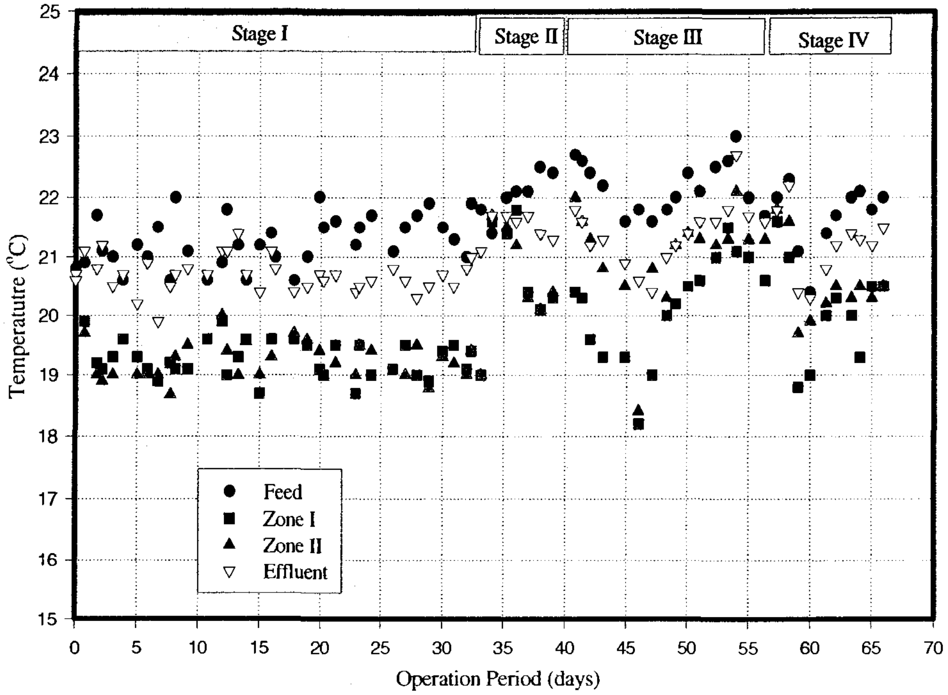


Figure 8.10 Changes in temperatures in the SMEBR system during the Phase III

8.5.3 Response of the Mixed Liquor Properties to the SMEBR Operation

8.5.3.1 Changes in Sludge Concentration

The development of the biomass concentration in the SMEBR system during Phase III was monitored by determining the MLSS and the MLVSS concentrations in the electro-bioreactor. Because the SMEBR system has two zones, the values of the MLSS and the MLVSS concentrations were presented as an average measurement in both zones (as it was done in Phase II). Figure 8.11 shows the time-dependent variations of the sludge concentration in the electro-bioreactor. During the first 5 days of Stage I, the MLSS concentration decreased from 3300 mg/L to 2750 mg/L. This decrease was attributed to a decrease in the pH values of the SMEBR system (Figure 8.5), that may have caused some microorganisms to die or to lose their viability. A few days after adjusting the pH influent, the MLSS began to be stabilized around 2700 mg/L until day 14.

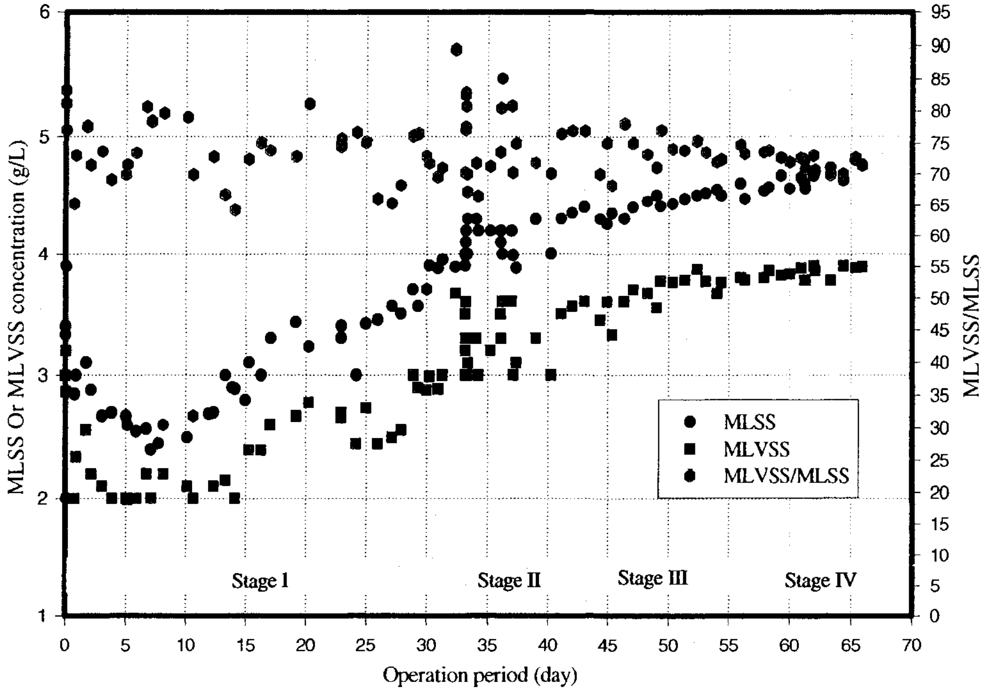


Figure 8.11 Changes of the MLSS and the MLVSS concentartions durnig the Phase III

The performance of the electro-bioreactor after 14 operation days was satisfactory; the sludge concentration increased slowly and reached an average of 3800 mg/L at the end of Stage I.

The MLSS concentration continued to increase after applying the DC field throughout Stages II, III, and IV. This trend indicates the viability of the microorganisms and the biodegradation processes. It appears that the performance of the organic degrading bacteria was not affected whereas the ammonia oxidization bacteria were exposed to the inhibition conditions of applying a DC field. This issue will be discussed in details in the next sections.

On the other hand, the investigation of the volatile fraction of total suspended solids revealed that MLVSS/MLSS was found to be stable within the range of 0.65 and 0.85 during Stage I, indicating no obvious accumulation of inorganic particulate compounds in the bioreactor. However, starting from the end of Stage II, the

MLVSS/MLSS ratio demonstrated some decrease; the MLVSS/MLSS ratio was less than 75 % beginning from day of 52 and it went down to 70 % by the end of the operational Phase III. This trend implies that there was an accumulation of inorganic matter which started to build-up in the electro-bioreactor after applying the DC field.

Because there is no clear correlation between the fouling rate and the MLSS concentration in the submerged membrane bioreactor applications as it was discussed in Chapter 7 (section 7.5.4.1.1), the development occurring in membrane flux during the operation of the SMEBR system in Phase III is completely attributable to the changes occurring in the physical/chemical properties of the MLSS solution after applying a DC field.

8.5.3.2 Changes in Specific Resistance to Filtration (SRF)

According to Larue and Vorobiev (2003), the flocs formed by the EC process are relatively large and contain less bound water. They are also more stable and therefore amenable to filtration. This observation was confirmed in this research by applying a DC field to the MLSS solutions. Starting from Stage II, the results demonstrated that by using the electokinetic phenomena in the SMEBR system, the floc size of the MLSS solution was significantly affected. Beginning by Stage II, large and dense flocs appeared and they enhanced the overall performance of the liquid/solid separation processes. This was shown visually during the preparation the samples for the filtration purposes. The effect of large flocs reflected also in the sedimentation velocity which increased dramatically after applying the DC fields to the MLSS solution.

To find an empirical evidence of the above results, the specific resistance to filtration (SRF) of the MLSS solution particles in the electro-bioreactor's zones was measured every 10 days or at the end of each stage during the operation period as shown in Figure 8.12.

All the measured filtration resistances were compared relative to the specific resistance to filtration of the MLSS solution at the beginning of the operation of the SMEBR system (r_o).

According to the Carman-Kozeny equation (Equation 4.4), the specific resistance to filtration (SRF) of the particles is inversely proportional to the square of particle diameter. Accordingly, the SRF is considered to be an indirect measurement of the size fractions of the particles.

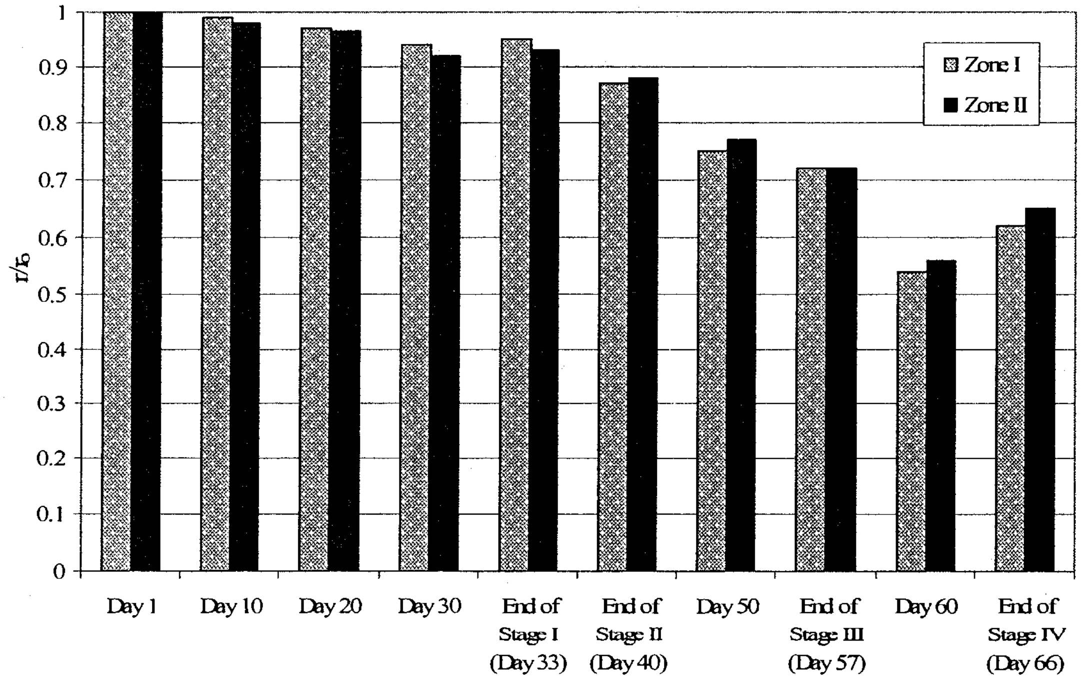


Figure 8.12 Changes of specific resistance to filtration of the MLSS solution during the Phase III

Obviously, from Figure 8.12, the results of the SRF tests during Stage I did not show a considerable improvement in the SRF after 10 days of operation. This could be attributed to the fact that the particle size of the flocs did not growth well during the first ten days of operation where the MLSS solution decreased during the first five days as shown in Figure 8.11.

A small improvement was observed in the SRF on day 20 and day 30 of the operational period which was attributed to a small increase in particle sizes and associated with an increase in the MLSS concentration. This explanation agrees with the study reported by Chang and Kim (2005) based on the effect of the biosolids concentration on cake resistance during membrane filtration. They found that particle size at the lower MLSS concentrations was smaller than at the higher ones.

On day 33 (the end of Stage I), no significant improvement was observed and the SRF decreased by 4 % (on average) compared to the initial phase of the operation.

Although the permeate flux trend was unsatisfactory during Stage II (Figure 8.2), a considerable improvement in the SRF was observed on day 40 (at the end of Stage II). The SRF decreased by 13% in comparison with the initial phase of the operation. This result is not in contradictory with the fact that an improvement in the SRF of the MLSS solution can improve the permeate flux. A reasonable explanation of the results of Stage II is the fact that the membrane module was not exposed to a chemical cleaning before its immersion in the electro-bioreactor.

The results from Stage II confirmed two important conclusions: i) the membrane module should be cleaned chemically and physically after each cycle of operation, and ii) it is very important to create coagulation in the MLSS solution before operating the membrane module, as it was reported also in section 8.5.1.

The above conclusions were confirmed in Stage III where the membrane module was exposed to a physical and chemical cleaning before its operation. In Stage III on day 50, the SRF decreased by 25 % and 23 % in Zones I and II respectively, and decreased by 38% on average in both zones by day 57 (the end of Stage III).

The significant decrease in the SRF was observed throughout Stage IV. On day 60, the SRF had decreased by 46 % and 44 % in Zones I and II respectively. This situation was clearly associated with the *PRPF* = 37 % as is shown in Figure 8.2.

Due to the mixing occurring between the two zones after the level switch failed on day 63, a decrease in the SRF was observed at the end of Stage IV; however, the SRF decrease was still higher than in previous stages (i.e. 38 % in Zone I and 35% in Zone II).

The above results are in agreement with the reported literature about the significant role of the smaller size particles in the activated sludge on the membrane fouling phenomenon (Lim and Bai, 2003). It can be concluded form the results obtained from Phase III that the small colloidal particles, that are known to have greater capacity to build-up fouling resistance within the membrane pores, were destabilized and formed larger aggregates after applying the DC field, and led to an enhancement of the membrane's permeability. In addition, the application of an aluminum anode seemed to give an overall better protection of the membrane module. These results agreed with the reported results obtained by Song et al. (2008) who conducted, in their study, that chemical coagulation by alum enhanced the membrane's permeability in a conventional submerge membrane bioreactor.

Since the colloidal fraction of mixed liquor plays the most important role in the membrane fouling, the coagulation of these colloids is a determining factor of a successful treatment process. According to the discussion presented in this and previous sections on the SRF and the MLSS concentration, it can be concluded that the size of flocs plays a more significant role on membrane fouling at lower levels of MLSS concentrations, than the MLSS concentration itself. This is in agreement with Chang and Kim (2005) who studied the effects of biosolids concentration on cake resistance using membrane filtration. They found that the SRF decreased as the MLSS concentrations increased, for specific MLSS concentrations (90, 250, 2900 and 3700 mg/L).

8.5.3.3 Changes in Zeta Potential

The improvement in membrane permeability within the SMEBR system can also be confirmed by measuring the zeta potential of the sludge flocs. According to the theoretical background presented in Chapter 4, the zeta potential reflects the surface charge of sludge flocs. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If particles have a large negative or positive zeta potential, the dispersion is stable and it prevents the flocs' formation. If particles have low zeta potential values then the dispersion instability permits the formation of flocs as there is no significant force to prevent the particles coming together and aggregating.

In Phase III, the potential for particle aggregation in the SMEBR system was verified daily by measuring the zeta potential of the particles in the supernatant after settling 50 ml of the mixed liquor for 30 min. The results of the zeta potential are presented in Figure 8.13. During the first stage (DC = 0 V/cm), no significant difference was observed in the zeta potential values in both electro-bioreactor's zones and the zeta potential fluctuated within the range of -26 to -37 mV, with average value of - 32 mV. According to the criteria mentioned in Chapter 4, this value was closed to the zeta potential value of -30 mV required to achieve sedimentation. This means that applying a low level DC field into the MLSS solution can reduce the forces that prevent the aggregation of particles; this case was demonstrated from the beginning of Stage II.

Starting from the Stage II (DC = 1V/cm), the zeta potential of the particles in the supernatant shifted from –28.2 to –15.2 mV in Zone I and from -27.4 to -11.3 mV in Zone II. This situation improved the aggregation and coagulation process; although this improvement did not significantly enhance the membrane flux for the reasons provided in the section 8.5.1. By the end of Stage II, zeta potential decreased to -19 mV in Zone I and to -21 mV in Zone II.

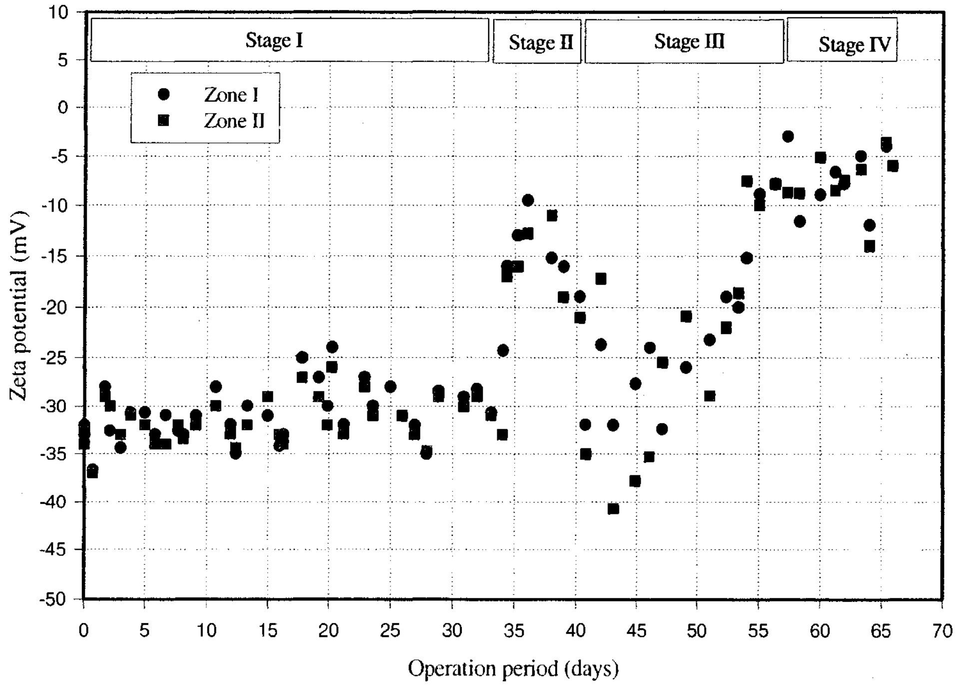


Figure 8.13 Changes in zeta potential in the SMEBR system during the Phase III

In Stage III, an increase in negative direction was observed in zeta potential values between the days 41 and 44 which might due to the mixing occurred in the two zones after starting Stage III. However, zeta potential stabilized at around -25 mV in both zones until day 51; thereafter, the zeta potential continued to decrease with time and reached -8 mV in both zones.

In Stage IV, the zeta potential decreased slowly to an average value of -4 mV in both zones, which means that the colloidal particles of the mixed liquor solution were closed to their isoelectric point (i.e. the point at which the colloidal particles are least stable). These values can explain the significant improvement of flux during Stage IV when the permeate flux lost only 38 % of its initial value.

8.5.4 Response of Biochemical Parameters to the SMEBR Operation

8.5.4.1 COD Removal Performance

Figure $8.14_{(a)}$ illustrates the variations of the COD concentration in the influent, supernatant liquors in the two zones, and the membrane effluent throughout Phase III; whereas Figure $8.14_{(b)}$ illustrates the corresponding COD removal efficiencies in the electro-bioreactor (% $R_{reactor}$) for both zones and for the overall performance of the SMEBR system (% R_{system}). The removal efficiency of the COD in the electro-bioreactor and of the whole system is expressed by equations (4.10) and (4.12) respectively.

While the removal efficiencies in the two zones varied between 80% and 88% during Stage I, Figure $8.14_{(b)}$ indicates that the overall system can provide consistently higher COD removal. The total COD removal efficiency of the system was maintained at a high level surpassing 93% because of the efficient filtration of the membrane module.

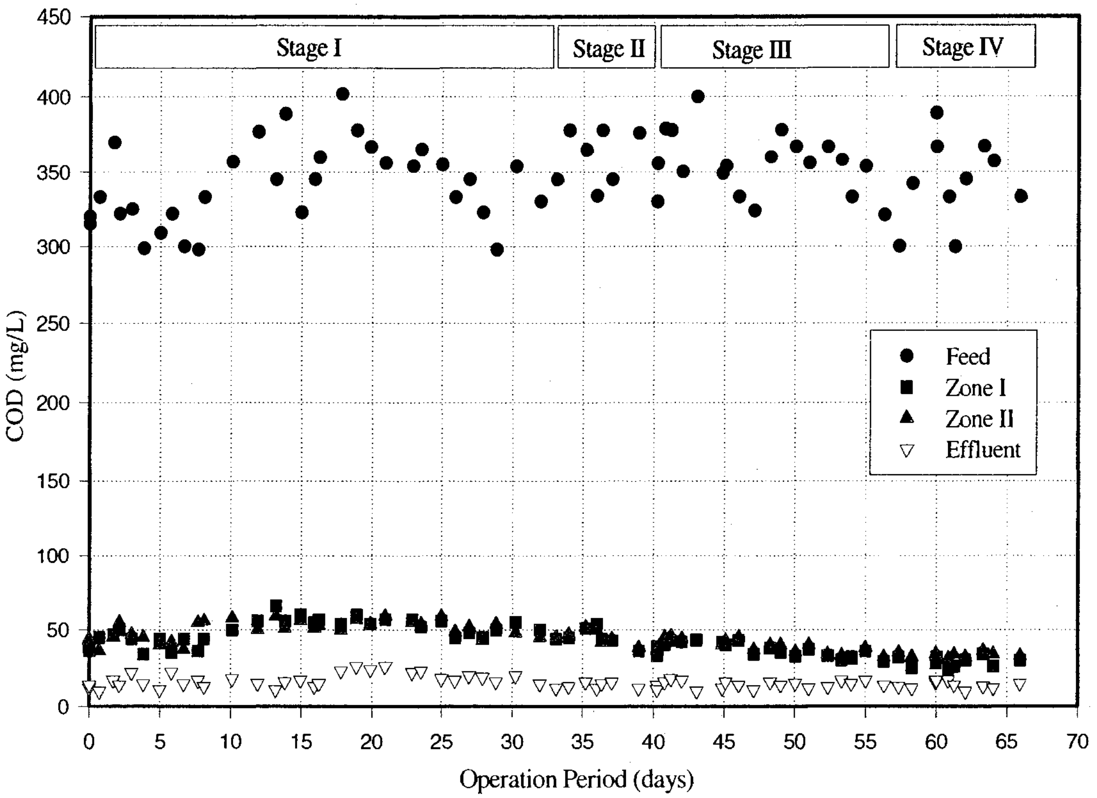


Figure 8.14(a) Change in the COD concentrations in the SMEBR system during the Phase III

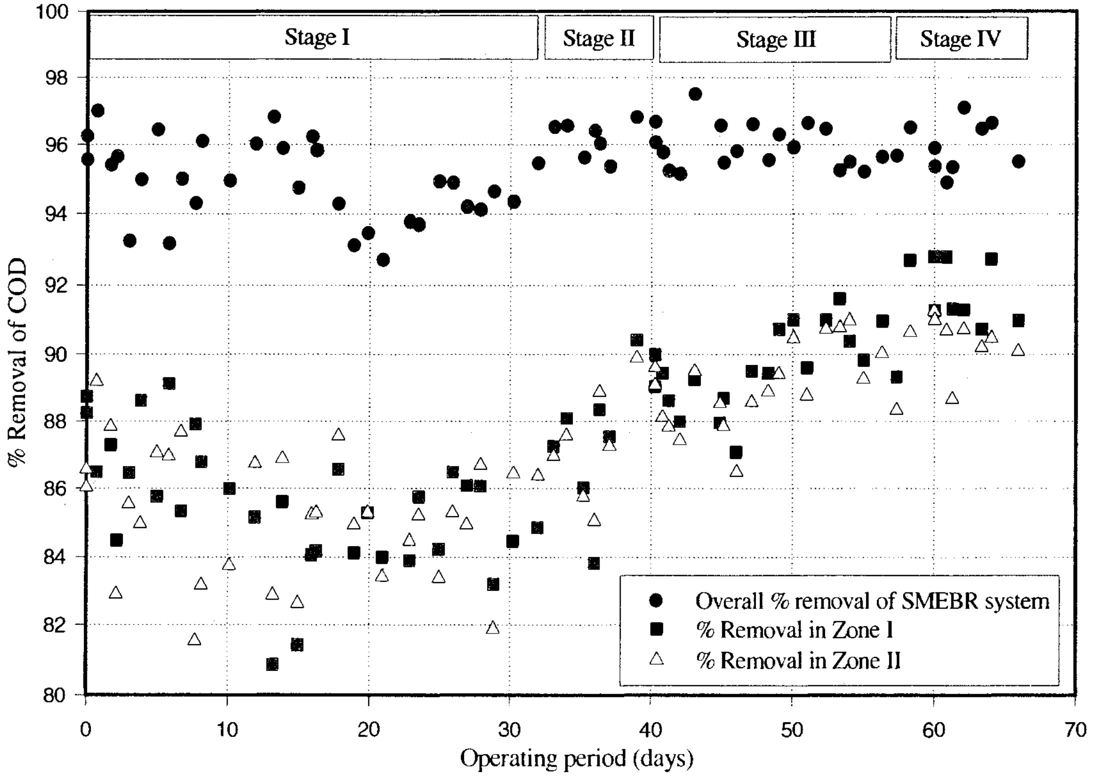


Figure 8.14 (b) Removal efficencies of the COD concentrations in the SMEBR system during the Phase III

This data confirmed that the membrane module played an important role in providing an excellent and stable effluent quality during the MBR processes (Le-Clech et al., 2006, Trussell et al., 2005).

During Stage I, most of the COD fraction (80 -88 %) was degraded by the microorganisms in the electro-bioreactor, while the membrane module contribution was between 5 % and 16 % (Figure 8.14$_{(b)}$). Similar result was obtained during Phase II of this research.

Although the overall COD removal efficiency remained stable at around 96%, beginning from Stage II until the end of Stage IV, the application of a DC field through the MLSS solution increased the COD removal efficiency in the two zones of electro-bioreactor.

This observable fact can be attributed to the effect of the electro-coagulation phenomenon. When a comparison between Stage I (DC = 0 V/cm) and the other stages is made, the designed SMEBR system can contribute 8 % of the COD removal within the electro-bioreactor. This conclusion is very important because as it was reported by Yamato et al. (2006), some fractions of organic matter in the mixed liquor have higher affinities with the membrane than do other fractions and consequently cause greater irreversible fouling. Defrance et al. (2000) reported that the membrane fouling is caused not only by the microbial floc but also by the supernatant containing colloids and solutes. Other researchers reported that for a microporous pore size membrane, the main components of the activated sludge system that contributed to membrane fouling are small size soluble and colloid components (Lee et al., 2001). Other studies also confirmed that the impact of the non-settleable organic fraction on membrane performance is generally considered as a negative one (Cicek et al., 2003; Bouhabila et al., 2001). Lee et al. (2003) reported that the relative contributions of supernatant containing colloid and solutes to the total fouling were 28-37%, while suspended solids was 63-72%. Consequently, applying a DC field to the mixed liquor can reduced the load contributed by the organic matter on membrane fouling. This conclusion may explain the good performance of the SMEBR system during Stage III as well as Stage IV where the fouling rates decreased dramatically.

8.5.4.2 Nitrification Performance

As it was mentioned in Chapter 7, the change in ammonia concentration is often used as an indirect measurement of the changes in the nitrification process (Pollard, 2006). The variations of the ammonia nitrogen (NH_3–N) concentrations in the influent, electro-bioreactor supernatant (in the two zones) and the membrane effluent are presented in Figure $8.15_{(a)}$. The corresponding removal efficiencies of the SMEBR system are shown in Figure $8.15_{(b)}$.

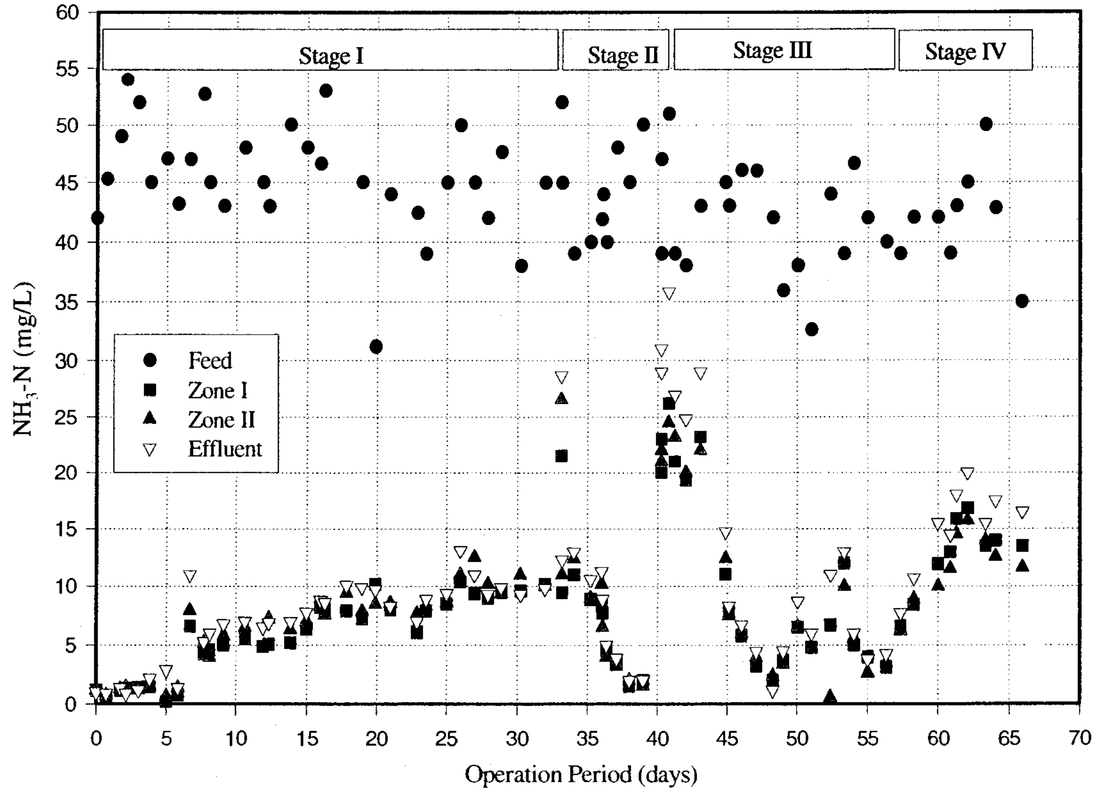


Figure 8.15 (a) Changes in the NH_3-N concentrations in the SMEBR system during the Phase III

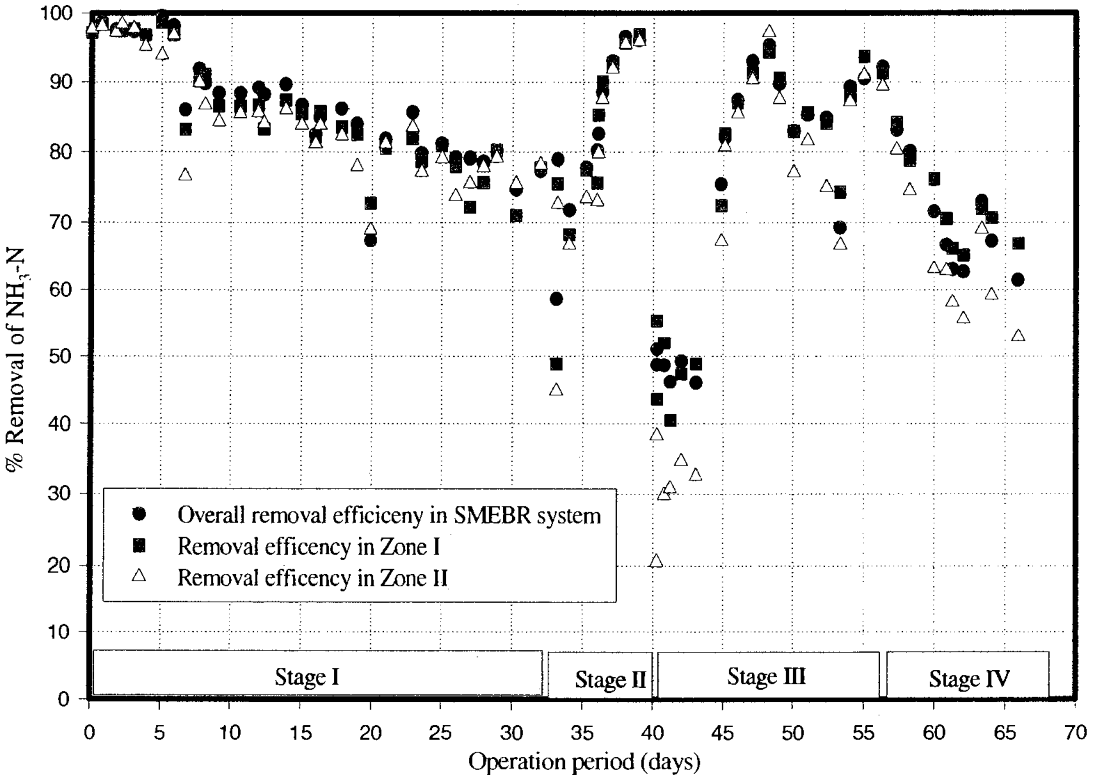


Figure 8.15 (b) Removal efficencies of NH_3-N concentrations in the SMEBR system during the Phase III

The influent NH_3–N varied between 32 and 54 mg/L, with an average of 45 mg/L. The effluent NH_3–N concentrations fluctuated in each stage of Phase III.

In Stage I, where DC = 0 V/cm, the effluent NH_3–N concentrations were below 1 mg/L during the first five days. In contrast to the result obtained in Phase II, a good oxidation of ammonia was observed during the first period of Stage I. The nitrification rate during the first 5 days of Stage I was 90~97%, and only a small fraction of free ammonia-nitrogen ions were found in the effluent. This result may be attributed to a sufficient generation of ammonia oxidizing bacteria before starting Phase III.

Beginning from the day 6, the NH_3-N concentration in the effluent started to increase and fluctuated until the concentration stabilized around 10 mg/L with an average removal efficiency between 70~80%. The increase in effluent NH_3–N after day 6 can be attributed to a decrease in the pH (5-5.8) during this period, as illustrated in Figure 8.5; this may have caused an inhibition for some nitrifying bacteria. According to Gieseke et al. (2006), the optimum range for ammonia oxidation bacteria occurs under neutral to moderately alkaline conditions (pH 7 to 8). The decrease in the pH value might explain the reduction in ammonia oxidation observed from day 6.

When Stage II progressed (DC = 1 V/cm, exposure time = 15 minutes ON / 45 minutes OFF), the effluent NH_3–N concentration reached 28.7 mg/L on day 34. This decrease in nitrification efficiency may have been the result of the shock exposure of the nitrogen bacteria to the DC field. However, the effluent NH_3–N concentration decreased again until it reached 2.1 mg/L at the end of Stage II, with NH_3–N removal efficiency above 93%.

In Stage III the same operating conditions as in Stage II was applied. The effluent NH_3–N concentrations increased until it reached 35.8 mg/L on day 41. However, the NH_3–N concentrations decrease again with time until it reached 4.5 mg/L at the end of Stage III.

The rapid increase in the NH_3–N concentration when the mixed liquor solution was exposed to the DC field in both Stage II and Stage III could be also attributed to the sensitivity of nitrifying bacteria to a DC field; it appears that their sensitivity is more significant during the first hours of exposure time to a DC. This suggests that accumulation of aluminum in the reactor can give rise to a severe inhibitory effect on the activity of nitrifying bacteria (Lee et al., 2001). Song et al. (2008) reported unclear vision about the nitrogen removal efficiency although they reported small variation at different alum dosage.

The same behavior was observed in Stage IV. When the mode of operation of the DC field was altered to be 15 minutes ON /105 minutes OFF, the NH_3–N concentrations began to increase with time and reached 17.6 mg/L by the end of Stage IV.

During the operational period, no significant difference in NH_3–N concentration in the elector-bioreactor supernatant between the two zones and the membrane effluent were observed, which implies that the NH_3–N removal was mainly achieved by the electro-bioreactor.

To further confirm the impact of the SMEBR operation on the nitrification process, the nitrate nitrogen (NO_3-N) concentration in the effluent, as another indicator, is presented with the effluent concentration of NH_3–N in Figure 8.16.

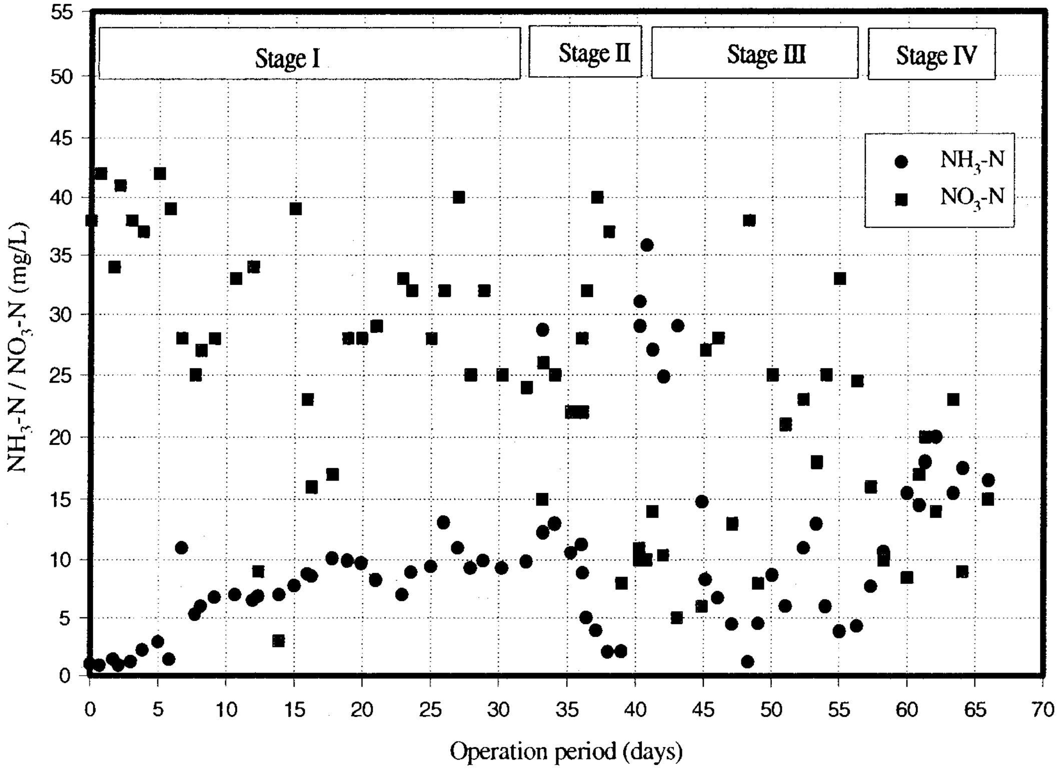


Figure 8.16 Changes in NH_3-N and NO_3-N concentrations in the effluent SMEBR system during the Phase III

The nitrification rate in the reference stage (Stage I) was observed at the starting stages by oxidation of ammonia to nitrate as shown in Figure 8.16. The nitrate nitrogen (NO_3-N) concentration in the effluent fluctuated in each stage also associated with the fluctuation of the NH_3–N concentration.

As it was the case in Phase II of this research, nitrite nitrogen (NO_2–N) was not detected during the whole operational period of the SMEBR system suggesting that the nitrification was the major process in the SMEBR system.

8.5.4.3 Phosphorous Removal Performance

Figure 8.17$_{(a)}$ shows the time-dependent variations of orthophosphate (PO_4-P) concentration of the influent, the supernatant liquors in the two zones, and the membrane effluent during the experimental period. Figure 8.17$_{(b)}$ shows the corresponding orthophosphate (PO_4-P) removal efficiency of the electro-bioreactor (% $R_{reactor}$) in both zones and in the entire SMEBR system (% R_{system}). The influent phosphorus as orthophosphate (PO_4-P) varied from 19 to 31 mg/L, with the average of 26 mg/L. During the first period of Stage I, the removal efficiency of PO_4-P in the two zones was approximately 95% and the removal efficiency in the effluent was about 97%. The sudden decrease in the PO_4-P removal in the two zones (less than 85%) and the relatively lower removal in the effluent appearing on day 6 corresponded to the lower MLSS concentration on that day. However, a few days later, the system increased its efficiency once more with an increase in the MLSS concentration in the electro-bioreactor. Although the phosphorus uptake fluctuated during the first stage due to the fluctuation in the MLSS concentration, the overall system showed good performance as the membrane module might have played an adsorbent support for phosphorous removal.

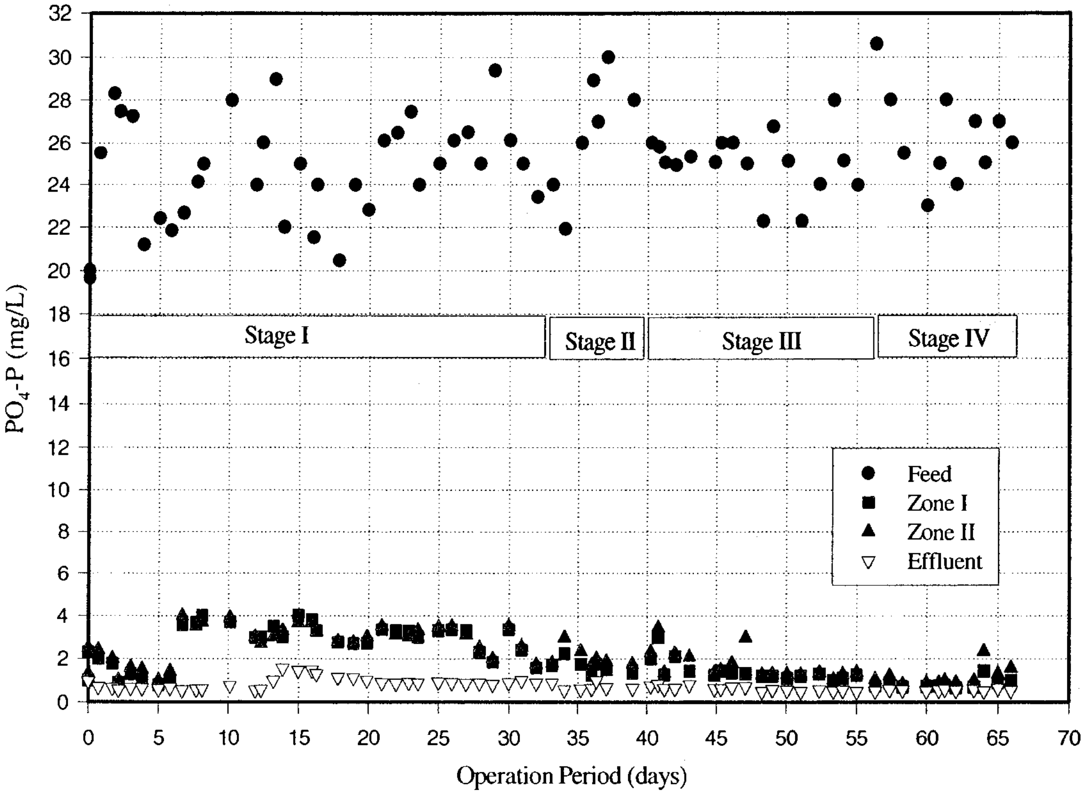


Figure 8.17 (a) Changes in PO$_4$-P concentrations in the SMEBR system during the Phase III

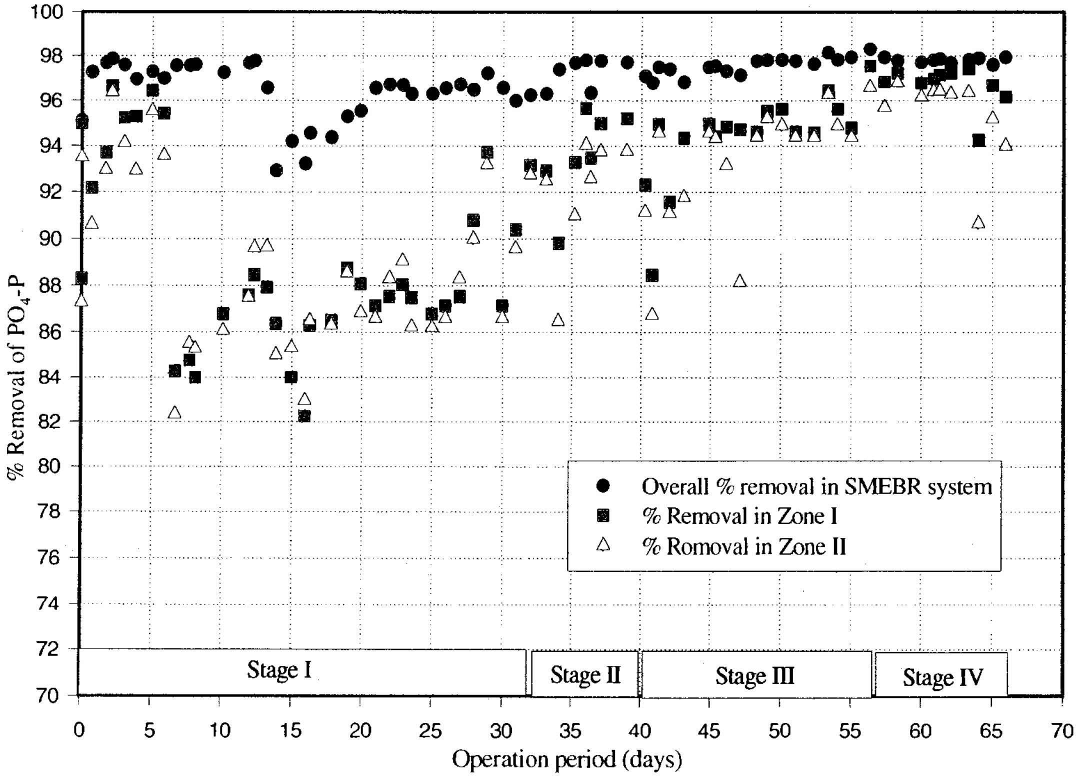


Figure 8.17(b) Removal efficienies of the PO$_4$-P concentrations in the SMEBR system during the Phase III

Starting from Stage II (day 33 to day 40), after applying a DC field into the MLSS solution, a dramatic increase in the PO_4-P removal was observed in the two zones. This can be understood from the electrokinetic phenomenon that occurred in Zone I. The metal ions (Al^{3+}) began to appear in the MLSS solution forming aluminum hydroxide which functions as sweep flocs. These sweep flocs have large surface areas which is beneficial for the rapid adsorption of soluble phosphorus (Kobya et al., 2006). The improvement in phosphorus uptake continuing during Stages III and IV was associated with the further increase of Al^{3+} ions from the electrolysis of the aluminum anode.

These results demonstrated that during the first stage of operation, where no DC was applied, the concentrations of PO_4-P in both zones of the electro-bioreactor supernatants were similar to each other; while after application of DC, little differences were observed between the two zones. The concentration of PO_4-P in Zone I was on average less than 2-4% the concentration of PO_4-P in Zone II (the same phenomenon was observed in Phase II of this research). This is attributed to the coagulation phenomenon that occurred in Zone I. As the aluminum ions (Al^{3+}) are produced in Zone I, as a result of the electrochemical process, the phosphorous molecules reacted with aluminum ions to produce $AlPO_4$ and precipitated out of the sludge. Alternately, the aluminum ions (Al^{3+}) react with the hydroxyl ions (OH^-) produced at the cathode to form $Al\ (OH)_3$ flocs in Zone I. The phosphorous molecule will get a better chance to be adsorbed onto these flocs and precipitated out to the bottom of the reactor. In Zone II, where no electro-coagulation process took place, there was less chances for the available phosphorous molecules to react with aluminum ions; therefore, the removal efficiency of phosphorus in Zone II was less than the removal efficiency of phosphorus in Zone I.

8.5.5 Impact of the Volumetric Loading on the SMEBR Performance

As it was mentioned in Chapter 7, operating the SMEBR system on the basis of constant pressure produced a fluctuation in HRT during the experimental stages (Figure 8.3). The HRT has significant relation with feed concentration and so affects the volumetric loading to the SMEBR system. For example, short HRT can induce large organic loading (OLR). Also the HRT affects the food to biomass ratios (F/M). The very high HRT reached in the system resulted in very low F/M ratio which might increase the % removal of COD, NH_3-N and PO_4-P.

Consequently, COD, NH_3-N and PO_4-P volumetric loading to the system changed continuously as shown in Figures 8.18, 8.19 and 8.20. These trends might have impact on the removal efficiencies and distorting the microbiological picture within the electro-bioreactor. Also, the fluctuation in the HRT affects the food to microorganism's ratio (F/M) as shown in Figure 8.21.

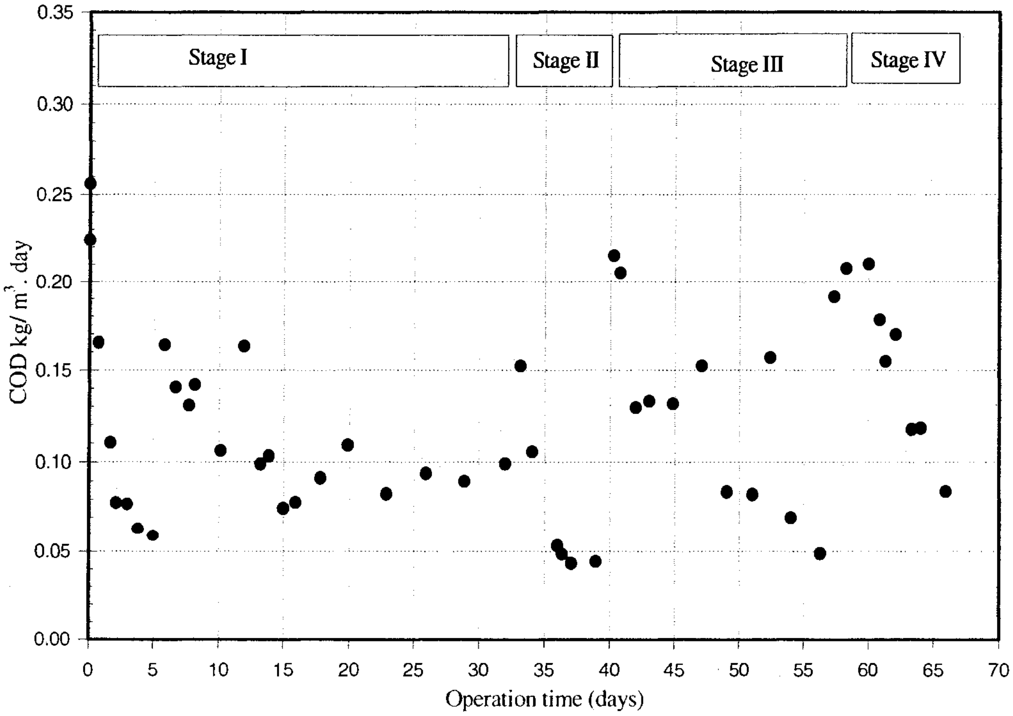


Figure 8.18 Changes of organic loading in the SMEBR system during the Phase III

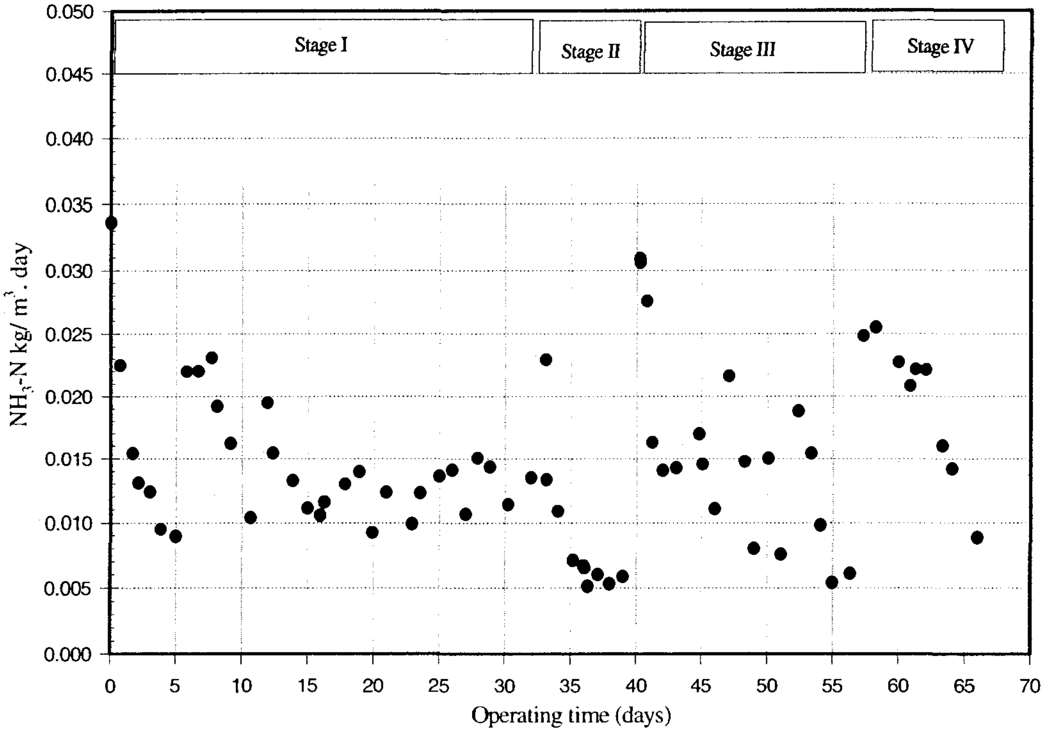


Figure 8.19 Changes of NH_3-N loading in the SMEBR system during the Phase III

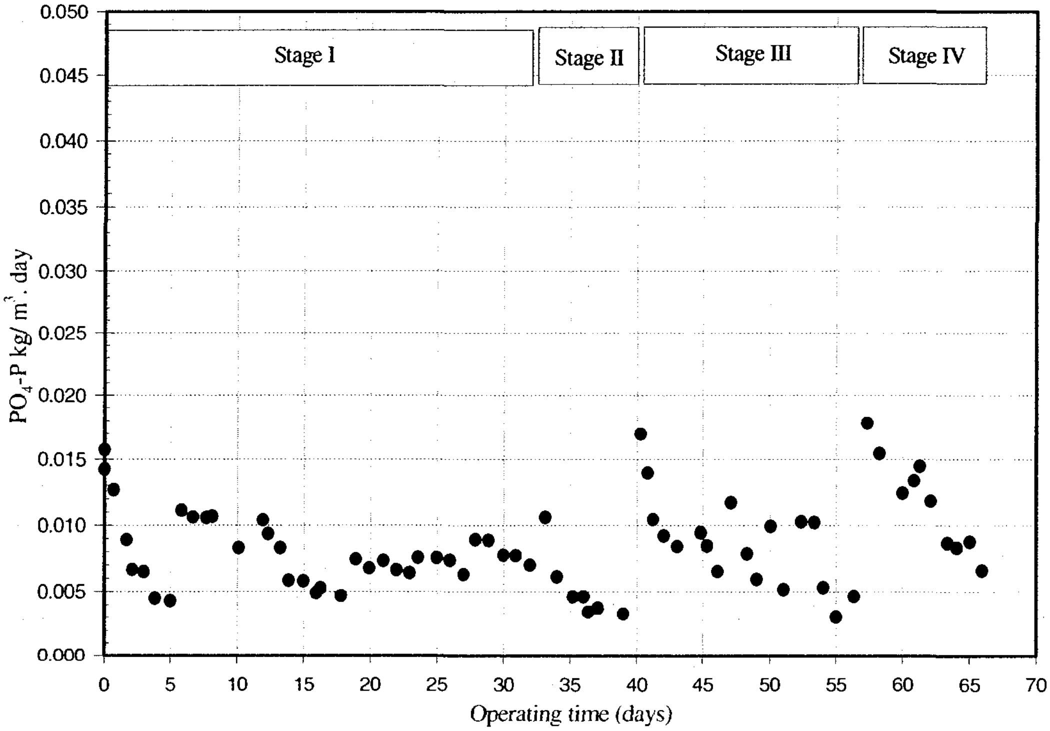


Figure 8.20 Changes of PO_4-P loading in the SMEBR system during the Phase III

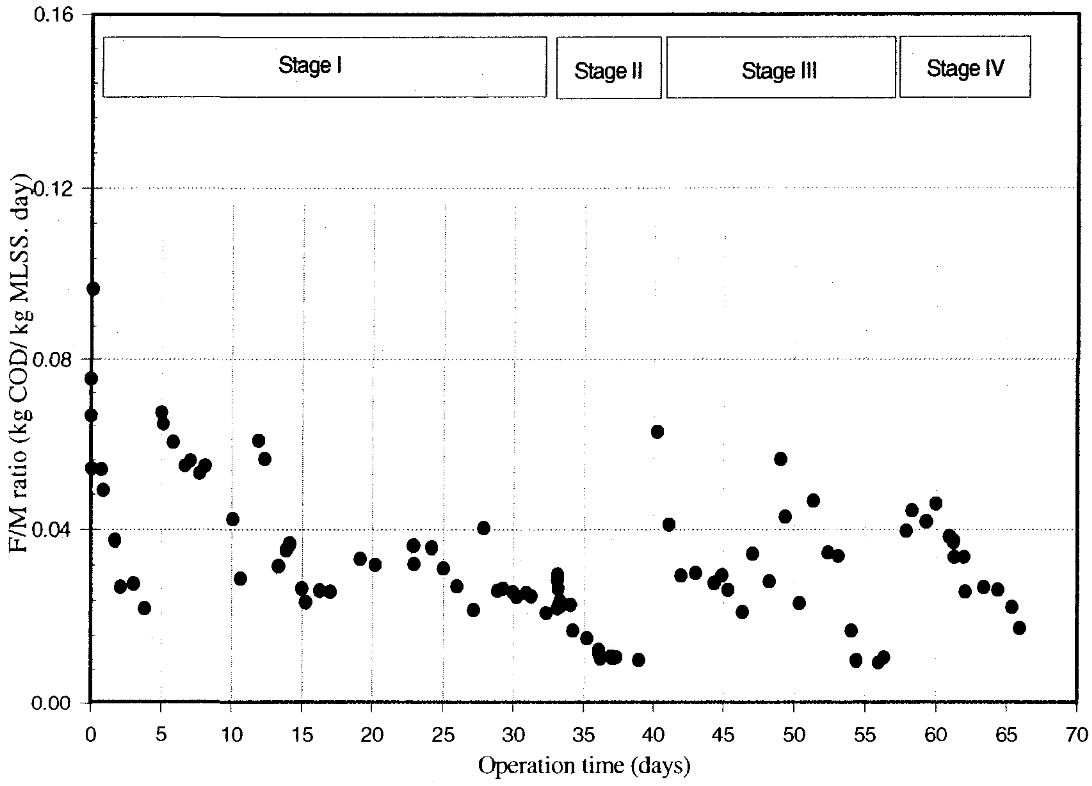


Figure 8.21 Development of F/M ratio in the SMEBR system during the Phase III

To analyze the impact in volumetric loading on the overall performance of the SMEBR system, the overall removal of organic, ammonia nitrogen and ortho-phosphorous were plotted versus the variations in their loading as shown in Figures 8.22, 8.23 and 8.24 respectively.

Any systematic trends can be drawn from Figures 8.22, 8.23 and 8.24. However, the overall % COD removal was within the range 93 and 97.5% during all stages of Phase III (Figure 8.22). This means that the variation in organic loading rate (OLR) did not affect the % COD removal. To further confirming this conclusion, the % COD removal was plotted against the HRT as shown in Figure 8.25, which demonstrates that % COD removal was less dependent on the variation of the HRT. This is in agreement with the reported study conducted by Tay et al. (2003) as explained in Chapter 7.

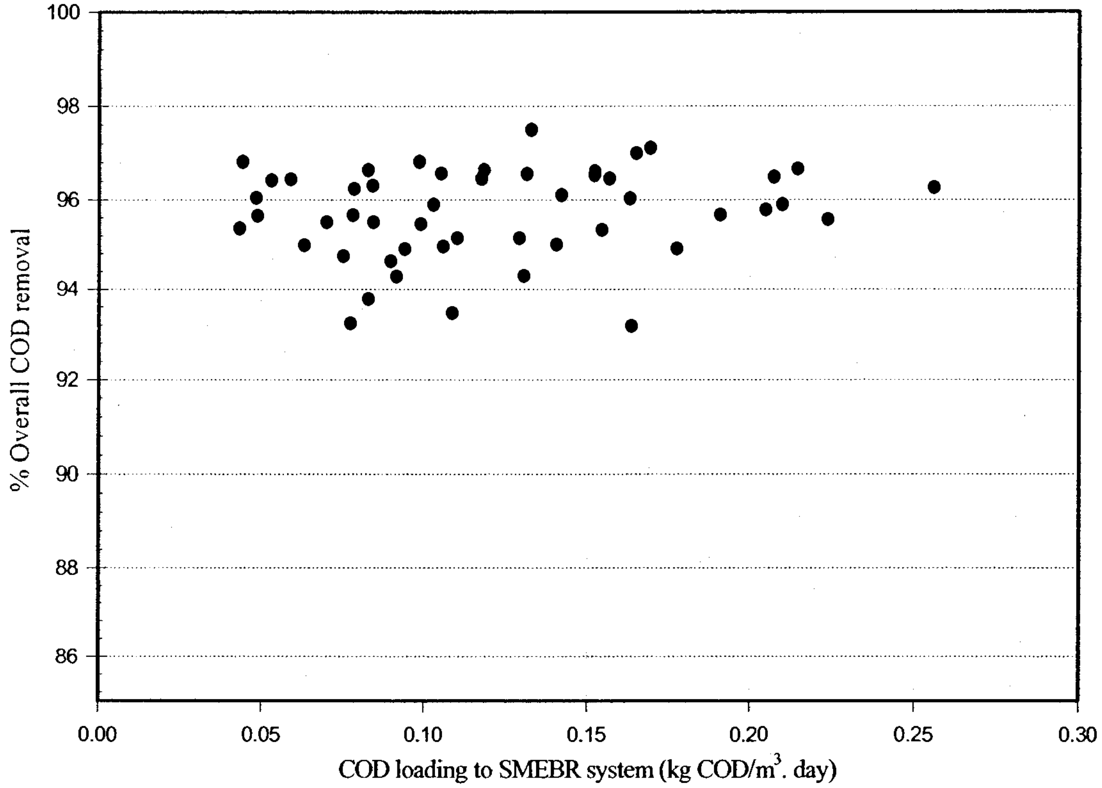


Figure 8.22 Overall COD removal versus organic loading in SMEBR system during the Phase III

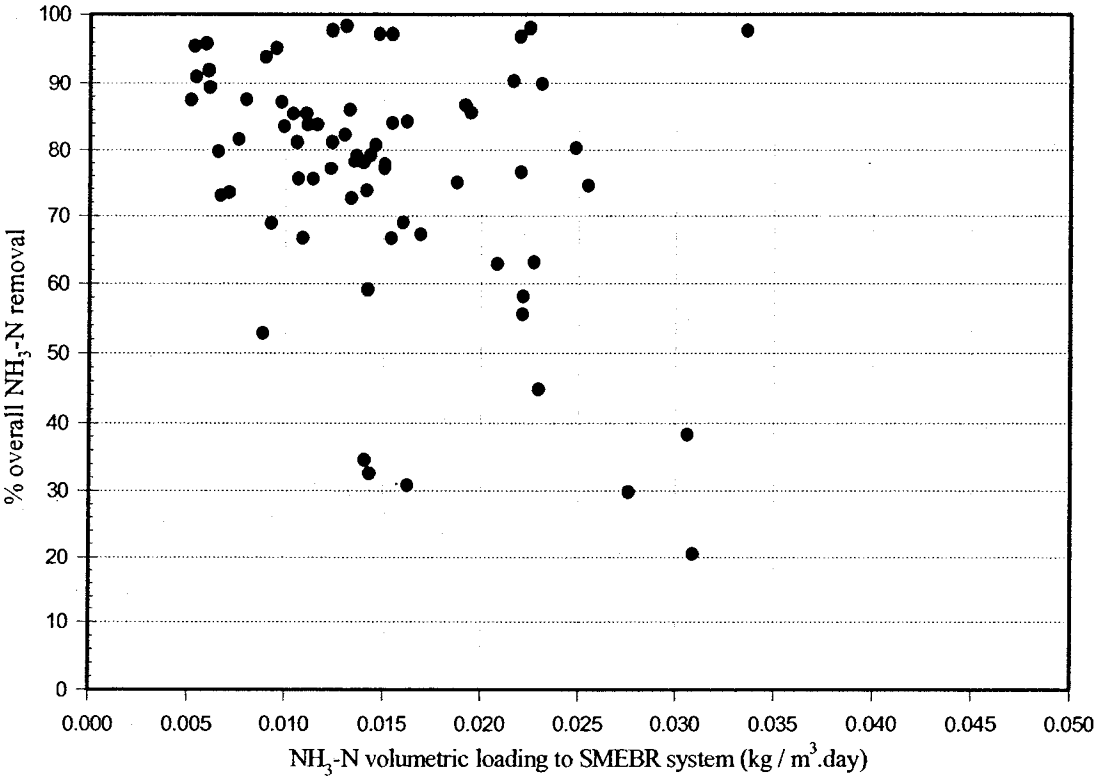


Figure 8.23 Overall NH$_3$-N removal versus ammonia nitrogen loading in SMEBR system during the Phase III

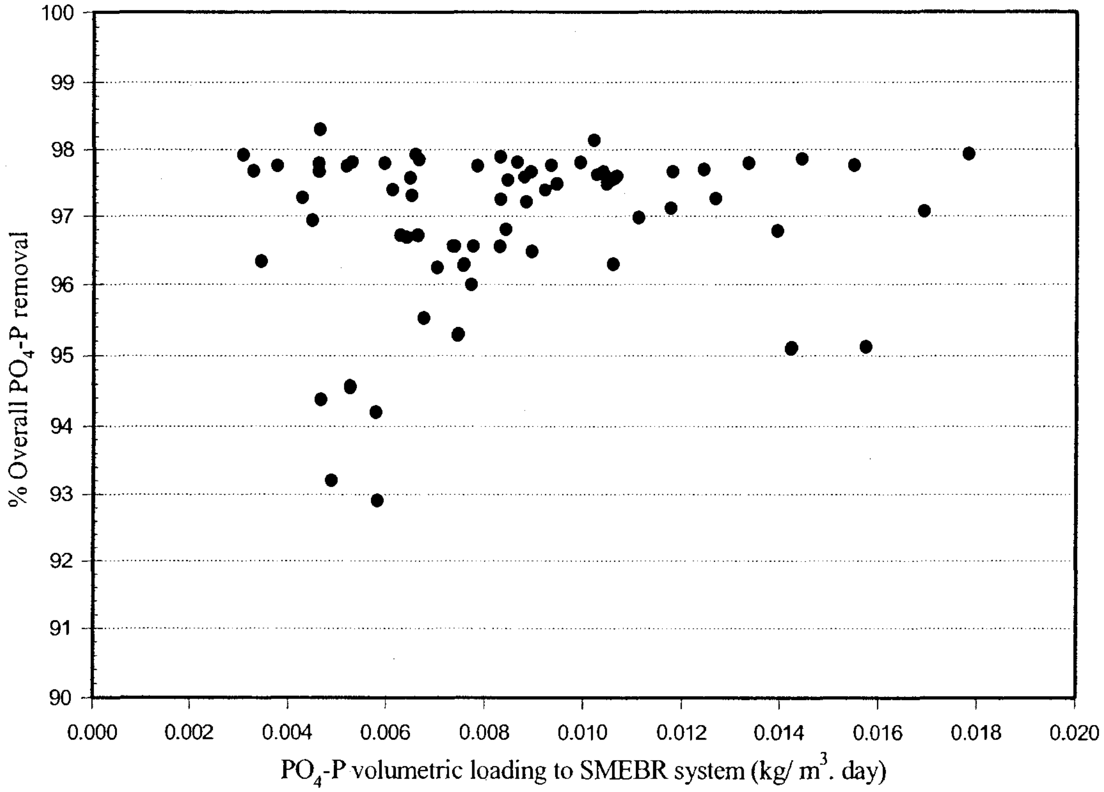


Figure 8.24 Overall PO_4-P removal versus ortho-phosphorous loading in SMEBR system during the Phase III

They reported that for six lab runs with HRTs of six days, three days (two runs), one day, 12 hours, and 6 hours, the submerged membrane bioreactor was capable of achieving over 90% COD removal, on average, almost independently of HRT. Another reason for the stability in COD removal efficiency may the designing SMEBR system itself, which can reduce the COD concentration by applying electrokinetic phenomena.

Figure 8.23 (variations in % NH_3-N removal against NH_3-N volumetric loading) has not show any trends neither. The percentage of NH_3-N removal was reproduced against the variations in the HRT as shown in Figure 8.26. This figure demonstrates that only in Stage II, the % NH_3-N removal was strongly dependent on the HRT, while during the other stages, the % NH_3-N removal was less dependent. This may be due to the fact that the decline in flux was sharply during the Stage II as shown in Figure 8.1.

Figure 8.24 demonstrates that about 86 % of the % PO_4-P removal was above 96% but 69% above 98%. When the % PO_4-P removal is plotted against the HRT (Figure 8.27), the % removal in PO_4-P was always greater than 96 % during the Stages II, III and IV in which the electrocoagulation took place. The only decrease in PO_4-P removal was observed in Stage I which might be due to the fluctuation in the HRT. However, because EC process in the designed SMEBR system can supply a continuous production of flocs which might be able to deal with the sudden increase in the volumetric loading of PO_4-P. This means that the designed SMEBR system can deal with sudden shock in volumetric loading which considers another advantage of the designed SMEBR system.

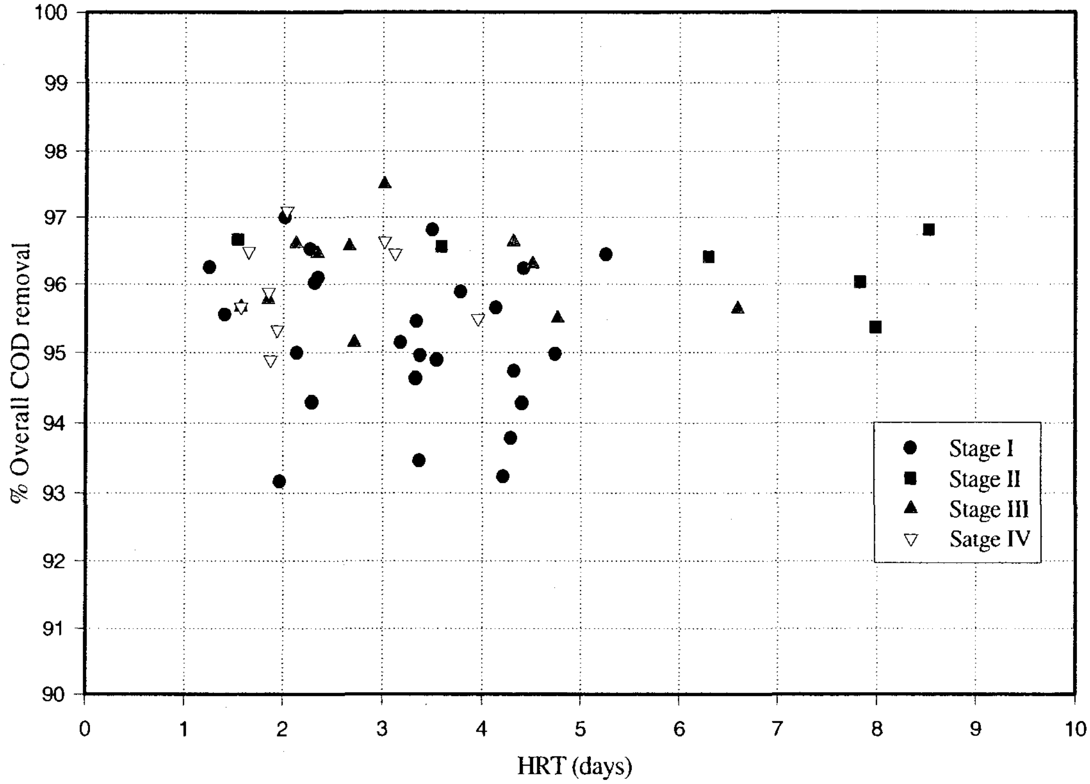


Figure 8.25 Overall COD removal versus HRT in the SMEBR system during the Phase III

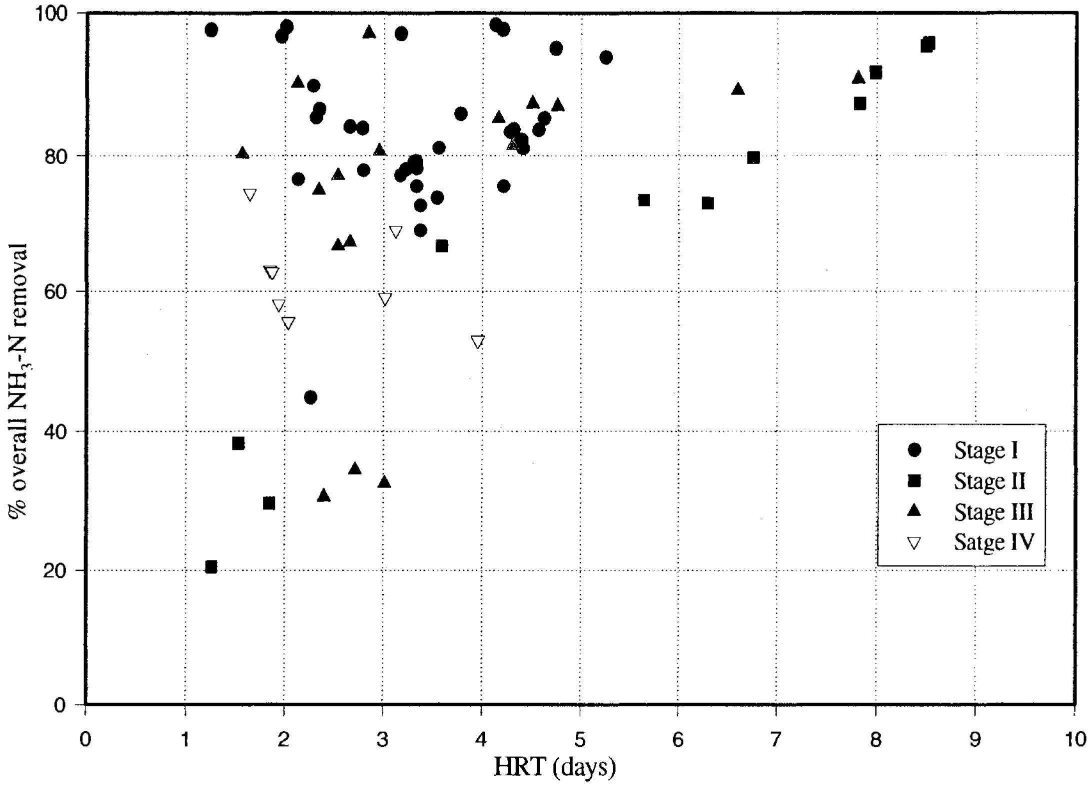


Figure 8.26 Overall NH_3-N removal versus HRT in the SMEBR system during the Phase III

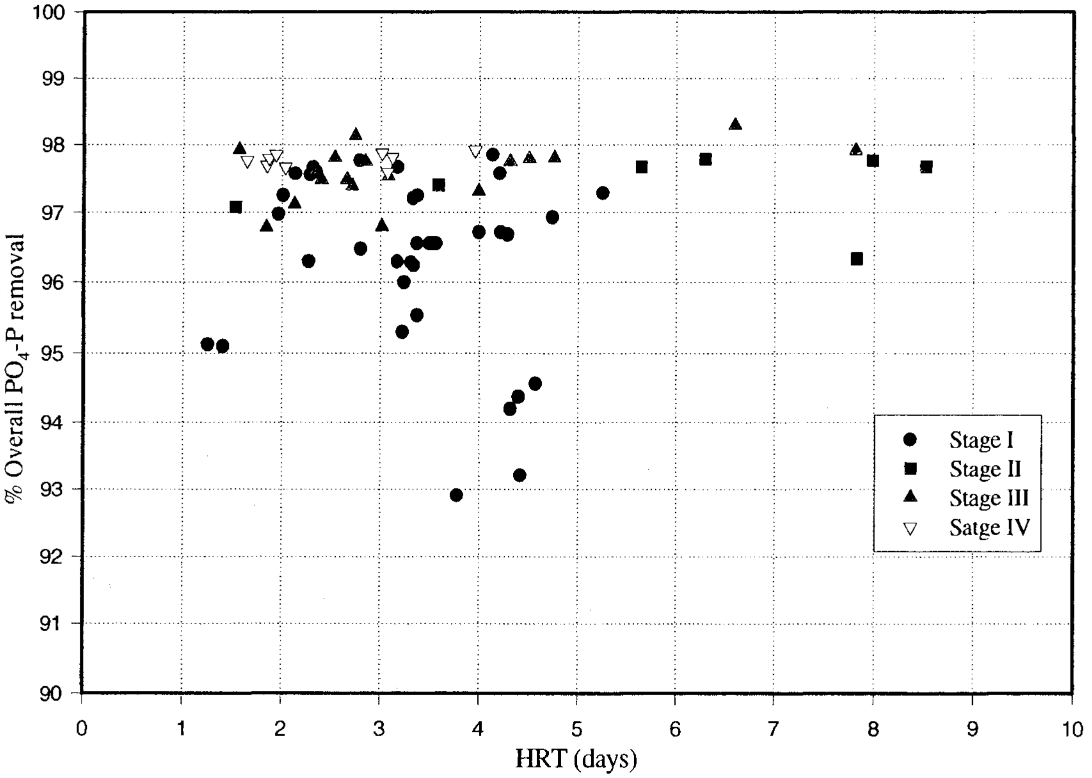


Figure 8.27 Overall PO_4-P removal versus HRT in the SMEBR system during the Phase III

8.5.6 Microbial Activity

As iron can affect the microbial activity, aluminum can also do so, therefore, in Phase III of this research, the specific oxygen uptake rate (SOUR) of the activated sludge was also determined (Equation 4.32) in each zone in order to analyze the effect of applying a DC field on microbial activity.

As shown in Figure 8.28, during the first stages of operation of Stage I (reference stage), an obvious reduction in the microbial activity was observed. This was attributed to the acidic conditions in the SMEBR system during this period of operation (section 8.5.2.1). After the pH in the system was adjusted to neutrality neutral level, an increase in the microbial activity was observed.

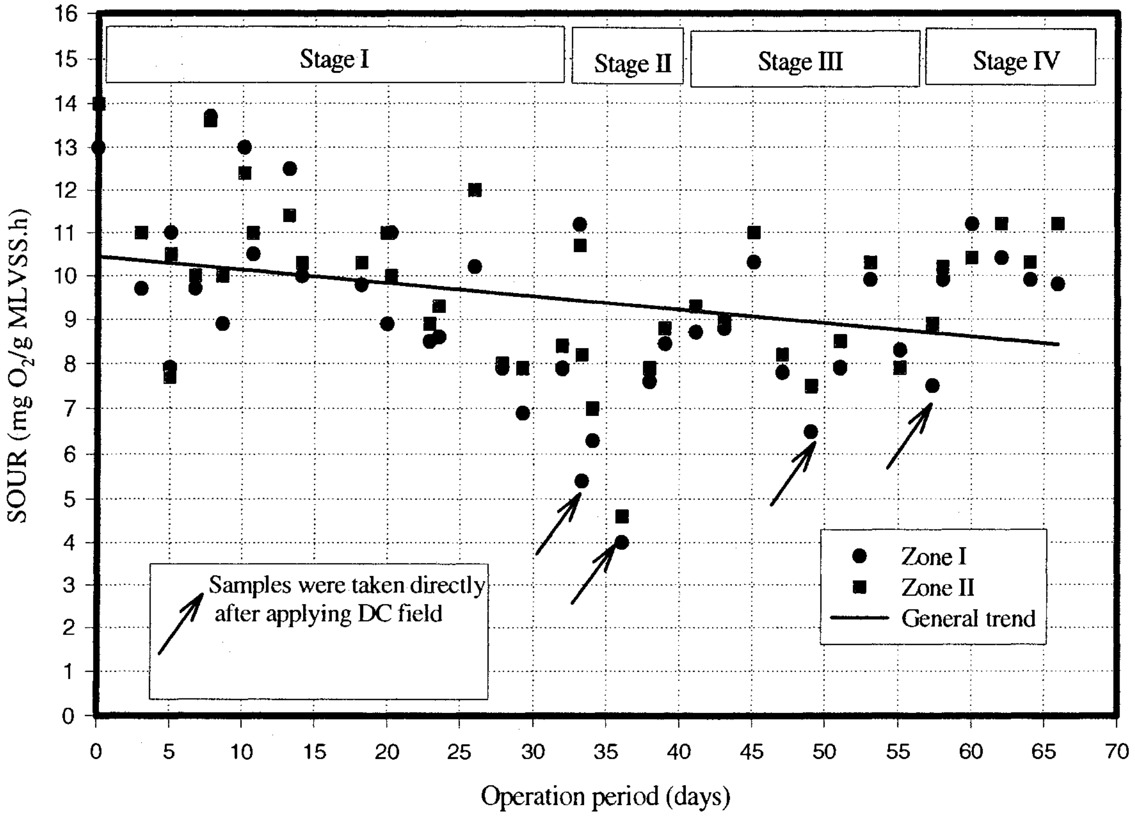


Figure 8.28 Changes of the SOUR in the SMEBR system during the Phase III

Starting from Stage II, a fluctuation in the microbial activity was observed during the SMEBR operation. It indicated that the weakness in the microbial activity was more pronounce when the samples from both bioreactor zones were taken immediately after applying a DC field to the MLSS solution. This behavior was also observed in Phase II of this research. These results imply that the microbial activity is very sensitive to a DC field, particularly during the application period of the DC field onto the MLSS solution.

Furthermore, the result from Figure 8.28 demonstrated that the decrease in microbial activity was less pronounces in Stage IV in comparison with Stages II and III. This might be due to the fact that the exposure time to a DC field in Stage IV was less than the other stages because of the different operational modes.

However, not only can an applied DC field decrease the microbial activity, but also the long SRT can be seen to have a negative impact on the activity of the microorganism (Khor et al., 2006).

With respect to the impact of applying DC on the decrease of microbial activity on the removal efficiency of the pollutants, the treatment efficiency, in terms of COD and phosphorus, was not affected by the decrease in microbial activity whereas the effect of the DC was more obvious on the bacteria that are responsible for the nitrification process. The same phenomenon was observed in Phase II of this research.

8.5.7 Change in Electrical Parameters

8.5.7.1 Change in Current Density

In any wastewater treatment process, the economic analysis is a matter of concern. As the designed SMEBR system is based on applying a DC, it is necessary to study the variations in electrical parameters (current density, energy consumption, electrode material consumption) during the operation of the SMEBR system, since these parameters have a direct impact on the economical analysis of the developed process.

In Phase III of this research, the voltage was constant during the operation period (1 V/ cm), while the current values changed with time. Figure 8.29 illustrates how the current density fluctuated during the operation of the SMEBR system. The current density was 14 A/m^2 at the beginning of Stage II and it reached 27 A/m^2 on day 41, after that the current density began to decrease with time until day 46, when it stabilized at around 15 A/m^2. The fluctuation in the current values during these days was attributed to the changes in conductivity and electrolysis of electrodes. An apparent explanation for these changes in electrical conductivity is the increase in the ionic content of the MLSS solution due to substrate degradation (Alshawabkeh et al., 2004) and electrolysis of the anode.

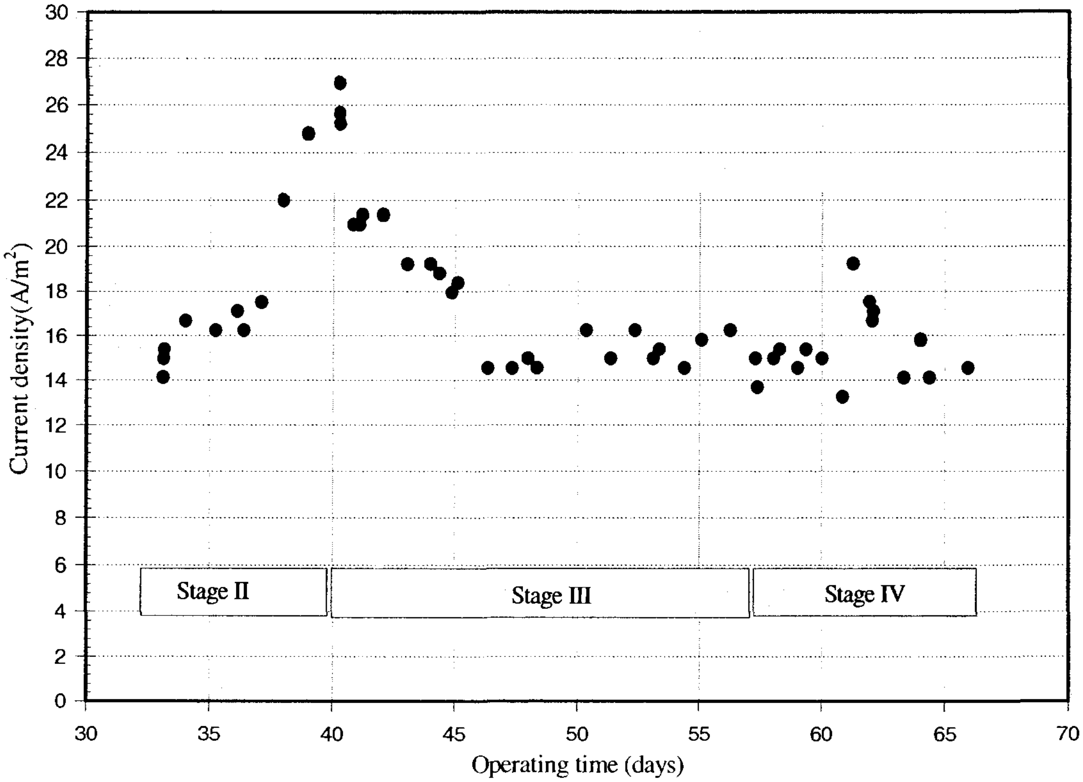


Figure 8.29 Changes of the current density in the SMEBR system during the Phase III

On day 63, the current density jumped to 19.5 A/m^2 due to the damage of the level switch. The SMEBR system was consequently shut down for maintenance and the electrodes assembly was taken from the elector-bioreactor which caused mixing the activated sludge content of the two zones. However, after two days of operation, the system had stabilized at around 15 A/m^2.

8.5.7.2 Energy and Anode Consumptions

The most important electrical parameter which may affect the cost of wastewater treatment by the SMEBR system is the energy consumption. Calculation of energy consumption (E) is expressed as (Kobya et al., 2006):

$$E = \frac{U \times I \times t}{V} \tag{8.3}$$

Where E is the energy consumption (kWh/m^3 wastewater treated). U is applied voltage (V), I is the current (A), t is retention time (s) (i.e. electro-coagulation time) and V is the volume of the treated wastewater (m^3).

Another parameter which can also affect the economical performance of the SMEBR system is the anode expenditure. Anode consumption (m) having a unit of kg Al/m^3 wastewater treated is calculated from Faraday's law in the following equation:

$$m = \frac{I \times t \times M}{Z \times F \times V} \tag{8.4}$$

Where M is the relative molar mass of the electrode concerned, Z is the number of electrons in oxidation/reduction reaction, and F is the Faraday's constant (96,500 C/mol).

In Phase III, the DC field was applied to the mixed liquor solution as a discontinuous operation throughout Stages II to IV, at different operational modes and different operating days. To calculate the total energy consumed during each stage, the average current in each stage was used in the calculation based on the results presented in Figure 8.29. To eliminate the difference in operation days in each stage, the result obtained from equations 8.3 and 8.4 were divided by the number of operating days in each stage. Table 8.3 summarizes the energy and anode consumptions for each stage in Phase III.

The results demonstrate (Table 8.3) that the energy consumption per cubic meter of the treated wastewater per operating day was more in Stage II in comparison to Stages III and IV.

Table 8.3 Energy and anode consumptions in the SMEBR system during the Phase III

Items	**Stage II**	**Stage III**	**Stage IV**
Operation time (days)	7	17	9
DC exposure time (minutes)	15 ON/ 45 OFF	15 ON/ 45 OFF	15 ON/ 105 OFF
Effective operating hours during each stage (h)	56	136	30.86
Average current during each stage (ampere)	0.5	0.35	0.37
Energy consumption (kWh)	15.4	26.6	6.4
Unitary daily energy consumed (kWh/ m^3.day)	2.2	1.56	0.517
Unitary daily electrode consumed (g/ m^3.day)	100	70	32

An energy reduction from 1.56 (kWh/ m^3.day) in Stage II to 0.517 (kWh/ m^3.day) in Stage IV was also observed. Furthermore, the electrode consumption reduced from 70 (g/ m^3.day) in Stage III to 32 (g/ m^3.day) in Stage IV. These were also associated with improvements in membrane flux in Stage IV, as it is shown in section 8.5.1. These results demonstrate the importance of the time operational mode on the SMEBR process.

Subsequently, in addition to the benefits of operating the SMEBR system at the operational mode of 15 ON minutes / 105 minutes OFF in Stage IV of Phase III, this mode demonstrated a decrease in the consumption of energy by 66.8% than the other operational mode that was applied during Stage III. This benefit was mainly due to a lesser amount of exposure time to the applied DC field. Furthermore, the electrode consumption for the operating mode of 15 ON minutes / 105 minutes OFF was reduced by 54.3% in Stage IV compared to the operational mode of 15 ON minutes / 45 minutes OFF in Stage III.

8.6 Conclusions

In Phase III of this research, the SMEBR system was operated at constant transmembrane pressure mode where aluminum was used as an anode and iron as a cathode. The operational period was extended for 66 days and divided into four sequential stages. The conclusions of Phase III can be summarized by the following points:

- Contrary of Phase II, the color of the MLSS solution in Phase III did not change with time during the operation and was found similar to the original color of MLSS solution. Also in this phase, water permeate quality had neither color nor odor.
- Starting from Stage II (with a DC field applied to the MLSS solution), the results demonstrated an increase in the pH of treated suspensions. Also, the influence of electrokinetic process did significantly affect the floc size of the MLSS solution. Large and dense flocs started to appear during Stage II, which enhanced the overall performance of liquid/solid separation processes.
- As Phase III extended during the four stages. The conclusions of each stage can be summarized by the following points:

- **The Stage I ~1–33 days**: The system was operated without a DC field. The HRT fluctuated between 1.2 and 6 days, which was due to a declined flux resulting from the fouling phenomenon. The average COD removal of the system was 95.2 % and an ammonia nitrogen removal efficiency of 80% was achieved by end of Stage I. The phosphorus removal was greater than 96.4 %.
- **The Stage II ~33–40 days**: The system was operated with a DC field with a potential gradient of 1 V/cm and with an operational mode of 15 minutes ON / 45 minutes OFF. The SMEBR system made significant improvement in COD and phosphorus removal (greater than 96% for COD and greater than 97% for phosphorus). The ammonia removal was 70%. However, the HRT increased to 9 days by the end of this stage reflecting an unsatisfactory filtration performance. Subsequently, it was suggested to begin the electro-coagulation process before operating the membrane module inside the electro-bioreactor. This would permit a proper electro-coagulation to take place before beginning the membrane filtration and thus decrease membrane fouling.

-**The Stage III ~40–57 days**: The system was operated with a DC field gradient of 1 V/cm and with operational mode of 15 minutes ON/45 minutes OFF, after washing the membrane (chemically and physically). Better membrane filtration performance was achieved in comparison with Stages I and II. During the first 5 days of the continuous operation, the percentage reduction in membrane permeability was 63 % in Stage III, while in Stages I and II was 80% and 82% respectively (based on five days on the continuous operation).

-The Stage IV ~57–66 days: The system was operated with DC field gradient of 1 V/cm and with a different operational mode of 15 minutes ON /105 minutes OFF. This achieved significant improvement in membrane filtration efficiency, the percentage reduction in membrane permeability was only 38 % equivalent to 52.5 % improvement in permeate flux in comparison with Stage I. Furthermore, this mode was an improvement over the previous mode in terms of the pH variation within the SMEBR system. The data from this stage confirmed that the operational mode of the DC field is a key parameter in the performance of the SMEBR system.

- In comparison with the two operational modes of DC applied during Phase III, the operational mode in the Stage IV (15 ON/ 105 OFF) demonstrated better results in terms of pH fluctuations within the SMEBR system. The pH values of all types of wastewaters in the system were within the range of 6.8 -7.3. This may due to the fact that the time interval where the DC was turned off was greater in Stage IV in comparison with that interval in Stages II and III. This result is considered another advantage of this operational mode in addition to the advantage obtained regarding the improvements in the permeate flux.
- Indirect observations can be drawn from the output data of Phase III presented by the fact that within the development of the MLSS during the operational period, the floc sizes had a significant effect on membrane fouling in comparison with the role of the MLSS concentration alone.

Chapter 9

General Conclusions and Future Work

Chapter 9 discusses and summarizes the major conclusions from Chapters 6, 7 and 8 and the issues generated during this study. It also addresses the principal factors necessary for the further development of the SMEBR system.

9.1 General Conclusions

In this research, the submerged membrane electro-bioreactor (SMEBR) system was designed and investigated as a novel wastewater treatment method to reduce membrane fouling and to enhance quality effluent.

It should be emphasized that the SMEBR system is not just an addition of the electrocoagulation (EC) to submerged membrane bioreactor (SMBR). It is a completely new design for wastewater treatment combining three fundamental processes (biological, membrane filtration and electrokinetic) in one hybrid reactor.

The novel designed SMEBR system that was based on applying a DC field between immersed circular electrodes around membrane filtration module showed an efficient treatment of the synthetic mixed liquor solution simulating municipal sewage.

Two different anode materials - iron and aluminum - were used to validate the SMEBR system for wastewater treatment. The designed system demonstrated an excellent performance in decreasing the fouling rate. The applied DC field in the SMEBR system enhanced the membrane filterability up to 16.6 % and 21.3 % using the iron and aluminum electrodes, respectively, comparing to simple submerged membrane bioreactor (MBR) (when the operating mode of DC was 15 minutes ON/ 45 minutes OFF). The significant improvement in membrane filterability was 52.5% (comparing to common MBR system) when using the aluminum anode at an operational mode of 15 minutes ON/ 105 minutes OFF. This indicated that the operational mode of the DC supply is a key parameter in the operation of the SMEBR system. Furthermore, the SMEBR system showed a high removal efficiency of major wastewater components such as COD and nutrients. The overall removal efficiency for COD was greater than 96% and greater than 98% for phosphorus. In conjunction, an average removal of NH_3-N was about 70 %. It should be emphasized that the phosphorous removal efficiency was higher than other studies on MBR without electrokinetics. Furthermore, the effluent of the SMEBR treatment using synthetic wastewater had no color and no odor. Table 9.1 summarized the detailed results obtained in Phases II (iron anode) and III (aluminum anode) of this research.

In terms of improving sludge properties, the SMEBR system improved the sludge dewatering conditions by reducing the specific resistance to filtration up to 46%.

Table 9.1 Summary of results of the Phase II and the Phase III

		Phase II		**Phase III**			
		Stage I	**Stage II**	**Stage I**	**Stage II**	**Stage III**	**Stage IV**
Anode Material		---------	Iron	---	Aluminum		
Operation time (days)		26	27	33	7	17	9
DC exposure time (minutes)		------	15 ON / 45 OFF	----	15 ON / 45 OFF	15 ON / 45 OFF	15 ON / 105 OFF
% COD removal of the system	Maximum value	99.3 %	98.4%	96.8%	96.8%	97.5%	97.1%
	Minimum value	89.4 %	93.7%	92.6%	95.4%	95.2%	94.9%
	Average Value	95.7 %	97.5%	95.2%	96.2%	96.2%	96.0%
% PO_4-P removal of the system	Maximum value	95.6%	98.7%	97.8%	98%	98.3%	98.1%
	Minimum value	88.5%	90.7%	93%	96.2%	97%	97.9%
	Average Value	90.1 %	97.6%	96.4%	97.3%	97.8%	98%

Table 9.1 Summary of results of the Phase II and the Phase III (Continued)

		Phase II		**Phase III**			
		Stage I	**Stage II**	**Stage I**	**Stage II**	**Stage III**	**Stage IV**
% NH_3-N removal of the system	Maximum value	97%	93%	98%	96%	93%	81%
	Minimum value	49%	15%	68%	58%	69%	62%
	Average Value	90%	70%	80%	70%	88%	68%
Unitary daily energy consumption (kWh/m^3.day)		---	---	----	2.200	1.560	0.517
Unitary daily electrode consumption (g/m^3.day)		---	---	---	100	70	32

In term of pH changes within the SMEBR system, the pH values of the effluent were between 5.5 and 8.5; the range recognized as the best for microorganism performance. This also means that the effluent of the SMEBR system does not require further adjustment of pH.

9.1.1 Conclusions Related to Design

9.1.1.1. SMEBR Design Zones

The selected designed of the SMEBR system divided the treatment unit onto two main zones. The localization of the electrokinetic zone and the membrane filtration zone was adequate and responded to all designing constraints. The overall results demonstrated that the proposed design confirmed the hypothesis regarding the positive interaction of the three main processes: biological, electrokinetic and membrane filtration.

Because the boundary zones were fixed in this study (based on previous studies on electrokinetics at Concordia), their impact on the overall performance of the SMEBR system was not investigated. It is speculated that the investigation of the optimum distance between the boundaries of the two zones in the electro-bioreactor would give even better results in terms of decreasing the fouling rate within the SMEBR system.

9.1.1.2 Electrodes

Although positive results of experimental work had been accomplished with iron and aluminum electrodes during Phases II and III respectively, a general comparison between using of these two electrodes can be drawn and summarized in the following points:

- In terms of water quality, the color or the mixed liquor solution changed with time when it was treated with the iron electrode (greenish first, and finally turned red and turbid), while the color of the mixed liquor solution did not show any change with using aluminum. The change in MLSS color when iron is used may require further treatment to remove.

- In terms of the efficiency fouling prevention, the aluminum anode demonstrated relatively better performance in comparison with iron. This conclusion can be confirmed from the results obtained from Stage II in Phase II and those obtained from Stage III in Phase III. During these stages, the mode of operation of the DC was the same (15 minutes ON/ 45 minutes OFF). Based on 5 days of continuous operation in both stages, the percentage reduction in permeate flux (PRPF) was 68 % in Stage II (Phase II) compared to 63 % in Stage III (Phase III). III (Phase III). This may also be due to the fact that the effective anode area was 2.5 times higher with the aluminum anode.

In general, electrocaogulation by iron has some limitations because iron can present in two oxidation states: ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions. It is highly disadvantageous to generate Fe^{2+} since it is highly soluble and therefore, is not capable of colloid destabilization by sweep flocculation thereby might cause poor electrocoagulation performance (Bagga et al., 2008). On the other side, aluminum is predominantly present as trivalent Al^{3+} in aqueous environments. Hence, it is hypothesized that employing aluminum anodes will generate Al^{3+} during electrocoagulation producing $Al(OH)_3$ precipitates capable of destabilizing colloid suspension and potentially improving membrane performance (Bagga et al., 2008).

9.1.2 Conclusions Related to the Operation Parameters

All the operational parameters are important in the SMEBR performance. However, it appears that there are some key parameters which can have more significant effect on the overall performance of the SMEBR system. These parameters are: DC exposure time and sequence of operation.

9.1.2.1. DC Exposure Time

While the other parameters are kept constant, the DC exposure time plays a significant role in a successful SMEBR design. This was demonstrated throughout the operation of Phase III when the DC exposure time changed from 15 minutes ON/ 45 minutes OFF (in Stage III) to 15 ON minutes / 105 minutes OFF in Stage IV. Practically, the DC exposure time may be related to the amount of dissolved metal supplying the mixed liquor solution and creating the coagulation. Low DC exposure time would not create the sufficient conditions for better coagulation, but similarly a high DC exposure time might produce a negative impact represented by a decrease in the growth of microorganisms. Although the present study demonstrated successful wastewater treatment, it seems there is an optimum range of DC exposure time could be studied in the future.

In comparing the two above mentioned operating modes of DC supply, 15 minutes ON/ 105 minutes OFF in Stage IV demonstrated better results in reducing the fouling rate (1.7 times lower than MBR alone during five days of continuous operation).

9.1.2.2 Sequence of Zone Operation

An important conclusion is drawn from this study regarding the method of beginning the SMEBR operation. The results showed that a better performance of the SMEBR system can be achieved if the electro-bioreactor zone undergoes operation before the operation of the membrane module starts. An initiation of electro-coagulation is necessary to prevent the fouling particles from moving towards the zone with the membrane module.

9.1.3 Conclusions Related to Energy Consumptions

In addition to the benefits of operating the SMEBR system with the operating mode of 15 ON minutes / 105 minutes OFF during Stage IV of Phase III, this mode demonstrated less consumption of energy by 66.8 % than the other operating mode of (15 ON minutes / 45 minutes OFF) during the same phase. This was mainly due to the reduced exposure time of the applied DC field. Furthermore, the electrode consumption for the operating mode of 15 ON minutes / 105 minutes OFF was 54.3% lower than the other operating modes. The energy consumption influences the overall costs of the wastewater treatment and can be easily optimized.

9.2 Contribution of this Study

The design studied in this research is the first of its kind and thus constitutes a novel approach to a hybrid wastewater treatment method by integrating biological processes, membrane and electrochemical processes into one operational unit called the submerged membrane electro-bioreactor – SMEBR.

There are a number of contributions made by this thesis including (a) designing of a new system for wastewater treatment; (b) assessing relationship between three processes: membrane, biological and electrochemical; (c) testing of two different electrodes within the SMEBR system; (d) establishing of appropriate current levels to be used in a bioreactor system; (e) improving the flux of effluent due to reducing of membrane fouling through the reduction of colloids and soluble organics in reactor; (f) establishing electrode and power consumption parameters for the SMEBR hybrid system; (g) improving sludge dewatering conditions by reducing the specific resistance to filtration.

Moreover, this hybrid method can be competitive with any other one presently used in wastewater treatment. The SMEBR contributes to: a) saving in the land needed for construction of treatment facilities by combined all secondary and advanced wastewater treatment units; b) protection waters by increasing quality of the effluent in terms of color, pH, Chemical Oxygen Demand (COD), and nutrient content; c) reducing the membrane fouling problems; d) omitting the requirements for chemical addition (the coagulation process occurs by electrokinetic phenomenon) leading to a higher quality of biosolids; e) initiating research in a new type of hybrid systems for more efficient wastewater treatment.

During the operation periods (about two months in each phase), the new designed method has proven the beneficial interactions among three main processes and avoided successfully the potential undesired impacts. The electrical field applied for electro-coagulation does not significantly affect the biological processes in the electro-bioreactor. The generated electrokinetic phenomena did not show evidence for the deterioration of membranes material. However, the performance of the new design on long term operation needs to be validated and this is addressed as a future work.

The significant improvement in permeate flux and phosphorous reduction made by the novel design of the SMEBR system could open the door for a cost-effective and environmentally sustainable technology.

One of the main advantages of the selected design of the SMEBR system was the implementation of the electro-coagulation phenomena instead of conventional coagulation to increase the size of the floc particles, and further enhancing the membrane filtration process and improving the effluent quality.

The developed system could find a direct application in the treatment of various wastewaters, including sewage, without an extensive pretreatment. Such a solution is required by several small municipalities, mining areas, agriculture facilities, military bases, and remote locations including those in cold regions. In addition, such a compact hybrid system can be easily adapted to a mobile unit.

9.3 Future Research Directions

During the present study on SMEBR several promising parameters remained unexplored or kept constant; subsequently, some additional investigations could be carried out. Sections 9.3.1 – 9.3.5 show suggestions for future research work.

9.3.1 Pilot Scale Investigations and Cost Analysis

Although the system showed good performance in a laboratory scale, a pilot scale investigation would be required to expose the system to a variable quality of wastewater influent.

Because cost analysis is a major factor in succeeding any new project, the feasibility of the new designed system as a wastewater treatment method needs detailed analysis in terms of costs. In this thesis, it was demonstrated that it would be misleading to go in details regarding costs based on the laboratory scale results. Therefore, during the pilot scale phase, a comprehensive study on the cost analysis is recommended.

9.3.2 Impact of Transmembrane Pressure

In this research, the transmembrane pressure was constant to eliminate the impact of transmembrane pressure on the results. However, in most applications of membrane filtrations processes, the flux is constant and the transmembrane pressure varies with time because this approach is less expensive. Consequently, the fouling mechanisms in constant flow applications and constant pressure applications are different. For this reasons, the operation of the SMEBR system at constant flux should be addressed in future work.

9.3.3 Impact of Sludge Retention Time (SRT)

In this thesis, the strategy of research was based on decreasing the wasted sludge. The SRT was constant (about 200 days), which increased the MLSS concentration in the electro-bioreactor. In general, the SRT is directly linked to the net production of excess sludge and affects biological performance. Furthermore, no-wasted the sludge might result in a non-steady state system because the kinetic conditions in the electro-bioreactor vary.

Integrating electrokinetic phenomena (mostly presented by electrocoagulation) to biological process makes the system more complex. The cumulative effect of coagulated sludge on biological and filtration performance is different in a SRT controlled system than a no-wastage system. Therefore, the impact of variations in SRT in the SMEBR system needs further investigation.

9.3.4 Impact of Hydraulic Retention Time (HRT)

Because the SMEBR system in this research was operated at constant pressure as mention in section 9.3.1 and low permeate flux, the HRT fluctuated rapidly in both experimental Phases II and III. It reached 24 days in Phase II and 9 days in Phase III which is not representative to the conventional operation of MBRs where the HRT is about few hours. It should be emphasized that only when the SMEBR system is really operated under steady-state conditions, sound conclusions can be drawn about the effect of the HRT on the SMEBR performance. Therefore, the impact of variations in HRT in the SMEBR system needs also further investigation.

9.3.5 Impact of Other Operating Parameters

- The impact of various operational and design parameters, such MLSS concentration and organic loading rates on filtration performance within the SMEBR system would be explored.
- Further research may also optimize some operating conditions, e.g. oxygen supply in the two zones, temperature and exposure time to the DC field (operation mode) beyond those tested in this research.

- More research could be carried out on new materials for electrodes.
- The zones' boundaries could be also optimized for pilot and full scale conditions.

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Appendix A

Analytical Methods

As mentioned in Chapter 4, different physiochemical and biochemical parameters were analyzed in this research to assess the performance of the submerged membrane electro-bioreactor (SMEBR) system. While Table 5.5 summarizes the analytical methods that have been followed to analyze or measure the physiochemical and biochemical parameters, this appendix provides detailed description of analyzing and measuring each parameter.

A-1 Procedure for pH, Oxidation-Reduction Potential (ORP), and Temperature Measurements

The values pH, ORP and temperature were measured using a pH meter model 215 glass electrode (Denver Instrument, USA). Calibration of pH, and DO meters was conducted once a day before use and room temperature (20 ± 1 °C) was set as default temperature.

A-2 Procedure for COD Analysis

To analysis COD samples, the following procedure was followed:

1- All the samples were filtered using 0.45 μm filter paper.

2- COD heater block was preheated to 150° Celsius.

3- The cap from a COD twist-cap vial was removed.

4- A 2.5 mL sample was added carefully to COD vial such that it formed a layer on top of reagents.

5- The twist cap was replaced.

6- The contents of the sealed vial were mixed by shaking.

7- Standards and blanks were processed exactly as the samples.

8- The twist-cap vial was placed in a COD heater block for 2 hours.

9- After 2 hours, the vial was removed from the heater block and allowed for cooling.

10- The suspended precipitate was allowed to settle and the outside of the vial was clean before taking the measurements.

11- As described by the manufacture, Method A was used for standard Range reagent (20-900 mg/L COD) or method B was used for low Range gent (5-150 mg/L COD).

(a) The wavelength of the spectrophotometer was set to 600 nm and using a procedural blank, zero the absorbance reading.

(b) Use the highest standard (up to 150 mg/L COD) to set spectrophotometer to zero absorbance at 440 nm.

12- The absorbance of each standard and sample on the spectrophotometer was read.

13- A graphic calibration curve was prepared by plotting the absorbance of the standards versus their known concentration.

14- The sample absorbance was compared to the graphic calibration curve to determine COD concentrations.

A-3 Procedure for Ammonia- Nitrogen (NH_3-N) Analysis

1- A 0.1 mL of sample was added to one AmVer^{TM} Diluent regent test N tube for high range ammonia nitrogen. This presented the prepared sample.

2- A 0.1 mL of ammonia-free water was added to one AmVer^{TM} Diluent regent test N tube for high range ammonia nitrogen. This presented the blank sample.

3- The contents of one ammonia salicylate regent powder pillow was added to each sample in step 1 and 2.

4- The contents of one ammonia cyanurate regent powder pillow was added to each sample in step 1 and 2.

5- The vials were caped tightly and shacked thoroughly to dissolve the powder.

6- The contents in each vial in the step 5 were left for 20- minute reaction period.

7- The vial of the blank sample was placed into the cell holder, and the Zero bottom was touched. The display showed 0.00 mg/L NH_3-N.

8- The vial of the sample was placed into the cell holder, and the Read bottom was touched. The display showed the concentration of NH_3-N in mg/L.

A-4 Procedure for Nitrate- Nitrogen (NO_3-N) Analysis

1- A 25 mL graduated mixing cylinder was filled with 15 ml of the sample

2- The contents of one NitraVer 6 Reagent powder were added to the cylinder.

3- The cylinder was shaken vigorously for three minutes.

4- The contents in the previous step were left for a 2- minute reaction period.

5- A 10 mL of the sample from step 4 was poured into a clean round sample cell.

6- The contents of one NitraVer3 Reagent powder were added to the sample in step 5. This presented the prepared sample.

7- The sample in step 6 was shaken gently for 30 seconds. A pink color was developed when the nitrate was presented.

8- The contents in the step 6 were left for 15- minute reaction period.

9- When the reaction period finished, a second 10 mL of the original sample is filled in another clean sample cell. This presented the blank sample.

10- The blank sample was placed into the cell holder, and the Zero bottom was touched. The display showed 0.00 mg/L NO_3-N.

11- The prepared sample was placed into the cell holder, and the Read bottom was touched. The display showed the concentration of NO_3-N in mg/L.

A-5 Procedure for Ortho-Phosphorus (PO4-P) Analysis

1- A 25 mL graduated mixing cylinder was filled with 25 mL of the sample.

2- A 1 mL of Molybdate reagent was added to the sample in step 1 using a 1-mL calibrated dropper.

3- A 1 mL of Amino Acid reagent solution was added to the contents in step 2 using a 1-mL calibrated dropper.

4- The contents in step 3 were mixed for several times. This presented the prepared sample. A blue color was developed when the phosphate was presented.

5- The contents in step 4 were left for 10- minute reaction period.

6- During the reaction period, a 25 mL graduated mixing cylinder was filled with another 25 mL of the sample. This presented the blank sample.

7- When the reaction period done, the blank sample was placed into the cell holder and the Zero bottom was touched. The display showed 0.00 mg/L PO_4^{3-}.

8- The prepared sample was placed into the cell holder and the Read bottom was touched. The display showed the PO_4^{3-} concentration as in mg/L.

A-6 Procedure for MLSS and MLVSS Analysis

1- Fiber filter no-ash glass disc of approximately 0.45 μm pore size was used and weighted before test.

2- The weighted filter disk was then placed in a filtering apparatus as shown in Figure 4.6.

3- A measured volume (10 mL) of waste water was passed through the filter and suction was applied.

4- The filter containing the residual was then washed and dried in an oven for two hours at 103 to 105 °C.

5- The sample was then cooled and weighted.

6- The difference in weight of the dry filters before and after solids were passed through was the MLSS [mg] of suspended solids per liter [L] of water filtrated.

To analysis MLVSS in waste samples, the following procedure was followed:

7- The suspended solids collected on the no-ash filter in the MLSS test were ignited in a furnace at 550 °C ± 50 °C for 20 minutes.

8- The resulted loss of weight was the MLVSS as mg/L.

A-7 Procedure for Measuring Specific Resistance to Filtration (SRF)

Figure A.1 shows the apparatus required to measure the sludge specific resistance to filtration (SRF). Ashless filter papers were used to determine the SRF (Cat. No. 1440-110, Fisher Scientific, Canada). About 100 mL sample of the mixed liquor suspension was required for each filterability test. The sample was placed in Buchner funnel, and immediately the vacuum started at 50 kPa. Then, a series of data V–t was measured, and a curve for t/V–V was obtained (See Equation 4.3). The slope from the graphic method represents the coefficient b in Equation 4.30.

A-8 Procedure for Measuring Oxygen Uptake Rate (OUR)

Oxygen uptake rates were determined immediately after samples (about 250 mL per sample) were taken from the elector-bioreactor. The OUR was measured by using a YSI DO meter, Model 52 and a DO probe inserted into the sample bottle, which was tightly sealed to prevent oxygen transfer from the outside. The decrease in DO concentration with respect to time was recorded and the slope of the concentration versus time plot gave the oxygen uptake rate.

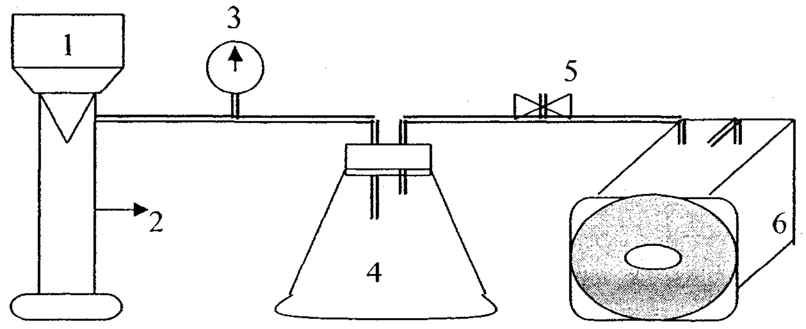

Figure A.1 Schematic diagram of sludge specific resistance measurement. 1-Buchner funnel; 2-Measuring cylinder; 3-Pressure gauge; 4-Suction flask; 5- Vacuum control valve; 6-Vacuum pump.