

Faculty of Science and Engineering
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**Development of a Novel Bioelectrochemical Filter for
Particulate-rich Wastewater Treatment**

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Abstract

Waste stabilisation ponds (WSPs) are widely used in tropical climate areas to treat municipal wastewater particularly that of remote communities. However, their operation depends on a range of uncontrollable natural factors (e.g. wind, sunlight), making it difficult to maintain a right balance between algal and bacterial activities for efficient treatment. Therefore, additional polishing steps are often required to prevent excessive discharge of suspended solids (SS) (mostly as algal biomass) and dissolved organic carbon (DOC) into the environment. One of the widely used polishing technologies is rock filters, which can facilitate entrapment of SS and aerobic oxidation of soluble organic matter. However, rock filters are usually constrained by their reliance on passive aeration, which is often insufficient to allow SS oxidation causing the problem of clogging. Hence, developing a reliable oxidative polishing technology is a necessity.

This thesis aimed at developing an alternative technology that can reliably treat particulate-rich effluent such as those generated from WSPs. For this, an emerging bioelectrochemical systems (BES) technology was selected as a platform and this technology harnesses the capacity of microorganisms to catalyse oxidation and/ or reduction reactions at solid-state electrodes. Microbial oxidation (removal) of organics can be facilitated via a BES anode with a concomitant generation of electrical current. Since organic matter removal could be electrochemically driven under anaerobic conditions and the electrode materials can be specifically selected to assist retention of organic particulate matter, a BES was considered as a suitable alternative to rock filters to polish WSP effluent.

The development of the technology first began with an assessment of a simple BES configuration (sediment-type). On developing a deeper understanding about limitations of this configuration, a unique and an innovative BES configuration was developed to treat wastewaters rich in particulate matter. Most of the experiments were conducted with primary sedimentation tank (PST) effluent, collected from a local municipal sewage treatment plant to mimic effluent of a failed WSP.

The sediment-type BES configuration was operated with graphite granules (substituting rocks in a rock filter) packed in anode and cathode areas facilitating a filtration of solids present in wastewater. Although simple to operate, the configuration had inherent limitations such as the spacing between cathode and anode. The higher electrode spacing and oxygen diffusion limitations into the cathode (due to biofouling of cathode) resulted in a poor removal of organic matter. The loss of organic matter was largely via fermentative pathways.

With an understanding of these limitations, a new tubular dual chamber filter-type BES configuration termed BES filter was designed and tested to retain and oxidise particulate matter and soluble chemical oxygen demand (SCOD) from wastewater. The BES prototype was composed of an outer anodic chamber (with approximately 10 L liquid volume) that encircles an inner cathodic chamber and the two chambers were separated with a cation exchange membrane. A short distance (2 cm) was maintained between the anode and the cathode. The unique feature was the use of a conductive carbon felt as both a physical filter and an attachment surface for biofilm formation. The BES filter effectively removed organic particulate matter from municipal wastewater (83% of SS removal). Also, the process was able to oxidise SCOD with a high coulombic efficiency (CE) of >80% (based on the SCOD removed).

The ability of the BES filter to entrap, decompose and oxidise fresh algal biomass was also verified. Results suggest that the filter type BES anode can effectively entrap (ca. 90%), decompose and anodically oxidise algal biomass without the need for a separate pre-treatment step. However, the BES filter had the following limitations: (1) inefficient hydrolysis of entrapped particulate matter; (2) the need for active pH control in both cathodic and anodic chambers; and (3) a huge cathodic oxygen reduction overpotential.

To address these limitations, a two stage sequential treatment process was developed. The 1st stage contained an electrolysis filter and a BES made up the 2nd stage of the process. The first electrolysis step was responsible for physical removal and *in situ* alkaline hydrolysis of entrapped particulate matter. The alkaline effluent enriched with hydrolysed soluble compounds was then loaded into the BES for oxidation of SCOD. The coupled system was continuously operated with primary sedimentation tank effluent (SS ~200 mg/L) for over 160 days. With no signs of clogging the process was

able to capture nearly 100% of loaded SS. A high CE of 93% (based on overall TCOD removed) was achieved. Results also suggest that the SCOD-laden alkaline liquor from the electrolysis step could effectively alleviate acidification of bio-anode and the acidity in the bio-anode facilitated discharge of effluent which was near neutral pH. The final effluent was both low in COD and SS. Since the two-stage process can be used without the need for any external chemicals, it has the potential for practical application. Future research is warranted to examine the performance of the process to effectively treat pathogens and nutrients in wastewater.

Overall, this thesis has explored the use of BES technology for particulate-solids treatment. The development of a novel “filter-type” BES configuration may enable the wastewater industry to effectively manage unwanted discharge of particulate solids. The technology developed is of particular benefit to manage discharge of algae from WSPs. The two-stage process could also become applicable to treat waste streams of other industries (e.g. abattoir, dairy, leather) rich in organic solids.

Declaration

To the best of my knowledge and belief, this thesis contains no material previously published by and other person except where due acknowledgement has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature:



Hassan Mohammadi Khalfbadam

Date: August 2016

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Abbreviations

Bioelectrochemical systems	BES
Cation exchange membrane	CEM
Coulombic efficiency	CE (%)
Counter electrode	CE
Data acquisition card	DAQ
Deionized	DI
Dissolved organic carbon	DOC
Dissolved oxygen	DO
Facultative ponds	FPs
Gas chromatograph	GC
Hydraulic retention time	HRT
Optical density	OD
Particulate chemical oxygen demand	PCOD
Primary settling tank	PST
Reference electrode	RF
Return activated sludge	RAS
Soluble chemical oxygen demand	SCOD
Stainless steel	SS
Suspended solids	SS
Total chemical oxygen demand	TCOD
Volatile fatty acids	VFAs
Waste stabilisation ponds	WSPs
Working electrode	WE

Chapter 1

Introduction

1.1 Background

Wastewater is a result of a range of domestic, industrial, commercial or agricultural activities. Untreated municipal wastewater typically contains carbon, pathogens and nutrients such as phosphorus and nitrogen. Nineteenth century treatment objectives were mainly to remove carbon and pathogen from wastewater to reduce the spread of diseases in the community. Today, there is also an emphasis on nutrient removal to minimise eutrophication in aquatic environments. Hence, to protect both the environment and the human health, treatment of municipal wastewater is now considered a basic necessity. Both active and passive treatment technologies are widely used to treat municipal wastewater. Active waste treatment is ‘hands on’ and is complex and typically (but not always) have significant energy, chemical and operator requirements (e.g. activated sludge treatment). In contrast, passive waste treatment is essentially a ‘set and forget’ approach, which utilises naturally-occurring chemical and biological processes to carry out treatment. Passive treatment technologies have little or no energy, chemical or operator requirements. Waste stabilisation ponds (WSPs) are one of the passive treatment technologies widely used to treat wastewaters of remote communities.

Since WSPs are highly reliant on natural environmental factors such as sunlight, wind etc., the technology is wide spread in warm climate areas where sufficient land is available (Alvarado et al., 2012; Senzia et al., 2002). WSPs facilitates removal of organic matter, suspended solids (SS), pathogens and some nutrients from wastewater (Pedahzur et al., 1993). Due to high reliance on environmental factors, often there is inconsistent and inadequate removal of both dissolved and particulate organic matter from effluent creating a challenge for utilities to comply with enforced discharged limits. Hence, most utilities rely on effluent polish up technologies to achieve the desired effluent quality for discharge. The current effluent polish up technologies however, also have their inherent limitations and hence there is a need to develop

reliable polish up technologies that is able to guarantee a consistent effluent quality from WSPs.

This research aims to develop a sustainable technology to polish WSPs effluent.

1.1.1 Wastewater treatment using WSPs

WSPs are man-made ponds in which wastewater is naturally treated with the aid of sun light, wind, microorganisms and algae. Often several ponds can be found linked in a series to achieve different levels of treatment. There are three types of ponds, (1) anaerobic, (2) facultative and (3) aerobic (maturation) and each of these ponds facilitate different levels of treatment and they have unique design characteristics (Wolverton & McDonald, 1979). A brief overview of each of the ponds are given in the following sections.

1.1.1.1 Anaerobic ponds

Raw wastewater primarily flows into anaerobic ponds. These anaerobic man-made ponds are deep (2 to 5 m) and receive high organic loads exceeding 100 g BOD/m³. They essentially facilitate primary treatment of influent wastewater specifically by retaining solids present in influent wastewater. In addition to the retained solids, some soluble organic matter in the wastewater also get removed through hydrolysis and fermentation processes taking place in these ponds. During fermentation, anaerobic bacteria converts organic carbon into methane and as a consequence, some organic matter (approximately 60 % of BOD) gets removed from wastewater (WHO, 1987).

According to Hernandez-Paniagua et al. (2014) some full-scale anaerobic ponds remove up to 18% of influent organic carbon as methane. Methane is a greenhouse gas (GHG) and it has potential consequences on climate change. Relative to carbon dioxide the global warming potential (GWP) of methane is 25 times higher as it dangerously prevents infrared radiation from escaping the planet (Guisasola et al., 2008).. Hence, there is a great importance to develop reliable strategies to mitigate emissions of methane from anaerobic ponds.

It is largely the suspended solids in the anaerobic ponds that are contributory towards methane emissions. It has been estimated that approximately 40 L of solids per person per year enters anaerobic ponds. Hence, to reduce methane emissions from WSPs, a strategy is required to reduce entry of solids into WSPs. Although an entry of solids

can be reduced with the aid of screens, a disposal of entrapped solids into landfill, will not reduce emission of methane into the atmosphere. According to Themelis and Ulloa (2007), landfills are the third largest source of methane emissions in the United States. Therefore, to achieve a true reduction of methane emissions, the solids need to be aerobically oxidised. Without a hydrolysis step, aerobic oxidation of solids is quite ineffective. Hence, any strategy devised to facilitate oxidation of solids, should have a built-in pre-hydrolysis step. An aerobic oxidation of solids, also will minimise emissions of other harmful gases such as hydrogen sulfide (H₂S).

Another important function of an anaerobic pond is the destruction of harmful pathogens. Worm eggs, parasites and pathogenic bacteria have been shown to undergo anaerobic decomposition in anaerobic ponds and effluent leaving an anaerobic pond additionally is also lower in suspended solids and carbon (compared to influent COD, the effluent COD is approximately 40-60 % lower) (WHO, 1987).

1.1.1.2 Facultative ponds

A typical facultative pond is usually 1.2 to 2.4 m in depth and is not mechanically mixed or aerated (Gloyna, 1971). The treatment of wastewater in facultative ponds is a result of algal and bacterial growth. Algal photosynthesis introduces dissolved oxygen to the top surface layers of the water and this supports the growth of aerobic and facultative microorganisms in the pond. The sludge deposits in the bottom layers of the pond facilitates the growth of anaerobic microorganisms. The anaerobic bacteria play a key role solubilising solids and complex organic compounds (hydrolysing/fermenting), making them more bio available for bacterial oxidation. The layer in between the top and bottom layers is referred to as the facultative zone and this zone is largely anoxic. This facultative zone is largely a result of a temperature induced water-density variation. The microorganisms in the deeper facultative zone use inorganic compounds such as nitrate, sulfate etc. as electron acceptors and contributes towards nitrogen removal (denitrification) and metal removal (as metal sulfides) from wastewater.

The presence of algae in the top aerobic and facultative zones is essential for a successful operation of a facultative pond. Exposed to sunlight, the algal cells carry out photosynthesis utilising CO₂ in wastewater and releases O₂ into the water body increasing dissolved oxygen in wastewater. O₂ has been observed exceeding saturation

levels in the top aerobic zone specifically on warm sunny days. This level of photosynthesis has shown to increase pH in the aerobic zone to as high as pH 10 due to utilisation of CO₂ and this high pH have shown to assist ammonia removal via volatilisation (Mara & Pearson, 1998). Although aerobic conditions prevail during the day, O₂ levels significant decrease during night due to lack of photosynthesis. Accordingly, both O₂ and pH fluctuates with a maximum during daylight hours to a minimum at night.

Photosynthesis in a pond is a result of three different organisms: (1) cyanobacteria, (2) algae and (3) purple sulfur bacteria.

(1) Cyanobacteria: Cyanobacteria were previously classified as blue-green algae. They are autotrophic organisms and produce O₂ as a by-product of photosynthesis. Given right environmental conditions, cyanobacteria will grow rapidly and tend to form blooms. The most common cyanobacteria found in ponds include *Oscillatoria*, *Arthrospira*, *Spirulina*, and *Microcystis* (Barrington et al., 2013; Vasconcelos & Pereira, 2001). The size and higher growth rates of cyanobacteria enables maintenance of a higher cyanobacterial density in ponds. This intern appears beneficial to maintain good aerobic conditions in facultative ponds.

Some of the cyanobacterial genera present in facultative ponds, however, produce toxins, including microcystins, which pose a significant health risk to both humans and ecological health (Barrington et al., 2013). Hence, there are major concerns about discharge of cyanotoxins with effluent into surrounding water bodies such as recreational waters. Additionally, cyanotoxins have also been shown to inhibit biological, physical, and chemical treatment of wastewater. Hence, wastewater utilities now a days aim to closely manage the cyanobacterial population and the cyanotoxins discharged from WSPs. Much research has been carried out to explore methods to inhibit cyanobacteria and their inhibitory cyanotoxins. Of a range of strategies examined, the use of H₂O₂ have been shown to selectively inhibit cyanobacteria.

(2) Algae: Compared to prokaryotic cyanobacteria, the eukaryotic algae can be found unicellular or multicellular, motile or immotile, and, according to their phylogeny they also have different combinations of photosynthetic pigments. They are also autotrophs and utilise inorganic nitrogen, phosphorus and a suite of microelements, to fix CO₂.

The photosynthetic end product of algae is O_2 . Unlike prokaryotic cyanobacteria algae are unable to fix nitrogen. Hence they rely on inorganic nitrogen such as nitrate (NO_3) or NH_3 to supplement nitrogen requirements. Therefore, algae also contribute towards removal of nitrogen from wastewater.

There are three major groups of algae and this grouping has been based on their chlorophyll pigmentation. Green and brown algae are commonly found in facultative ponds and there is only occasional occurrence of the red algae. The dominance of an algal species appears to be temperature dependent. Unlike cyanobacteria, algae do not produce toxins. Hence the wastewater utilities aim to foster growth of algae in facultative ponds while suppressing growth of cyanobacteria.

(3) Purple sulfur bacteria: Purple sulfur bacteria are anaerobic photosynthetic prokaryotes. These organisms will carry out photosynthesis provided there is light (of the correct wavelength), CO_2 , nitrogen (N), and a reduced form of sulfur (S) or H. Unlike cyanobacteria or algae, there is no production of O_2 during photosynthesis. Instead, these organisms produce elemental S or sulfate (SO_4) and the conversion of odorous sulfide compounds in wastewater to the above odourless compounds is of significant benefit to manage operations of facultative ponds.

Dissolved oxygen introduced through surface aeration and by algae is used by aerobic and facultative microorganisms to oxidise organic matter in wastewater. While CO_2 , the oxidation end product would largely escape into the atmosphere, some would dissolve in wastewater and remain in the system. Algae then has the opportunity to tap into this dissolved CO_2 to carry out photosynthesis. While algal photosynthesis is of value to facilitate enhance oxidation in facultative ponds, it also negatively impacts facultative ponds by re-introducing dissolved or particulate organic matter back into the pond. In other words, the mutualistic relationship that exist between algae and bacteria in a facultative pond is not entirely beneficial for the process of wastewater treatment. This relationship essentially creates internal cycling of organic matter as depicted in Figure 1.1.

Internal cycling of organic matter require management, if facultative ponds are to perform optimally. Wasting of algal biomass from facultative ponds would reduce organic cycling and availability of O_2 . A reduction of O_2 will reduce bacterial abundance (i.e. will reduce cycling of organic matter). Overall wasting of algae will

also enable control of the bacterial biomass. Wasting also may create avenues to better manage the abundance of cyanobacteria in facultative ponds. Implementing a wasting strategy similar to what is practiced in activated sludge plants is difficult due to the low densities of algae found in facultative ponds. If wasting was carried out similar to an activated sludge plant, the volume of wastewater that would need to be discharged from a facultative pond would be significant. Adopting a wasting strategy developed around a filtration mechanism on the other hand may facilitate wastewater utilities to implement biomass wasting from facultative ponds.

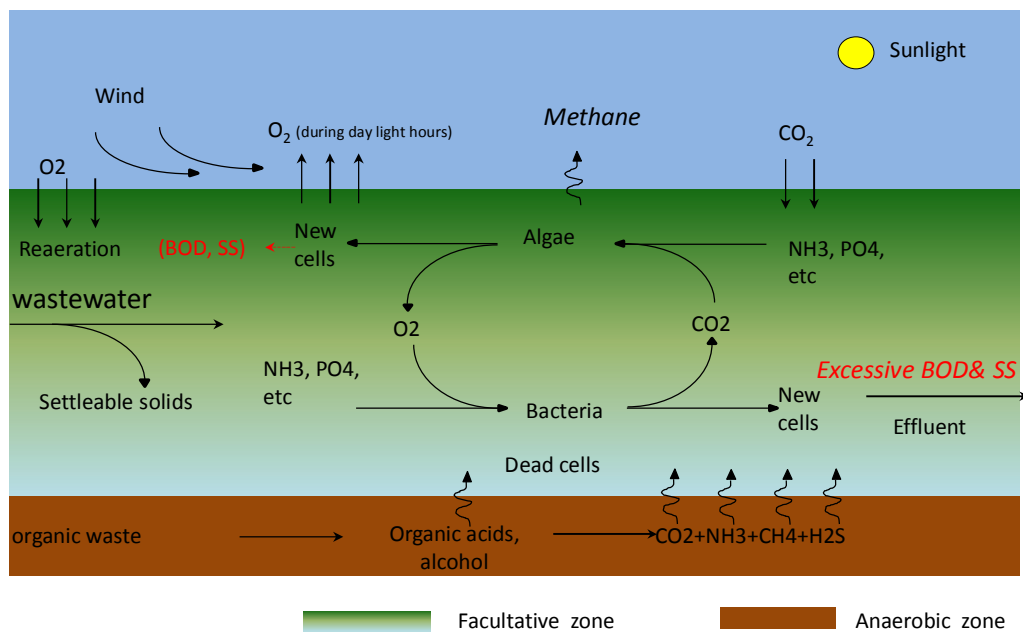


Figure 1.1 Schematic representation of processes taking place in a facultative pond (adapt from (Tchobanoglous, 1991))

1.1.1.3 Maturation ponds (Tertiary lagoons)

Maturation ponds are designed to further polish effluent of facultative ponds. These ponds, which are designed for tertiary treatment, facilitates removal of pathogens, nutrients and algae. Compared to anaerobic and facultative ponds, maturation ponds are very shallow (0.9 – 1 m in depth) and this allows light penetration to the bottom and maintenance of aerobic conditions throughout the entire pond. For the maturation pond to operate effectively, the wastewater BOD flowing into the pond should be

maintained low. Specifically, 80 % of BOD in wastewater has to be treated upstream of maturation ponds (Mara & Pearson, 1998). When operated properly, maturation ponds are able to successfully remove faecal coliforms from wastewater.

The size and the number of maturation ponds depends on the wastewater retention time (usually 3 – 10 days) that needs to be maintained to achieve a specific bacteriological quality in the final effluent. The pre-requisites for pathogen destruction in a maturation pond include (1) sufficient hydraulic retention time (HRT); (2) temperature; (3) high pH (>9) and high light intensities. The high pH often is facilitated via algal photosynthesis. An operation of maturation ponds together with algae and/or fish harvesting, have been shown to additionally facilitate effective removal of nitrogen and phosphorus from the wastewater effluent (Mara & Pearson, 1998).

1.1.2 Factors effecting the failure of WSPs

According to WHO (1987), a failure of a WSP is a result of (1) a significant discharge (often > 200 mg/L) of suspended solids (including algae); and (2) an excessive discharge of soluble COD in effluent. Many natural (wind, temperature, rainfall, solar radiation, evaporation, and seepage), physical (surface area, water depth, short-circuiting) and chemical (pH, toxic metals, O₂) factors influence a failure of WSPs. According to Mara et al. (Mara et al., 1998), when factors influence an excessive growth of algae, a failure of a WSP is inevitable.

WSPs have a very high reliance on natural factors to treat wastewater. With climate change, there is much instability surrounding some natural factors, specifically wind, temperature, rainfall and solar radiation and as a consequence, maintaining a stable effluent quality from WSPs are increasingly becoming difficult. Increasing temperatures and solar radiation have implications on algal growth and high rainfall and wind creates challenges to maintain a low level of suspended solids discharge (Tharavathi & Hosetti, 2003).

A limited discharge of soluble COD and algae from facultative ponds is paramount for an effective operation of maturation ponds. As described above, maturation ponds carry out an important role, specifically in terms of pathogen removal. An effective

removal of pathogens can only be guaranteed, with a good penetration of sunlight. For this it is imperative to maintain a low suspended solids concentration in effluent of facultative ponds. WSP effluent is not at all times discharged into recreational or sensitive water bodies. Although pathogen destruction would then receive less importance, maintenance of a low discharge of suspended solids and soluble COD from WSPs would continue to be important to manage eutrophication in receiving water bodies (Goldman et al., 1972). Current regulations require suspended solids concentrations in WSP effluent to be less than 30 mg L⁻¹. It is a challenge for the wastewater industry to maintain such low suspended solids in effluent of WSPs without some reliance towards added tertiary polish up processes. These effluent polish up processes, enable the wastewater industry to continue use WSPs to treat wastewater specifically of remote communities (Ellis & Mara, 1983; Kothandaraman & Evans, 1972; Mara & Johnson, 2007).

1.1.3 Technologies to polish WSPs effluent

A review by Middlebrooks (1995) highlights availability of a range of technologies to polish WSP effluent. Centrifugation, coagulation-flocculation, microstraining and rock filtration are some of the technologies that have been examined to polish WSP effluent. The simplicity (in terms of operation and maintenance) of WSPs is a result of conceptual simplicity of the treatment technology. Hence, it is important to maintain this simplicity when introducing add-on technologies such as tertiary polish up processes. Although effective removal of SS can be achieved using above mentioned technologies, most introduce some level of complexity to the overall treatment process. For example, technologies such as centrifugation, coagulation- flocculation and dissolved air flotation (DAF) and micro-screening have been found to be highly successful to remove suspended solids (specifically algae) from WSP effluent. However, these technologies demand skilled labour, electrical energy and chemicals, all of which are not readily available at remote/under developed locations (Harrelson & Cravens, 1982; Middlebrooks, 1995; Truax & Shindala, 1994; USEPA, 1983).

The rock filters on the other hand, are simple and is a passive treatment technology. The main advantages of rock filters are its simple construction, low construction cost and simple operation. The use of rock filters has primarily been to remove algae from

WSP effluent. These systems are consisted of submerged beds rocks (size 5 to 15 cm in diameter) and WSP effluent is percolated horizontally (Figure 1.2) or vertically through the bed rocks. The highest level of performance have been observed with vertical flow rock filters (Middlebrooks, 1995; USEPA, 1983).

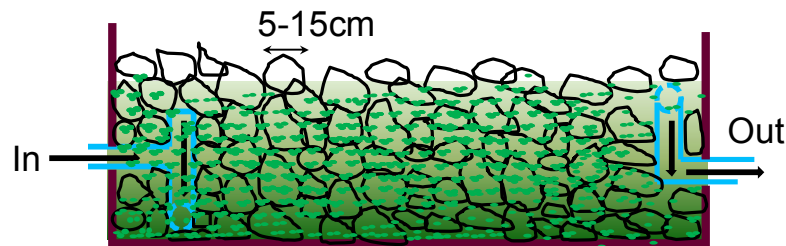


Figure 1.2 Schematic of a rock filter bed (adopted from (Powell, 1998))

The removal of SS (specifically algae) takes place with settlement or attachment of solids onto rock surfaces. Active biofilms residing on rock surfaces then induce decomposition of the settle solids. The oxidation of the hydrolysed solids is dependent on a passive diffusion of atmospheric oxygen into biofilms on bed rocks. Overall a rock filter is not just a physical filter, it is also a self-cleansing biological filter (Shelef & Azov, 2000). Due to the self-cleansing properties of the rock filter, some systems in the United States have operated largely maintenance free for over 20 years (e.g. The Veneta, Oregon system) continuously producing effluent with less than 30 mg/L of suspended solids (Middlebrooks, 1988). According to the literature, there are many advantages and disadvantages associated with rock filters. The advantages and disadvantages are summarised in Table 1.1.

Table 1.1 A Summary of the reported advantages and disadvantages of rock filters for polishing of WSPs effluent (Middlebrooks, 1995; USEPA, 1983)

Advantages
<ul style="list-style-type: none">• Provides a simple method to economically remove SS from WSPs.• The technology does not demand skilled labour, electrical energy or chemicals making it a suitable technology to facilitate waste treatment in remote communities.• The self-cleansing properties guarantee low maintenance.
Disadvantage
<ul style="list-style-type: none">• Maintaining low suspended solids (e.g. 30 mg/L) and soluble organic matter concentrations throughout in effluent is challenging.• The in situ hydrolysis of solids increase discharge of ammonia in effluent.• Accumulation of slime and no provisions to clean.

One of the main limitations of rock filters is its inconsistent removal of both SS and dissolved organics from wastewater. One reason for inconsistent treatment could be hydraulic overloading. According to USEPA (1983) a hydraulic loading rate of less than 250 L/m³ d of media allows a more consistent effluent quality to be achieved from rock filters.

In addition to hydraulic overloading, a limited diffusion of dissolved oxygen from atmosphere into the bed rock has largely contributed towards poor polish up residual COD. With limited dissolved oxygen reaching bed rock biofilm, there is a higher discharge of dissolved organic carbon in effluent. The reason for the higher discharge of dissolved organic carbon is anaerobic hydrolysis and fermentation of entrapped suspended solids. Dissolve oxygen limitations in rock filters are often overcome with injection of air into rock filters. Forced aeration, however, not only elevates dissolved oxygen concentrations, it also stimulates excessive growth of biomass and/or build-up of slime inside rock filters, increasing hydraulic pressures (biological clogging of void spaces of bed rock) (Brissaud et al., 2007; Mara & Johnson, 2006).

Another challenge associated with rock filters is discharge of ammonia. Although discharge of dissolved organic matter could be managed via forced aeration, managing the discharge of ammonia in effluent is challenging (Chen et al., 2000; Johnson, 2005). Rock filters are not effective at removing residual nitrogen released with decomposition of SS. This limitation of rock filters has prevented a broader application of rock filters to polish WSP effluent.

In summary, of all polish up technologies available for WSPs, rock filters are by far the best when considering the aforementioned advantages. Rock filters, however, has its inherent limitations and with stringent discharge limits being enforced, it is increasingly becoming important to address the limitations of rock filters. Entrapment (SS via filtration), hydrolysis (SS) and oxidation (hydrolysate) is the three-step treatment process that is embedded in rock filters. While an alternative technology is necessary to overcome limitations of rock filters, the maintenance of the three-step treatment approach of rock filters perhaps is necessary to develop an effective biological treatment technology.

1.1.5 Bioelectrochemical systems (BES): a technology ideally suited to substitute rock filters

The mind set towards wastewater treatment is changing. The traditional approach of aerobic treatment is increasingly being recognised unsustainable. The need for a large amount of electrical energy to provide aeration is one of the biggest negatives of aerobic treatment (Henkel et al., 2011). There is also an increasing recognition of the chemical energy present in wastewater. Two technologies have been recognised capable of harness this chemical energy. They are (1) anaerobic digestion and (2) bioelectrochemical systems (BES). Of the two technologies, anaerobic digestion is a well-established technology and it is currently used in commercial scale (Aiyuk et al., 2006; Pham et al., 2006). BES on the other hand, have immense potential but due to inherent limitations, the technology is yet to be embraced by the wastewater industry (Rozendal et al., 2008).

BES technology is reliant on electrochemically active microorganisms and these organisms are capable of extracellular electron transfer. When placed in an anodic chamber of an electrochemical cell, these microorganisms are able to use the electrode

as the final electron acceptor during oxidation of organic matter. In this instance, the microorganisms are behaving as a biocatalyst facilitating the oxidation reaction of the electrochemical cell. The anodes of such electrochemical cells are referred to as bioanodes. A bioanode, oxidising wastewater, when electrically coupled with a cathode (facilitating a reduction reaction), makes way for chemical energy of wastewater to be recovered as electrical energy (Figure 1.3). This however, is only feasible if the Gibbs free energy change of the overall electrochemical reaction is negative, and such BES are referred to as microbial fuel cells (MFCs). Often due to unfavourable conditions of the cathode, the Gibbs free energy change of the overall reaction becomes positive. Then electrical energy needs to be invested for electrode reactions to proceed and such BES are referred to as microbial electrolysis cells (MECs).

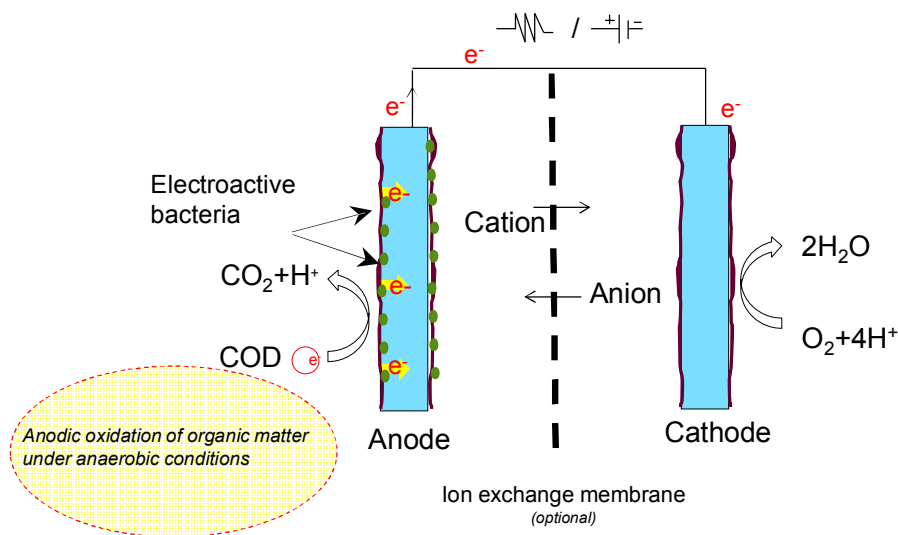


Figure 1.3 Schematic of a bioelectrochemical system

The electrons reaching cathode via the external circuit, facilitates a reduction reaction in the cathodic chamber. Often electron acceptors such as oxygen will receive these electrons and get reduced forming water. To maintain a continuous electron flow, an ionic balance should also be maintained between anodic and cathodic compartments. Specifically, for every electron flowing through the external circuit (i.e. a flow of negative charge from anode to cathode), a cation (from anode to cathode) or an anion

(from cathode to anode) needs to migrate to maintain electroneutrality (Logan et al., 2006).

For an oxidation and reduction reaction to proceed in anodic and cathodic compartments respectively, electron donors (i.e. wastewater COD) of the anodic chamber are best kept separated from acceptors (dissolved oxygen) in the cathodic chamber. Often an ion exchange membrane facilitates the separation of the anodic and cathodic chambers while allowing ions to migrate between chambers. The use of a cation exchange membrane allows cations such as H^+ , Na^+ to crossover from the anodic chamber to the cathodic chamber. A use of an anion exchange membrane on the other hand, allows anions such as OH^- , Cl^- to crossover from the cathodic chamber over to the anodic chamber. Having a membrane separating the anodic and cathodic chamber also allows maintenance of anaerobic conditions in the anodic chamber. What is unique of BES is the ability to facilitate an oxidation reaction in the anodic chamber in complete absence of oxygen (Clauwaert et al., 2008; Rozendal et al., 2006).

The failure of rock filters has largely been attributed towards a limitation of oxygen to facilitate an effective polish up of wastewater. Although this is one of the biggest limitations of rock filters, there are many fundamental benefits of this technology, such as (1) retention of solids through filtration; and (2) hydrolysis and oxidation of retained solids – a self-cleansing filter. If the above fundamental aspects of a rock filter could be embedded into an anode of a BES, the aforementioned limitation of the rock filter can be successfully addressed.

1.1.5.1 BES also have inherent limitations

There are several inherent limitations of BES and if this technology is to become commercially viable, these limitations needs to be addressed. Although some effort has gone towards innovating strategies to overcome these limitations, breakthrough technologies are yet to materialise to enable commercialisation of BES technology for waste treatment. A significant part of BES literature ignores these crippling limitations and have largely been reporting possible applications of the BES technology. Rozendal et al. (2008), highlights the following limitations of BES.

A. Limited metabolic diversity

Real wastewater contains a wide range (both complex and simple) of organic compounds, where some are soluble and the rest are in the form of solids. If bulk of the above organic matter is to be oxidised in a BES, a large and versatile anodic microbial community will be required specifically to facilitate degradation of particulate and/or polymeric organic substances, such as cellulose (Ren et al., 2007; Rismani-Yazdi et al., 2007). BES studies with real wastewater thus far have failed to achieve power densities similar to that have been achieved with synthetic media containing easily biodegradable substrates (e.g. acetate). For example, a single-chamber MFC was able to achieve a power density of 494 mW/m² anode surface area with a synthetic acetate medium and when this medium was replaced with domestic wastewater, the power density dropped to a low 146 mW/m² anode surface area (Liu & Logan, 2004). This observation could be a result of (i) a lack of metabolic diversity or activity (to facilitate degradation of complex organic compounds) among the electrochemically active anodic microbial community or (ii) non-electrogenic removal of carbon (e.g. through methanogenesis).

Accordingly, if much of the chemical energy in real wastewater is to be retrieved as electrical energy using BES, the complex organic compounds in wastewater first needs to be hydrolysed over to simple compounds. Considering more than half of the complex organic compounds in real wastewater are in the form of solids and if the overall objective is to develop a BES technology to substitute rock filters, developing a technology that facilitates hydrolysis of solids is imperative.

B. Biofilm acidification

During anodic oxidation of carbon, protons are liberated and if the protons are not actively neutralised or removed, the biofilm becomes acidified, negatively impacting BES performance. Torres et al. (2008) demonstrated the importance of alkalinity to achieve satisfactory performance of BES where a current densities as high as 10 A/m² anode surface area was achieved with a phosphate buffer concentration of 100 mM. The alkalinity of most domestic and industrial wastewaters are in the order of 50 to 200 mg/l as CaCO₃ and this is only equivalent to a phosphate buffer concentration of 1 to 4 mM (Tchobanoglous & Burton, 1991). The low alkalinity of wastewater, hence, limits the performance of bioanodes, and it is essential to increase alkalinity of

wastewater if BES is to be successfully used for treatment of wastewater.

Similar to build up of acidity in the anodic compartment, there is alkalinity build up in the cathodic compartment. An excessive build-up of alkalinity in the cathode, impacts cathodic reaction kinetics, which intern results in potential losses (Rozendal et al., 2006). Majority of research reported in literature have dosed acid and base to the cathode and anode respectively to maintain a near neutral pH and the need for external chemicals to maintain process stability in this instant is highly undesirable and demands development of alternative strategies to manage pH in BES.

Some effort has gone towards management of alkalinity in the cathodic chamber. Freguia et al. (2008) proposed a loop concept to maintain hydraulic flow from anode to the cathode compartment. The wastewater COD while getting oxidised in the anodic compartment, collects acidity and this acidity is used to neutralise alkalinity in the cathodic chamber. This configuration assumes an active abstraction and transportation of protons away from the anodic biofilm. Often achieving the above is notoriously difficult and as a consequence, acidification of anodic biofilm continues to remain problematic in this configuration. Additionally, another pre-requisite of this configuration is a complete anodic oxidation of organic matter present in wastewater. Failing to achieve a complete oxidation of organic matter, causes biofouling of cathode, impacting cathodic performance due to a decrease of oxygen transfer to the cathode (Zhang et al., 2010).

C. Cathodic overpotentials

According to Rozendal et al. (2008), full-scale BES are anticipated to achieve volumetric current densities exceeding 1000 A/m^3 . Potential losses at electrodes (i.e. overpotentials) are common and as a consequence achieving aforementioned current densities has been considered unrealistic. The potential losses of bioanodes are insignificant compared to potential losses observed with chemical cathodes and even with the use of excellent electrocatalysts such as platinum, the potential loses of cathodes remain significant. Slow kinetics of oxygen reduction has been identified as one of the reasons for the high cathode overpotentials (Zhao et al., 2006).

Conventional electrochemical systems with platinum catalysed cathodes on the other hand have managed to overcome cathode overpotentials to an extent by maintaining a very low cathodic pH (<1) (He & Angenent, 2006). The availability of a higher proton

concentration (at lower pH) guarantees no proton limitation for the cathodic oxygen reduction. Accordingly, an engineering solution to maintain a very low pH in the cathodic compartments of BES would be useful to address the above technological limitation.

D. Conductivity and electrolyte ohmic losses

Domestic and many industrial wastewaters mostly have low conductivities (~1 mS/cm). The low conductivity results in considerable electrolyte ohmic losses. For example, when exposed to low conductivities, at a current density of 10 A/m² anode surface area, an electrolyte ohmic loss of up to 1 V can be expected for each cm distance between anode and cathode (Rozenal et al., 2008). While electrolyte ohmic losses can be minimised by maintaining a very short distance between the anode and cathode, an increase of the ionic strength of wastewater can also further decrease electrolyte ohmic losses.

In summary, there is much to gain by combining two technologies. Specifically, by embedding filtration and self-cleansing aspects of a rock filters into BES. While this integration requires innovation, to deliver an implementable outcome, the limitations of BES also needs to be resolved. This thesis aims to systematically address the above two challenges.

1.2. Aims and Objective of this research

The overall aim of this study is to develop a technology that could facilitate oxidation of organic solids associated with wastewater. There is a specific focus to develop a technology that simulates a rock filter. Embracing the fundamentals of a rock filter the aim is to develop a self-cleansing filter that facilitates, entrapment, hydrolysis and oxidation of organic solids similar to a rock filter, but one that has managed to overcome all limitations of a conventional rock filter.

Objectives:

1. To examine the potential to use the simplicity of a sediment-type BES configuration to oxidise solids associated with wastewater (Chapter 2).
2. To develop an innovative filter-type BES configuration that simulates the fundamental operation of a rock filter (Chapter 3).
3. To examine whether a filter type BES configuration could facilitate entrapment, hydrolysis and oxidation of algal biomass without any reliance on a separate pre-hydrolysis step (Chapter 4).
4. To develop an add-on technology to the BES-filter to enable the BES to overcome most of its operational limitations (Chapter 5).

1.3 Thesis structure

This thesis is organised into six chapters. As mentioned earlier in this chapter (Chapter 1), the simplicity and cost advantages of rock filters has made it the most widely used polish up technology for WSPs. In terms of construction, operation and capital costs, a sediment type BES has much similarities to rock filters and with a minor configurational change, a sediment type BES can be made to operationally simulate a rock filter. **Chapter 2** investigates the suitability of a sediment-type BES configuration to oxidise SCOD and organic solids present in wastewater. This chapter specifically examines the pros and cons of this BES configuration with an aim to understand critical aspects that needs to be taken into consideration when developing a new technology to simulate rock filters.

Chapter 3 describes a new filter-type BES configuration engineered to address limitations identified in chapter 2. Chapter 3, examines limitations of the new configuration and steps that needs to be taken to overcome these limitations are reported. **Chapter 4** aims to consolidate the new filter-type BES configuration by demonstrating that the configuration is able to facilitate entrapment, hydrolysis and oxidation of algal biomass without any reliance on a separate pre-hydrolysis step.

Chapter 5 is devoted towards development of an add-on technology to the BES-filter to enable the BES to overcome most of its operational limitations. This chapter combines all knowledge established in Chapters 2 to 4 to finally develop a two-step

configuration that enables treatment of SCOD and solids in wastewater while smartly overcoming inherent limitations of BES.

The final **Chapter 6** discusses and summarises insights obtained in this thesis. Future research directions and outlook are also addressed.

Chapter 2

Assessing the suitability of sediment-type bioelectrochemical systems for organic matter removal from municipal wastewater: a column study

Extended from:

Khalfbadam, H. M, Cheng K. Y, Sarukkalige R, Kayaalp AS, Ginige MP. Assessing the suitability of sediment-type bioelectrochemical systems for organic matter removal from municipal wastewater: a column study. *Water Science and Technology*. 2016 Jun 9; *wst2016263*. doi: 10.2166/wst.2016.263

Chapter Summary

This study examines the use of bioelectrochemical systems (BES) as an alternative to rock filters for polishing waste stabilisation ponds (WSPs) effluent, which often contains soluble chemical oxygen demand (SCOD) and suspended solids mainly as algal biomass. A filter type sediment BES configuration with graphite granules (as the surrogate for rocks in a rock filter) was examined. Three reactor columns were set up to examine three different treatments: (i) open-circuit without current generation; (ii) close-circuit - with current generation; and (iii) control reactor without electrode material. All columns were continuously operated for 170 days with real municipal wastewater at a hydraulic retention time (HRT) of five days. Compared to the control reactor, the two experimental reactors showed significant improvement of SCOD removal (from approximately 25% to 66%) possibly due to retention of biomass on the graphite media. However, substantial amount of SCOD (60%) was removed via non-current generation pathways, and a very low Coulombic efficiency (6%) was recorded due to a poor cathodic oxygen reduction kinetics and a large electrode spacing. Addressing these challenges are imperative to further develop BES technology for WSP effluent treatment.

2.1 Introduction

Wastewater stabilisation ponds (WSPs) are an energy-efficient low maintenance technology used to treat municipal wastewater particularly of rural communities (Mara et al., 1998). A typical WSP consists of non-mechanically mixed anaerobic, facultative and maturation ponds, which are operated in a series (Mara et al., 1992). Facultative ponds (FPs) are designed to facilitate oxidation of dissolved organic carbon (DOC) and are reliant on the mutualistic relationship between bacteria (supply CO₂ for photosynthesis via oxidation of organic matter) and algae (supply O₂ for oxidation of organic matter via photosynthesis) (Mara et al., 1992). Typically, the treatment efficiency of FPs is highly affected by environmental factors such as wind (for dissolution of O₂), sunlight, and temperature, which are highly variable (Pedahzur et al., 1993; Tharavathi & Hosetti, 2003). The variations in meteorological factors do not enable FPs to maintain stable effluent quality and as a consequence maturation pond performance failures are frequent resulting in a discharge of effluent with high soluble chemical oxygen demand (SCOD), suspended solids (SS, could be as high as 200 mg/L) concentrations and pathogens into the environment (Ellis & Mara, 1983; Mara et al., 1992). Hence, much effort has gone towards developing strategies to minimise SCOD and SS (specifically algae) discharges from WSPs.

Middlebrooks (1995) reviewed a range of technologies that could be used specifically to remove suspended solids from WSP effluent. Considering simplicity and cost advantages, rock filters were identified suitable to polish WSP effluent. The rock filter operation requires WSP effluent to filter through a submerged porous rock bed. The algae and other pond detritus (not wastewater solids) that make up the SS of WSP effluent settle out and accumulate on the rock surfaces, where biological degradation takes place over time. Although the porous rock bed would to an extent facilitate passive aeration, development of anaerobic conditions in the rock filter due to excessive build-up of solids often occur, compromising the treatment performance particularly in terms of SCOD removal. Excessive build-up of solids also results in blockage and emissions of odour from rock filters. To some extent these challenges of rock filters have been addressed by the development of aerated rock filters (Mara & Johnson, 2006). The need for an electrical power supply to provide aeration increases operational costs and is a major drawback of aerated rock filters (Johnson et al., 2007).

Accordingly, there is a need to explore other more economical and simple alternative technologies that could substitute aerated rock filters.

Bioelectrochemical systems (BES) represent a novel technology that may potentially enable a more energy-efficient wastewater treatment. These systems typically consist of separated anode and a cathode chambers. Removal of organic matter in the wastewater can be facilitated by electrochemically active bacteria residing in the anodic chamber of a BES. These bacteria can catalyse the oxidation half reaction (i.e. oxidation of organic matter) and transfer the electrons to an inert solid-state anode under anaerobic conditions. The released electrons move through an external circuit to reach the cathode compartment and soluble electron acceptors such as dissolved oxygen (DO) receive the electrons to enable current production (Logan et al., 2006; Rozendal et al., 2008). Since organic matter removal could be achieved anaerobically, BES could be a promising technology to address the aforesaid issues associated with rock filters.

With BES negating direct requirements of oxygen to facilitate oxidation of soluble and sediment organic matter of a rock filter configuration, oxygen reduction in the cathodic compartment hypothetically can be mediated via passive diffusion of oxygen into the cathodic compartment. The rock filter configuration can be replicated in the anodic chamber of a BES by substituting rocks of rock filters with conductive materials such as graphite granules. As such, not only the filtration aspects of a rock filter could be achieved, but also the removal of organic matter (both soluble and insoluble COD) could be facilitated via anodic oxidation. Simplicity and cost effectiveness are the other two important attributes of rock filters and a sediment type BES configuration enable these two valuable aspects of a rock filter to be accomplished.

Sediment BES have thus far been deployed in natural systems or in less engineered and managed systems (e.g. constructed wetlands) (Zhao et al., 2013). One example is its use with sensors deployed at remote locations to enable long-term monitoring of environment (Shantaram et al., 2005) . The finite charge stored in the batteries of sensors, do not enable most sensors to operate for long-term without replacement of batteries, and when deployed at remote locations replacement is not logistically feasible and sustainable. Sediment BES provides an alternative renewable energy

supply for remote locations and replaces the reliance on batteries. The sediment BES supplies alternative power using renewable sources (i.e. from organic matter in the sediment) and is reliable with no maintenance required for a long-term supply of power (Donovan et al., 2008; Tender et al., 2008).

The configuration of a sediment BES is simple where a clear boundary between the anode and the cathode is not maintained using membranes or separators. Sediment BES relies on a naturally occurring oxygen gradient to facilitate a separation between the anode and the cathode (Bojun Xu 2015). To facilitate a gradient, the anode is deployed within or close to the sediment where DO is limited and the cathode is installed in the overlying water column where the condition is oxidizing (e.g. with a higher DO) (Hong et al., 2009; Reimers et al., 2001; Song et al., 2010; Yuan et al., 2010).

It was expected that such a redox gradient would exist in rock filters, where the surface region exposed to the atmosphere is oxidizing and the bottom region reducing. With rock filters demonstrating excellent entrapment of SS, a similar or a better level of entrapment was expected of graphite granules (which substitute rocks of rock filters) in the proposed sediment BES anode. Accordingly, the aim of this study was to evaluate the potential of using a sediment BES as an alternative method to remove organics from wastewater. A number of operational strategies were examined to identify limiting factors to achieve better organic removal from wastewater. Specific objectives of the study included examining: (1) the influence of cathodic aeration on anodic oxidation of carbon; (2) the impact of external resistance on current generation and anodic oxidation of carbon; (3) the effects of electrode spacing on anodic oxidation of carbon.

Three column reactors were fabricated as “sediment-type” BES and performance were evaluated at three different operational settings: (i) open-circuit without current production; (ii) close-circuit operation with current production; and (iii) control reactor without electrode to account for the effect of electrode material. Effluent of a poorly performing FP was emulated using primary sedimentation tank influent (approximately 200 mg-COD/L, 195 mg-SS/L) of a local wastewater treatment plant and was used as influent to the sediment BES reactors for a period of 170 days. During

this period, parameters such as COD removal, current generation and polarisation performance were monitored and quantified.

2.2 Materials and Methods

2.2.1 Sediment-type BES column reactors

Two identical polyethylene (PE) column reactors (R1 and R2) (height 1.5 m, internal diameter 0.05 m) were constructed for this study (Figure 2.1). The height of the column (1.5 m) was chosen to mimic the depth of rock filters (Middlebrooks, 1988). R1 and R2 were configured as sediment BES reactors and as detailed in Figure 2.1, graphite granules (3-5 mm diameter, specific surface area 1.3 m²/g, porosity of 48%, KAIYU Industrial (HK) Ltd.) were packed at both the anodic and the cathodic ends of the column. Unless specified otherwise, a 330 Ω resistor was used to externally connect the anode and the cathode to enable current generation in R2. A third column (R3) (height 0.82 m, internal diameter 0.05 m) contained no electrode was used as a control to account for the effect of the electrode surface. The three columns had an identical net liquid volume (1.61 L). Both R1 and R2 consisted of anodic and cathodic zones. The anodic zone (55.5 cm height, 0.52 L net working volume) constituted the bottom section of the columns, whereas the cathode zone (13.5 cm height, 0.12 L net working volume) constituted the top section where graphite granules were partially exposed to the atmosphere. Graphite rods (5 mm diameter) were horizontally inserted into the anodic and cathodic compartments to enable current collection. Anodic and cathodic compartments were hydraulically connected. The distance between the anodic and the cathodic zones was initially fixed at 90 cm, but was reduced by approximately three times (to 26 cm by reducing height of column) from day 130 to 170 to evaluate the effect of electrode spacing.

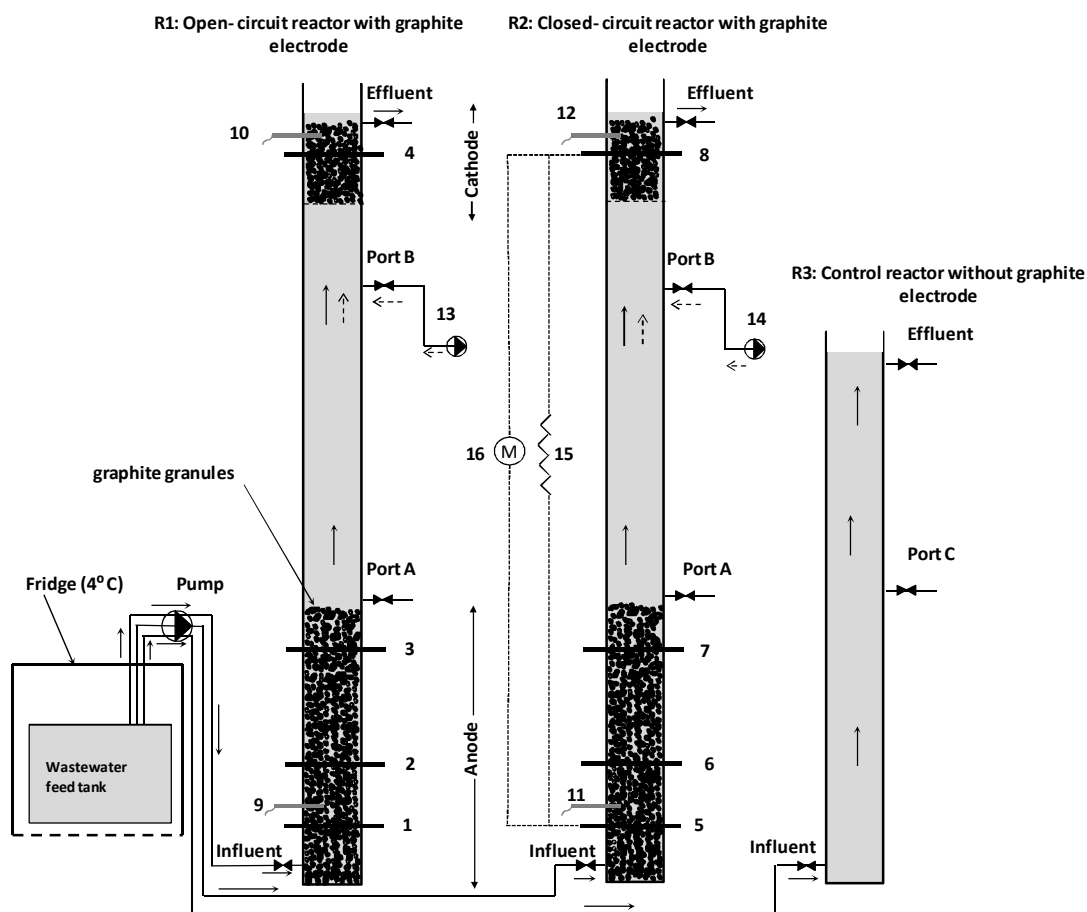


Figure 2.1 Schematic diagram of three column reactors used in the study (not scaled). [(1-8) electrode rod, (9-12) reference electrode, (13-14) air pump, (port A) sampling port at the middle of anode compartment, (port B) sampling port at below the cathode compartment, (port C) sampling port at the middle of R3 column, (15) external resistance and (16) digital multimeter].

2.2.2 General operation of the column reactors

Primary influent was collected from a local municipal wastewater treatment plant (Subiaco, Perth, Western Australia) weekly and was filtered through a 2 mm pore size sieve to remove large particles prior to storage at 4°C. The SCOD of wastewater varied between 147 and 229 mg/L. The wastewater was continuously fed from the bottom and was discharged from the top of columns at different influent flow rates (0.17-0.22 mL/min) and organic loading rates (0.03-0.046 kg COD/m³.d) to achieve a hydraulic retention time (HRT) of 5 days in all columns. The start-up of the reactors was initiated by adding one percent (v/v) of return activated sludge as inoculum. The three columns

were operated at ambient temperature throughout 170 days of operation. Samples were taken from the columns at the locations as illustrated in Figure 2.1.

2.2.3 Performance characterisation and determination of the effects of different process variables

2.2.3.1 Impact of cathodic aeration on the performance of sediment-type BES reactor

The effect of various cathodic aeration rates (10, 20, 30, 40, 120, 150 and 200 mL/min) on the performance of R2 was evaluated from day 39 to 78 (40 days period). Freshly collected wastewater was loaded into R2 at a flow rate of 0.22 mL/min (HRT of 5 days) and the current and SCOD removal of R2 was monitored with different aeration rates into the cathodic chamber.

2.2.3.2 Effect of external resistor on the performance of the sediment-type BES reactor

The impact of external resistance on current generation and SCOD removal was monitored by applying varying levels of external resistance (10, 330 and 1000 Ω) on R2 during days 101 to 130 (i.e. over a period of 30 days).

2.2.3.3 Effect of electrode spacing on the performance of sediment-type BES reactor

The effect of electrode spacing on the performance of both R1 and R2 was evaluated over days 131 to 170 (40 days period) by reducing the electrode spacing of both R1 and R2 from 90 cm to 26 cm. A distance of 26 cm was chosen according to Ghangrekar and Shinde (2007). Even with forced aeration of cathode, they did not find anodic performance being compromised with a short electrode distance of 20 cm. The effect of this change of electrode distance was quantified using polarisation curves analysis and the derived electrochemical characteristics (maximum power, current and internal resistance) of the two systems were compared.

2.2.4 Analyses and calculations

The voltage (i.e. the potential differences between the anode and the cathode) (V) of R2 was measured using a digital multimeter placed across the external resistor and the anodic and cathodic cell voltages of both R1 and R2 were measured against respective reference electrodes (Ag/AgCl). The current (I, mA) of R2 was calculated from the voltage according to Ohm's Law, $I = \frac{V}{R}$, where V (mV) is the measured voltage across an external resistor R (Ω). Power (P, W) was determined according to equation $P = V \times I$. Volumetric current and power densities were obtained by normalising I and P with the net working volume of the anodic zone (1.09 L).

COD in the collected sample (filtered through 0.45 μm) was measured using HACH reagents (cat no. TNT 821; method 8000, LR) and a spectrophotometer (GENESYS 20, Thermo Scientific). The coulombic efficiency (CE) (i.e., the percentage of electrons recovered as anodic current from the removed SCOD) was calculated as detailed in the literature (Logan et al., 2006). Polarisation curves analyses were carried out with a stepwise decrease of external resistance (from 1 M Ω to 1 Ω) of both R1 and R2 reactors. Prior to the polarisation curves analysis the reactors were allowed to reach a steady open circuit potential over a period of approximately 3 hours. The internal resistance of R1 and R2 were determined from the slope of the linear segment of polarisation curves.

2.3 Results and Discussions

2.3.1 Reactors start up and initial assessment of the sediment-type BES reactors

During days 0 to 15, both R1 and R2 were operated in open circuit mode. Upon seeding both reactors with activated sludge (on day 1), the electrode potentials and cell voltages of R1 and R2 declined suggesting creations of reducing conditions in both reactors. A gradual deposition of organic (includes biomass) and inorganic matter on electrode surface is likely to have contributed towards a rapid decline of cell voltage in R1 and 2 during the initial 5 days of reactor operation. While a reduction of anodic potential was expected, a substantial decline in cathodic potential of both reactors was not anticipated due to exposure of cathodes partially to the atmosphere (Figure 2.2A, C and D). The reducing cathodic conditions indicate limitations of passive oxygen

dissolution from atmosphere. Accordingly, after closing the external circuit of R2 (day 15) only a negligible amount of current (< 0.05 mA) was recorded (over a period of 33 days) (Figure 2.2B). Such a low current was a result of a huge cathodic overpotential, as reflected by a remarkable decrease in both the cell voltage (from a OCV of ca. 700 mV to 70 mV) and the cathodic potential (from ca. +140 mV vs. Ag/AgCl to ca. -360 mV vs. Ag/AgCl) of R2 (Figure 2.3A-D).

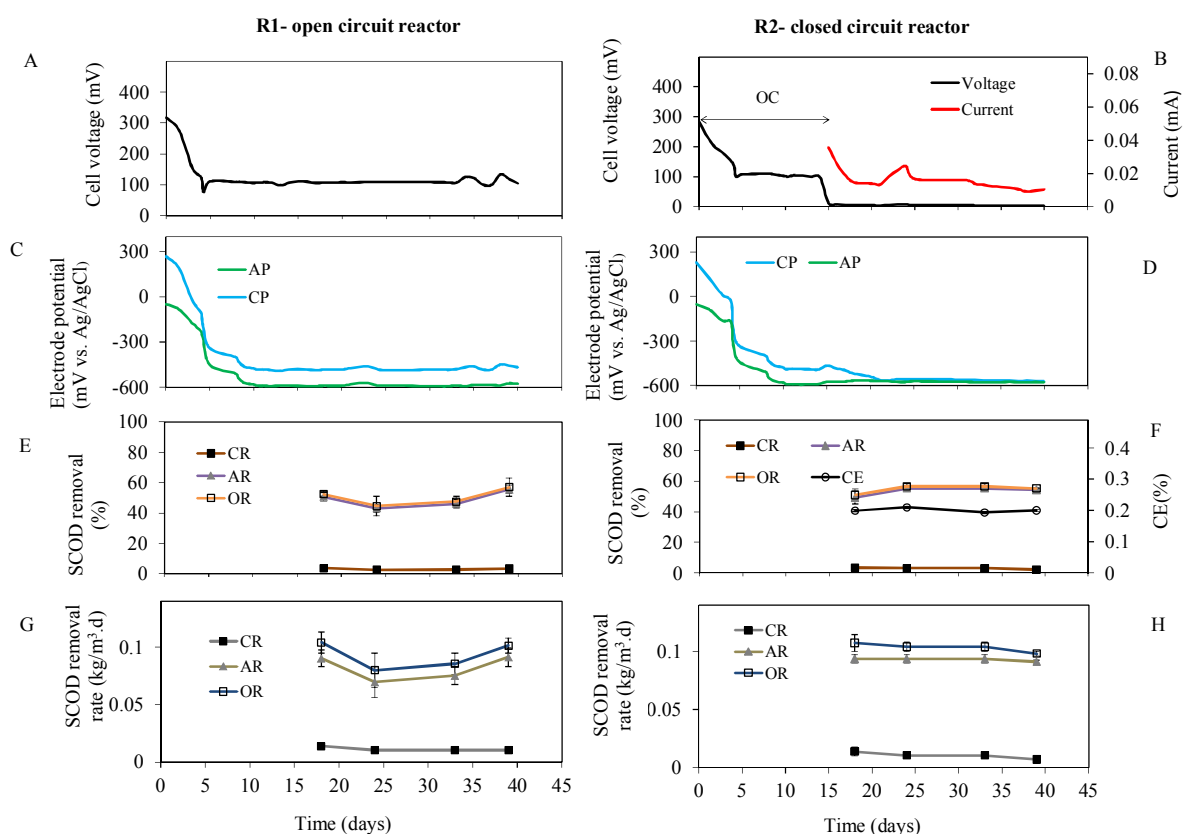


Figure 2.2 Changes in (A) voltage of open circuit column reactor; (B) voltage, produced current at close circuit reactor; (C and D), electrode potentials of open and close circuit reactor; (E) soluble chemical oxygen demand (SCOD) removal at open circuit reactor; (F) SCOD removal and coulombic efficiency at close circuit reactor; (G and H), volumetric rate of SCOD removal at open and close circuit reactor during start-up of the reactors. AP: anodic potential; CP: cathodic potential; CR: cathodic removal; AR: anodic removal, OR: overall removal; CE: coulombic efficiency. OC: open circuit.

The CE of R2 was only 0.2% and this implies the limited ability of the anodic biofilm to retrieve electrons from oxidation of organic matter. In general, low CEs are expected with the use of sediment BES for municipal wastewater treatment (Sajana et al., 2014; Villasenor et al., 2013; Zhao et al., 2013). Since no membrane separator was used, the presence of SCOD at the cathodic compartment/ region was generally considered as the reason of poor CEs. The success of sediment BES with remote sensors on the other hand was due to prevalence of low dissolved organic carbon and higher DO in the overlaying water column where the cathode is located (Lee et al., 2015; Tang et al., 2015).

In spite of the poor CE, the SCOD removal efficiency of R2 was 54%. Interestingly, a similar level of efficiency (53%) was observed with R1. The above SCOD removal efficiencies were largely noted around the anodic zones of both reactors (Figure 2.2E, F). COD removal of both reactors mostly remained stable with only some minor fluctuations as can be noted in Figures 2.2E and F. Many factors including toxins and capability of graphite granules in soaking up a range of compounds from the wastewater could have contributed towards the above variations of COD removal. The total COD (TCOD) removal efficiencies of both reactors were on average 85%. This indicates that approximately 31% of COD was entrapped as SS by the sediment BES reactors. Accordingly, the sediment BES appears to have successfully acted as a filter.

Considering R1 was operated in an open circuit mode, the SCOD reduction observed could be a result of organic matter oxidation by bacteria using oxygen, nitrate or sulfate as final electron acceptors or fermentative bacteria or methanogenic archaea and the carbon was subsequently lost from the reactor as CO₂ or methane. The similar level of SCOD removal of R1 and R2, and the very low CE of R2 (0.2%) suggested that SCOD removal in both reactors was via similar pathway(s). As shown in Figures 2.2C and D, the cathodic and anodic potentials of both R1 and R2 were below -500 mV vs. Ag/AgCl. Such low potentials are highly favourable for the growth of methanogens (He et al., 2005). Hence, methanogens would have likely contributed towards the observed reduction of SCOD in both R1 and R2. In contrast to R1 and R2, the SCOD removal in R3 (control) was only 25% (data not shown). The absence of graphite media resulted in a limited retainment of biomass in R3 and this may have contributed towards the observed 29% reduction of SCOD removal. This result suggests that the addition of graphite media could already improve COD removal,

most likely by (1) acting as a filter bed to entrap SS and (2) assisting biomass retention in the system. However, due to the very poor electrochemical performance of the sediment BES configuration (R2), the effect of graphite to support bioelectrochemical oxidation of organics was negligible.

2.3.2 Impact of aeration on cathodic performance of sediment-type BES column reactor

The open circuit R1 could be considered as a rock filter. With no penetration of DO into the anodic region of R1, the SCOD removal in the anodic region had to take place via fermentative or anoxic pathways. The primary sedimentation tank influent used in this study had negligible levels of nitrate and sulfate (< 1 mg/L) (data not shown). Hence, methanogenesis appears to be a major pathway for SCOD removal in the anodic region of R1. Methane is a potent greenhouse gas and hence its emission must be avoided (Hernandez-Paniagua et al., 2014). One option to minimise methane emission and accelerate organic removal in rock filters is via active aeration (Mara & Johnson, 2006). However, even with active aeration creation of anaerobic pockets inside the rock filter would be inevitable. To this end, BES could be a better alternative because the anode may act as a favourable electron acceptor by-passing the methanogenesis. However, for the anode to effectively act as a microbial electron acceptor in the sediment BES, an efficient cathodic reaction is required.

Maintaining an oxygen gradient by simply exposing the cathode to the atmosphere is difficult due to the presence of SCOD throughout the column (including the cathodic zone). Forced aeration near the cathode would increase the availability of DO, and was expected to improve the current. Table 2.1 and Figure 2.3 detail the influence of cathodic aeration on current production and SCOD removal. Clearly, increasing the aeration rate at the cathode concurrently increased the current and the SCOD removal (Table 2.1). However, at aeration rate of 120 ml/min, no further increase of current mediated removal of SCOD was recorded. Only a marginal (2.48%) increase of current and SCOD removal (CE increased from 0.2 to 3.3%) were achieved with aeration.

The current generation appears to have had some influence towards non-current mediated SCOD removal pathways in the anodic area of R2. This can be inferred by

examining the SCOD removal of the anodic area of R2 (Table 2.1). Initially there is a gradual increase of SCOD removal, which might have been due to a combined influence of current and other non-current mediated oxidation pathways. A subsequent decrease in the SCOD removal (in the anodic area) with an increase of current mediated pathways then suggested a decline of non-current mediated oxidation pathways in the anodic area of R2. Since anodic potentials largely remained unchanged (i.e. below -530 mV vs. Ag/AgCl) the reason for the decline of SCOD removal in the anodic area of R2 remains unclear.

Significant SCOD removal (ranging from 3 to 16 %) was taking place in the cathodic area after the forced aeration (Table 2.1). Since the removal was recorded within the cathodic zone, it is very likely that aerobic microorganisms around the cathode were responsible for this observation. This also implied that some aerobic microorganisms had reduced the DO availability in the cathodic region. However, since increasing the aeration rates beyond 120 ml/min did not increase the current further, factors other than DO had become limiting in R2.

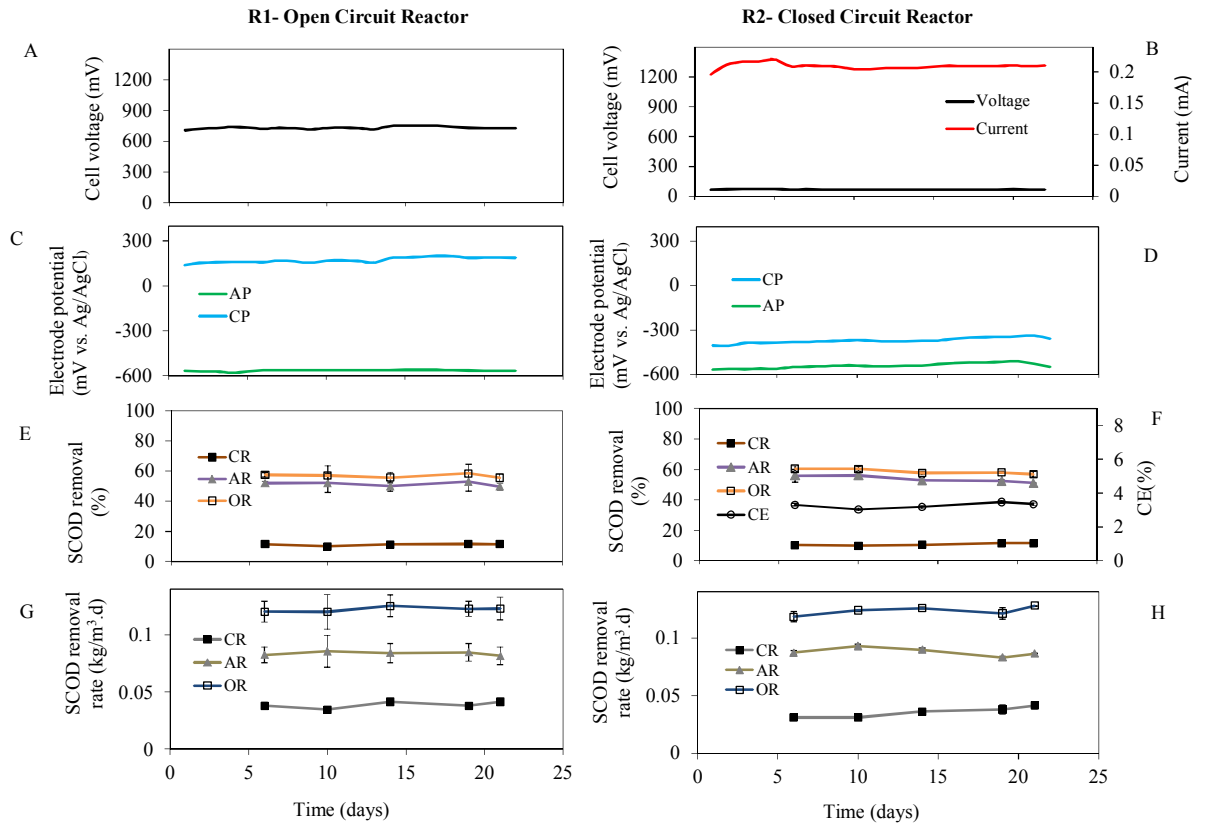


Figure 2. 3 Changes in (A) voltage of open circuit reactor; (B) voltage, produced current at close circuit reactor; (C and D), electrode potentials of open and close circuit reactor; (E) COD removal at open circuit reactor; (F) COD removal and coulombic efficiency at close circuit reactor; (G and H), volumetric rate of COD removal at open and close circuit reactor during cathodic aeration of reactors. AP: anodic potential; CP: cathodic potential; CR: cathodic removal; AR: anodic removal, OR: overall removal; CE: coulombic efficiency.

Table 2.1 The effect of cathodic aeration rate on the current and soluble chemical oxygen demand (SCOD) removal performance of R2 at external resistance of 330 Ω .

Cathodic aeration rate (ml/min)	Current (mA)	SCOD removal (%)			
		SCOD removed via Current	SCOD removed in anodic area	SCOD removed in cathodic area	Overall SCOD removal
0	0.010	0.12	51	2.7	53.7
10	0.015	0.18	53	3	56
20	0.025	0.29	53.8	3.3	57.1
30	0.04	0.47	55.5	7.2	62.7
40	0.16	1.89	55.5	7.5	63.0
60	0.18	2.48	55.8	8.3	64.1
120	0.21	2.48	54.4	10.3	64.7
150	0.21	2.48	52	14	66
200	0.21	2.48	52.9	16	68.9

2.3.3 Impact of external resistance on current generation and COD removal of sediment-type BES reactor

With improved oxygen availability in the cathodic zone of R2 (via forced aeration), the effect of external resistance (10, 330 and 1000 Ω) on SCOD removal was quantified (Figure 2.4). As expected, when a higher external resistance was used, the current declined and coincided with only a slight reduction of SCOD removal. When the external resistance was decreased 100-fold from 1000 Ω to 10 Ω , the current increased by only 3-fold, although the CE was increased up to 5% and the overall SCOD removal marginally increased to approximately 8%. Jadhav and Ghangrekar (2009) and Sajana et al. (2013) also reported a similar result where the decrease of external resistance resulted in only a marginal increase of SCOD removal. The reason for the inability to achieve higher SCOD removal efficiencies even with a decrease of external resistance (by 100 folds) could be an inherent issue associated with sediment BES configurations and this warrants further investigations.

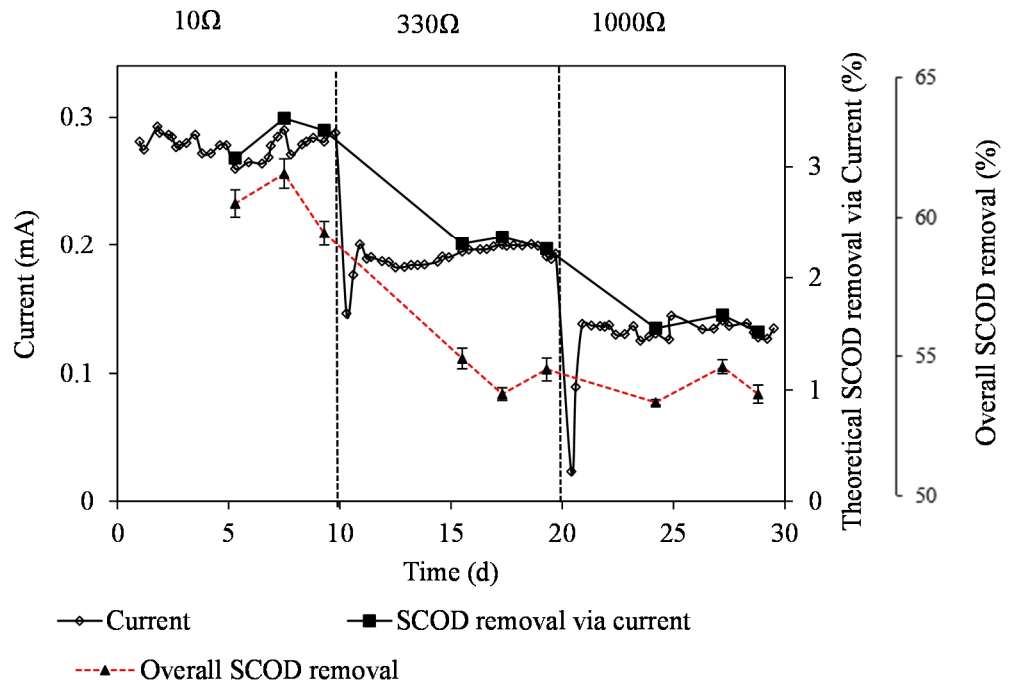


Figure 2.4 Effect of external resistance on current generation and COD removal of R2.

2.3.4 Effects of electrode spacing on the performance of sediment-type BES reactor

The performance of a BES is affected by many factors (e.g. electrode material, pH etc.) of which electrode spacing has been recognised as having a significant influence on current generation (Lee & Huang, 2013). Extending the distance between the cathode and anode leads to larger ohmic losses (Rozendal et al., 2008). The configuration of a sediment BES is such that it does not allow a very close distance between the cathode and anode. The distance between cathode and anode of R1 and R2 was initially fixed at 90 cm. To examine whether the performance of the reactors could be further improved by reducing the distance between electrodes, electrochemical properties of R1 and R2 were compared at two electrode spacings (90 cm and 26 cm) (Figure 2.5).

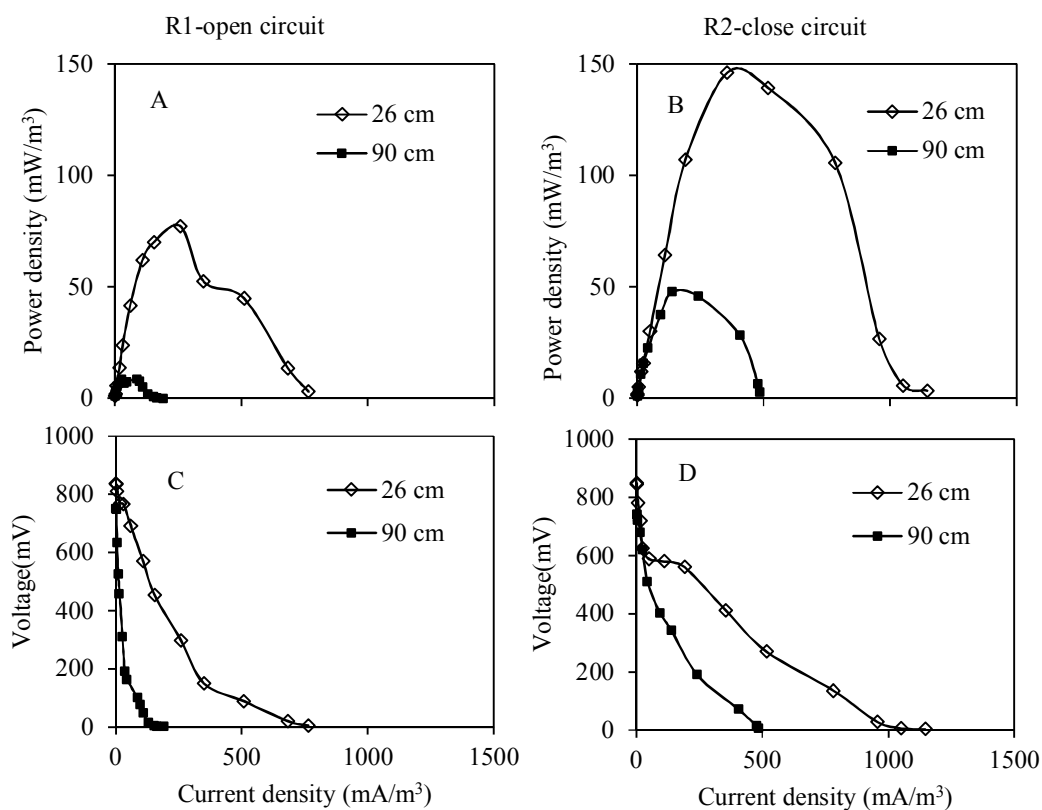


Figure 2.5 Comparison of (A, B), power curves; (C, D), polarisation curves of R1 and R2 with two electrode spacing distances.

The electrochemical performance of R2 improved with the shorter electrode spacing. The maximal power density increased from 50 to 150 mWm⁻³ and the maximal current density increased from 536 to 1148 mA m⁻³ when the electrode spacing was reduced from 90 cm to 26 cm. The internal resistance of R2 reduced from 1420 to 1218 Ω. Compared to R2, R1 showed a much reduced electrochemical improvement. The increase of current density (from 191 to 765 mA m⁻³) and power density (from maximal 9 to 77 mWm⁻³) comparatively was much lower than R2. Decrease of electrode spacing resulted in a 4% increase of SCOD removal in R2 but did not bring about a noticeable improvement in R1. CE of R2 increased from 3.2% to 6% with an external resistance of 330 Ω (Figure 2.6). The results demonstrate challenges associated with sediment BES specifically with regards to electrode spacing.

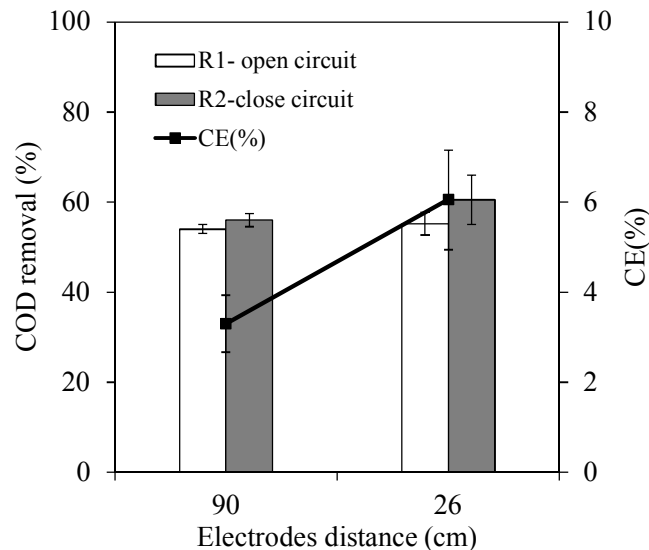


Figure 2.6 COD removal and coulombic efficiencies of R2 operated with two different electrode distances.

2.3.5 Implications of the findings

This study illustrates the significant limitations associated with using sediment BES configuration in the context of wastewater treatment. The difficulties to achieve higher current using sediment BES have also previously been demonstrated for powering remote sensors (i.e. with very low concentrations of SCOD and high DO in the overlaying water where the cathode is submerged). While the proposed use of BES to substitute rock filters represents a promising option, the results of this study clearly highlight the need for a configuration different to a standard sediment BES in order to achieve a positive outcome. The study identified several factors that need addressing when substituting rock filters with BES technology. These are (1) maintenance of low internal resistance (by minimising electrode distance); (2) ensuring no limitation of electron acceptor; and (3) maintenance of low SCOD concentrations in the waters surrounding cathode to prevent a reduced environment around the cathode. When treating wastewater often this may require maintenance of a clear boundary between the anode and the cathode using membranes or separators. These factors need to be considered for the development of a BES configuration suitable for wastewater treatment.

2.4 Conclusions

In this study, a filter type sediment BES configuration was examined as an alternative to rock filters. The following conclusions can be derived from the results of this study.

- Addition of electrode material substantially improved COD removal, possibly due to improved biomass retention and filtering effect.
- Approximately 60% SCOD removal was via non-current mediated pathways.
- The column reactor prototype, which was similar to a sediment BES did not enable efficient removal of SCOD. The current mediated SCOD removal was very low (5%, CE 6%).
- A highly reduced cathode and a large electrode spacing were detrimental.
- A Sediment-type BES configuration is not a suitable alternative for a rock filter to polish SCOD from effluent of WSPs. A more suitable BES configuration that can address challenges identified in this study is needed to realise the perceivable benefits of using BES to polish effluent of WSPs.

Chapter 3

Bioelectrochemical system as an oxidising filter for soluble and particulate organic matter removal from municipal wastewater

Extended from:

Khalfbadam, H. M., Ginige, M. P., Sarukkalige, R., Kayaalp, A. S., & Cheng, K. Y. (2016). Bioelectrochemical system as an oxidising filter for soluble and particulate organic matter removal from municipal wastewater. *Chemical Engineering Journal*, 296, 225-233. doi:10.1016/j.cej.2016.03.067.

Chapter Summary

A bioelectrochemical system (BES) configuration was designed and tested as a polishing process to remove soluble chemical oxygen demand (SCOD) and suspended solids (SS) from municipal wastewater. The configuration was designed such that the anodic carbon felt could behave as a filter enabling removal and bioelectrochemical oxidation of particulate and soluble organic matter from wastewater. Three reactors (approximately 10 L liquid volume) were set up to evaluate three different operational settings: (i) close-circuit operation enabling current production; (ii) open-circuit operation without current production; and (iii) control reactor without electrode to account for the effect of electrode as a filter. The reactors were operated for over 200 days during which key process parameters (SCOD removal, SS removal, turbidity, electricity production, electrolyte pH) were quantified. The results indicated that current production (maximal current of approximately 120 mA) could increase the SCOD removal efficacy from 11% to 77% at a SCOD removal rate of approximately 0.1 kg SCOD/m³.d. No measurable difference between SS removal efficiencies in open and close circuit (83%), and clogging of the electrode filter were observed. A high coulombic efficiency (more than 80%, based on the SCOD removed) and low internal resistance (2.7 Ω) were achieved, indicating that the configuration is suitable

for handling real wastewater containing particulate matter. However, active maintenance of a neutral pH at the anode and an acidic cathodic environment ($\text{pH} < 7$) were essential to sustain the optimum performance of the system. Overall, this study affirms the potential of using a BES to serve as both a physical filter and an oxidising medium for effluent polishing.

3.1 Introduction

Waste stabilisation ponds (WSPs) are widely used in tropical climate areas to treat wastewater such as domestic sewage when availability of land is not limiting (Alvarado et al., 2012; Senzia et al., 2002). Compared to conventional activated sludge processes, WSPs are simple and cheap to operate, and are particularly suitable for remote small communities (Mara et al., 1998). A WSP system designed to treat municipal wastewater typically consists of non-mechanically mixed anaerobic, facultative and maturation ponds (Wolverton & McDonald, 1979). Collectively, these ponds are employed to remove suspended solids (SS), organic pollutants, human pathogens and some nutrients from wastewater (Pedahzur et al., 1993). However, inadequate and inconsistent removal of pollutants and pathogens are not uncommon and hamper the widespread use of WSPs.

Typically, poor performance of WSPs is reflected with excessive biological oxygen demand (BOD) and SS in the effluent. According to (Mara et al., 1998), inadequate removal of BOD and SS is largely a result of excessive algal growth in facultative ponds (FPs). Although a well-managed FP requires a sufficient algal population to facilitate aerobic BOD removal, an excessive growth of algae could lead to an extra BOD (100 µg/l of chlorophyll results in 10 and 3 mg/l of SCOD and BOD, respectively) and SS loading (up to 200 mg/L) (Ellis & Mara, 1983; Shipin et al., 1999). Further, the dependence on environmental factors such as wind to assist BOD removal in FPs is unreliable and does not enable a stable effluent quality. Carryover of BOD from FPs into maturation ponds also compromise pathogen removal. Overall, achieving effluent discharge limits of WSPs are critical and in the recent past several add-on units have been proposed to polish up effluent of WSPs.

One add-on unit that has been widely used is rock filters. Rock filters have been specifically designed to trap and remove algal solids and the associated BOD (Mara & Johnson, 2006; Short et al., 2007). With proper design and operation, rock filters can facilitate passive aeration increasing BOD oxidation. However, excessive biomass build up over time reduces passive aeration and creates anaerobic conditions in the rock filter compromising BOD removal. In some instances, forced aeration of rock filters has been suggested to improve BOD removal (Mara & Johnson, 2006).

However, an elevated oxygen supply may cause profound biomass build up inside the filter leading to clogging.

Bioelectrochemical systems (BES) are a technology that can potentially circumvent the above limitations of rock filters. BES harness the capacity of microorganisms to drive oxidation and/ or reduction reactions at solid-state electrodes (Cheng et al., 2006). Due to the separation of the two half-reactions, removal of organics from the wastewater can be facilitated in the anodic compartment where the anode serves as an electron acceptor for microbial oxidation. The electrons accepted by the anode are conveyed as a measurable current via an external circuit towards the cathode compartment, where a wide range of soluble species including dissolved oxygen can be used as a final electron acceptor. Since organic matter removal could be electrochemically driven under anaerobic conditions, a BES could be a good alternative to rock filters to polish effluent of WSPs. In addition to oxidizing soluble organics, the BES anode media can be specifically selected to entrap and oxidize organic particulate matter in WSP effluent. However, the use of a BES in this context has not been explored yet.

In this work, the sediment microbial fuel cell of (Yuan et al., 2010) was re-engineered as a new “BES filter” configuration and this was evaluated as an alternative to conventional rock filters for SS and SCOD removal. A unique feature of this design is the forced passage of influent wastewater through the anodic carbon felt, whereby most suspended organic matter in wastewater is physically removed.

The main aim of this study was to assess the suitability of the BES filter to remove both soluble and particulate organic matter from real wastewater. Specific objectives included: (1) quantifying effects of current production with SCOD removal; (2) optimizing effective reduction of oxygen at the cathode; (3) examining influence of loading rates on soluble and particulate organic matter removal; and (4) elucidating the impact of particulate matter on current production and Coulombic efficiency.

The BES filters were retrofitted into lab-scale column reactors (9.64 L working volume) and the performance was characterized at three different settings: (i) close-circuit operation with current generation; (ii) open-circuit operation without current generation; and (iii) control reactor without electrode (to account for the effect of electrode as a filter). To emulate effluent of a failed WSP, primary sedimentation tank

effluent (200 mg-SCOD/L, 150 mg-SS/L) of a local municipal sewage treatment plant was fed predominantly into the BES reactors for more than 200 days. During this period, key process parameters such as SCOD removal, SS removal, turbidity, polarisation behaviour, and electrolyte pH were quantified and compared.

3.2 Materials and Methods

3.2.1 The configuration of BES-filtration column reactors

Three identical column reactors (height=1.5 m, internal diameter= 0.1 m) made of transparent polyvinylchloride (PVC) were constructed and set up. Two of these reactors (R1 and R2) were configured as dual-compartment BES reactors (Figure 3.1). The third column reactor (R3) contained no electrode and was used as a control to account for the effect of electrodes. Each BES filter had a height of about 1.5 m and consisted of two concentric cylindrical stainless steel mesh current collector columns, one with a diameter of 6 cm (anodic) and the other with a diameter of 4 cm (cathodic) (Figure 3.1A, B, C). The anodic current collector had its two ends open, whereas the cathodic collector only had its top end open (i.e. the bottom end was enclosed). The two compartments were separated by a cation exchange membrane (CEM) (Ultrax CMI 7000, Membrane International Inc.), which had a surface area of 0.168 m². The membrane was mounted onto the outer surface of the cathodic current collector and was sealed with epoxy glue (Bostix, Australia) to create an isolated internal cathodic compartment. Carbon felts (MGM-Carbon Industrial, Ltd Co., China) were used as both the anode and the cathode and were mounted (with plastic cable ties) onto the respective stainless steel current collectors (Figure 3.1D, i.e. on to the outer surface of anode and to the inner surface of cathode). A short distance (2 cm) was maintained between the anode and the cathode, forming a gap-compartment (3.8 L) to which the wastewater influent was introduced from the bottom end of the unit. Since the cathodic collector was enclosed at the bottom end, the influent was forced to enter the gap-compartment. Continuous loading enabled the wastewater influent to percolate through the anodic felt, facilitating physical removal of SS from the wastewater. As the cathodic current collector was completely sealed with the CEM and its bottom end

was closed, the cathodic compartment was operated in isolation from wastewater (i.e. the anodic compartment).

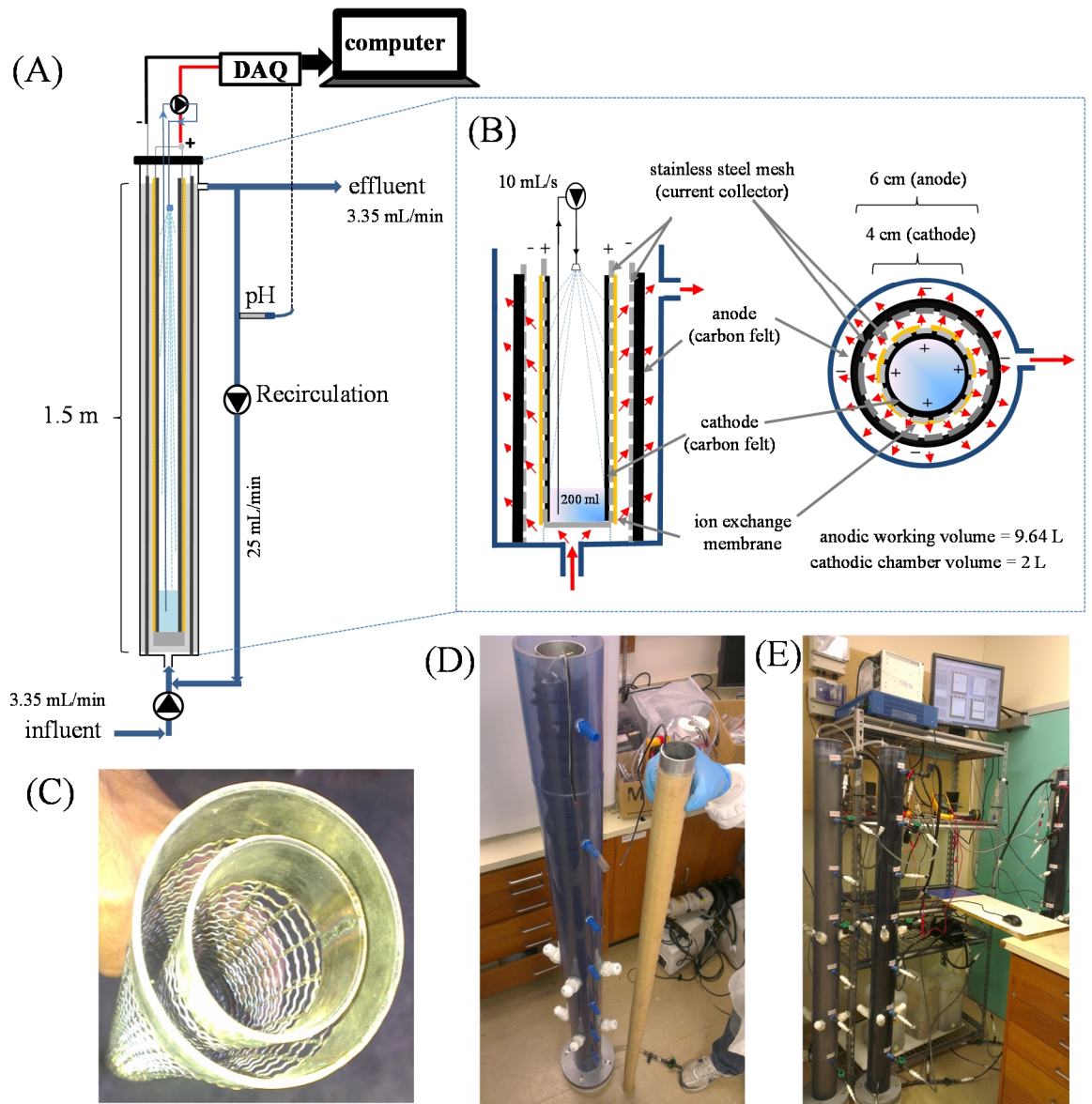


Figure 3.1 Details of the construction of the BES filter unit. (A) Process diagram (B) Cross section and top aerial of process set up, (C) stainless steel mesh current collector, (D) electrodes and cation exchange membrane after mounted onto the stainless steel mesh, (E) BES filter retrofitted into the column reactors in the laboratory. Red arrows indicate wastewater flow path. (DAQ: data acquisition card).

3.2.2 Operational modes of BES-filtration column reactors

Three reactors (R1) Close circuit BES filter- with electrode, (R2) Open circuit BES filter – with electrode and (R3) Control reactor- without electrode were used to evaluate three treatments. Unless stated otherwise, a 1 Ω resistor was used to connect the anode and the cathode of R1. PST effluent of a local wastewater treatment plant (Subiaco, Perth, Western Australia) was collected weekly and transported to the laboratory. The SCOD and suspended solids of the PST effluent was 191-235 mg/L and 110-150 mg/L, respectively. The wastewater was stored at 4°C and was continuously fed into the reactors at different influent flow rates (1.67 to 26.8 mL/min) to obtain different hydraulic retention times (HRTs) (0.25 to 4 days) and organic loading rates (OLRs) (0.05 to 0.9 kg SCOD/m³.d). The influents were introduced to the bottom of the reactors and after passing through the anode felt, the wastewater was continuously recirculated at a rate of approximately 18 L/h within the anodic chamber to optimize mass transfer. Any overflow from the anodic compartment was discharged from the reactor by gravity via an effluent port located near the top of the reactor. All reactors were operated at ambient temperature (22-25°C).

One percent (v/v) of returned activated sludge (RAS) collected from a local municipal wastewater treatment plant (Subiaco, Perth, Western Australia) was used as an inoculum for all reactors. In this study, the cathodic compartment was operated either fully immersed in water or exposed to air. In the fully immersed mode, the cathode was entirely submerged in an aerated catholyte (2000 mL). In the air-exposure mode, the cathode (~90% of the surface area) was directly exposed to the atmosphere and a small volume (200 mL) of catholyte was continuously re-sprinkled at flow rate of 10 mL/s. The sprinkling approach was to negate the requirement of active aeration and to facilitate oxygen transfer to the cathode. Unless stated otherwise, pH of anolyte and catholyte were controlled using 4M NaOH and 1M HCl, respectively.

The performance of the reactors were examined in three different stages. Stages 1 and 2 were operated in a continuous mode using real wastewater for a period of 107 and 25 days, respectively. Synthetic wastewater (particulate-free) was used in batch mode during stages 3 for a period of 53 days. Carbon free synthetic medium was used in some experiments, and it had a composition as described in (Cheng et al., 2008). The step changes carried out to the reactors during stage 1 are detailed in Table 1.

3.2.3 Impact of SCOD loading on BES filtration column reactors

The effect of various SCOD loading rates (SCODLR) (0.9, 0.42, 0.22, 0.11 and 0.05 kg/m³.d) on the performance of R1 and R2 was evaluated over a period of 25 days. Fresh wastewater was collected prior to application of each SCODLR. pHs of anolyte and catholyte were controlled at 7 and cathodic compartment was operated in the air-exposed mode, where the total working volume of the catholyte was reduced to 200 mL, enabling the exposure of the cathode directly to the atmosphere. Stable SCOD removal, SS removal and turbidity removal were monitored regularly to evaluate SCOD and particulate matter removal efficiencies of the system.

3.2.4 Oxidation of particulate matter by BES filtration column reactors

3.2.4.1 Extraction of particulate matter from PST effluent

Freshly collected PST effluent was loaded into 1-L Imhoff cones and was allowed to settle for five hours. Thereafter, two distinct layers of sediment were visualised at the bottom of each cone. The lower layer, which contained mostly inert sand-like particles was carefully discarded through a decant port. The upper layer was carefully harvest through centrifugation (4000 × g for 30 minutes). The supernatants were discarded, and the pellet was resuspended in DI water, centrifuged once again and the supernatant was discarded. This washing step with DI water was repeated twice to remove residual soluble organics from the suspended particulate matter. The extracted particulate matter (mixed liquor suspended solid (MLSS) concentration 25 g/L) had a total COD (TCOD) of 12,972 mg/l and SCOD of 31 mg/l, respectively.

3.2.4.2 Evaluation of the use of BES filter for particulate matter removal via current production

Prior to examining the influence of particulate matter, the entire anolyte of the BES filter was discharged and the anodic chamber was flushed with 50 litres (about 5 times the anodic chamber volume) of DI water to remove any residual SCOD. Subsequently the anode compartment was filled with a carbon free synthetic medium for approximately one week (adopted from (Cheng et al., 2008)). Thereafter, the anodic

activity of the biofilm was reconfirmed by adding several acetate aliquots (10 mL of 2M acetate) at different times. This was to ensure that the anodic biofilm remained active after the reactor flushing step. Once a background current of near zero was achieved, 2.5 g (dry weight) of the pre-concentrated particulate matter pre-mixed with 100 mL of synthetic medium was injected into anodic compartment of R1 and the current was continuously monitored until the current approached the near zero background level again. At this point, the anodic biofilm activity was checked once again by spiking 10 mL of 2M acetate. pH of anolyte and catholyte were controlled at 7 and cathodic compartment was operated in the air- exposed mode as described above.

3.2.5 Process monitoring, calculation and analysis

A potentiostat (VMP3, BioLogic) was used to measure cell voltage (i.e. the potential differences between the anode and the cathode) and pH electrodes (Ionode, Australia) were used to monitor online the anolyte pH of R1 and R2, the catholyte pH of R1, and the pH of R3. All data was collated (every 50 s) using a Labview program and data acquisition hardware (National Instrument, USA).

The current (I , mA) of R1 was determined from the cell voltage according to Ohm's Law, $I = \frac{V}{R}$, where V (mV) is the measured cell voltage across an external resistor R (Ω). Power (P , W) was calculated according to equation $P = V \times I$. Volumetric current and power densities were obtained by normalising I and P with the net working volume of the anodic chamber (9.64 L).

TCOD and SCOD were measured using HACH reagents (cat no. TNT 821; method 8000, LR) and a spectrophotometer (GENESYS 20, Thermo Scientific). Coulombic efficiency (CE) (i.e., the percentage of electrons recovered as anodic current from the removed SCOD) of the anodic reaction was determined as detailed in past literature (Logan et al., 2006). Polarisation curves were derived to examine the electrochemical performance of the BES filters (R1 and R2) and this was carried out by a stepwise decrease of the external resistance from 1 M Ω to 1 Ω . Polarisation tests were carried out on both R1 & R2 at three different time intervals (on days 20, 64 and 78) on observing a stable maximum current on R1. The internal resistance of reactors were

derived from the slope of the linear part of the polarisation curve (Logan et al., 2006). Influent and effluent particulate matter was quantified by measuring SS and turbidity. SS was measured according to standard methods for examination of water and wastewater (Young et al., 2007) Nephelometric turbidity units (NTU) were measured using a portable turbidity meter (HACH 2100).

3.3 Results and Discussion

This study was conducted over a 230 day period, during which the reactors were assessed for SCOD removal, electrochemical performance and SS removal characteristics. The results obtained from three different stages of the study are discussed in the following sections.

3.3.1 Stage 1 – Process start up and initial assessment of the BES performance

Stage 1 consisted of the initial 107 days of operation of all three reactors, and the step changes carried out in this stage are detailed in Table 3.1 and Figure 3.2.

Upon inoculation of the anodic chambers with activated sludge (on day 2), a rapid increase in cell voltage and decrease in anodic potentials was recorded in both R1 and R2. This suggests that the activated sludge could readily create a reducing environment in both reactors (under open circuit mode) (Figure 3.2B and C). At day 8, the external circuit of R1 was closed with a 1 Ω external resistor to facilitate acclimatisation of electrochemically active microorganisms on anode (Figure 3.2A). However, no noticeable current ($< 1\text{mA}$) was recorded. This was expected as a lag period before onset of current is a common occurrence during initial days of acclimatisation (Figure 3.2A).

Since closing the circuit resulted in a remarkable decline in both the cell voltage and cathode potential of R1 (Figure 3.2B, C), on day 13 the catholyte of R1 and R2 were actively aerated to ensure that the cathodic reaction was not limited of oxygen. This resulted in a noticeable increase in current of R1 and cell voltage of R2 (Figure 3.2A, C). However, such increase was only transient and the current began to decline gradually, coincided with an anolyte acidification and a catholyte basification (from

7.7 to 8.5) (Figure 3.2D). Daily replacement of the catholyte did not avert the pH drift of catholyte. Hence, on day 29 the catholyte pH of R1 and R2 was manually adjusted to pH 4 (using 2 M HCl). As expected, this resulted in an immediate increase in current and cell voltage in R1 and R2, respectively (Figure 3.2A, B).

Table 3.1 Step changes to the reactors during stage 1 of this study.

Step	Day	Description
1	2	1% (v/v) of activated sludge was added into the reactors as a mixed culture microbial inoculum.
2	8	R1 was closed with an external resistor of 1 Ω .
3	13	Cathode chambers of R1 and R2 were filled with deionised water (2000 ml) and aerated using compressed air at a flow rate of 50L/h.
4,5	29,31	20 ml of 2M HCl was added into the cathode chambers of R1 and R2.
6,7	36,41	Repeat of experiment to demonstrate reproducibility.
8	56	Anolyte pH of R1 and R2 were controlled manually at around pH 7 using 4M NaOH.
9	60	Online feedback control of pH (set point 7) established on the anode compartment of R1 using 4M NaOH.
10	70	Investigation of optimum catholyte pH and establishment of online pH control (set point 2). Exploration of strategies to improve proton diffusion and oxygen reduction on cathode.
11	75	R1 & R2 spiked with 10 ml of 2M acetate.
12	90	External circuit of R1 switched to open circuit.
13	94	R1 switched back to closed circuit with 1 Ω resistor.
14	104	Operation modes of R1 and R2 were switched from continuous mode to batch mode
-	20,64,78	Polarisation curve analysis

However, such increase again was only transient (a few hours) and the current (R1) and cell voltage (R2) reduced to even lower values to that recorded prior to the adjustment of pH. This trend coincided with a decrease in the respective analyte pH, which could be due to release of protons from the microbial anodic reaction (Figure 3.2A, D). A similar pH decline in R2 was recorded even when it was operated in open circuit mode. Hence, a cross contamination between catholyte and anolyte (due to membrane leakage) was suspected, and both R1 and R2 were dismantled and rebuilt.

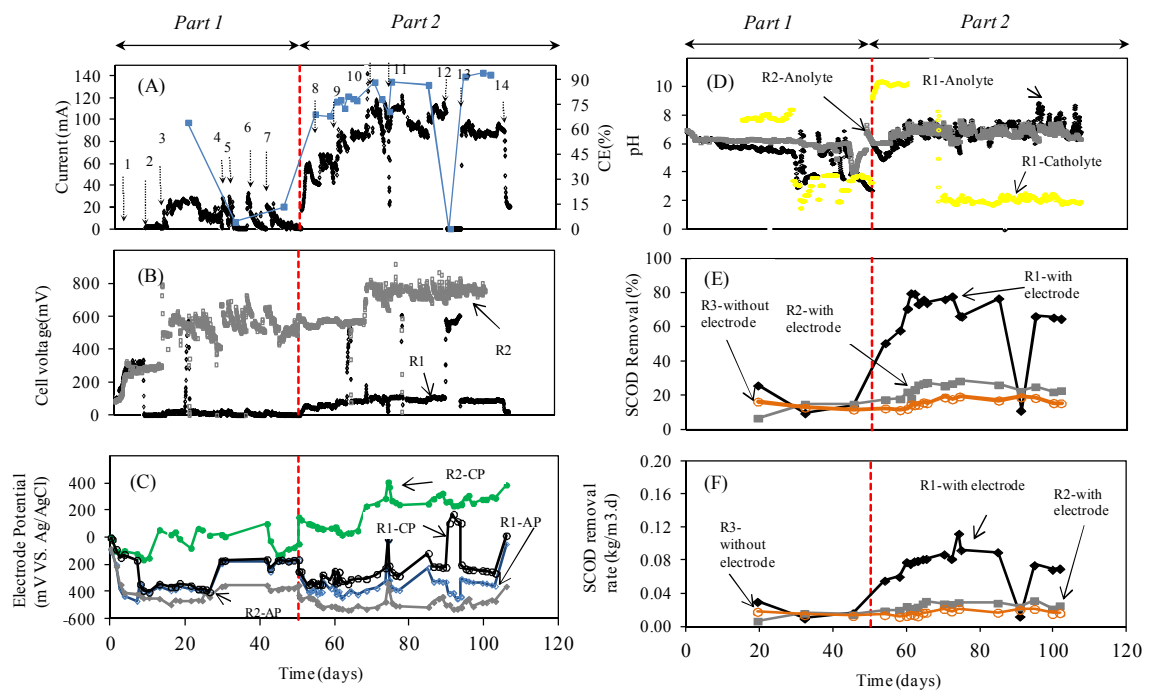


Figure 3.2 Changes in (A) current (black line) and CE (blue line) of R1 , (B) cell voltage of R1 and R2 , (C) electrode potentials of R1 and R2, (D) electrolytes pH of R1 and R2, (E) SCOD removal of R1, R2 and R3, (F) SCOD removal rate of R1, R2 and R3. The vertical red dotted line separates part 1 (before fixing the membrane) and part 2 (after fixing the membrane). Numbered arrows in (A) represents different actions made to the reactors as detailed in Table 1. (R1: close circuit reactor, R2: open circuit reactor, R3: control reactor CE: coulombic efficiency, CP: cathodic potential, AP: anodic potential).

3.3.1.1 Solution pH control was critical to enable current production

On rectifying the membrane leakage at day 50, an increase in current was recorded in R1 (Figure 3.2A). However, the anolyte was gradually acidified (pH decreased from 6.2 to 5.4), causing the current to decrease again (from 57 mA to 41 mA) (Figure 3.2D). When the anolyte was manually neutralised (pH 7), the current of R1 increased to 67 mA and the SCOD removal efficiency increased from 50 % to 58 % (Figure 3.2E). Hence, neutralization of anolyte was critical for the anodic SCOD oxidation. Indeed, it has been generally observed that a neutral pH favours anodic microbial reactions in BES (Cheng et al., 2010; He et al., 2008; Ruiz et al., 2015). To ensure the anodic reaction was not limited by acidification, a feedback control of the anolyte pH was implemented for R1 from day 60 onwards. Thereafter, the current of R1 gradually increased reaching a stable level of approximately 85 mA (Figure 3.2A) and a SCOD removal efficiency of 75.5% (Figure 3.2E).

Upon the improvement of the anodic reaction, the cathodic reaction appeared to be limited by an increase of pH due to inefficient proton transfer across the cation exchange membrane (Rozendal et al., 2006). An experiment was conducted to determine the dependency of current (R1) and cell voltage (R2) on catholyte pH (Figure S3.1A; Appendix 1). As expected, both parameters increased with decreasing catholyte pH, suggesting that acidic condition (pH 2) was beneficial to the process (Lefebvre et al., 2011). With an acidified catholyte, the cathodic potentials of both R1 and R2 increased (Figure 3.2C) and the current of R1 and the voltage of R2 increased from 85 mA to 110 mA and 570 mV to 800 mV, respectively (Figures 3.2A & B). SCOD removal of R1 also increased slightly from 74% to 76.1% and the average CE increased from 78% to 88.5% (Figure 3.2A & E).

3.3.1.2 The BES filter could be operated with an air-exposed cathode

Apart from solution pH control, the availability of oxygen as an electron acceptor for cathodic reduction is also imperative for the current production. In this study, two strategies for supplying oxygen to the cathode were examined at the end of stage 1: (1) the cathode was entirely submerged in an aerated catholyte; (2) the cathode (~90% of the surface area) was exposed to the atmosphere and was continuously re-sprinkled with a small volume of catholyte (Figure S3.1B; Appendix 1). The sprinkling approach

was to negate the requirement of active aeration and to facilitate oxygen transfer to the cathode. When the cathode was operated in a fully-submerged mode, current was produced only when the catholyte was actively aerated (0-38 h, Figure S3.1B; Appendix 1). When the aeration was terminated, both the current and the dissolved oxygen concentration in the catholyte declined immediately (the dissolved oxygen decreased from 8.8 to 0.5 mg/l within 1h) (Figure S3.2; Appendix 1). This suggests that dissolved oxygen is an effective electron acceptor for the BES filters.

On the other hand, a similar level of current (105 mA) was achieved with the sprinkling method. When the sprinkled catholyte was acidified to pH 2, the current almost instantly increased by 3-fold (~ 300 mA) and gradually stabilised at approximately 150 mA, which was 50% higher than the current obtained prior to acidification (Figure S3.1B; Appendix 1). Overall, the results suggested that the BES filter configuration could be operated with an air-exposed cathode without the need to actively aerate the catholyte, and an acidic condition was favourable for the cathodic reaction. The BES filter was operated with the air- exposed cathode as an effective aeration strategy for the subsequent stages.

3.3.1.3 The BES filter could efficiently convert the electrons from the wastewater into measurable electrical current

The BES filter (R1) could efficiently convert the electrons from the wastewater into measurable electrical current, as indicated by a high CE of 88% (Figure 3.2A). This value is remarkably higher than other similar studies (Table 3.2). Such a high CE% implies that there was only a small fraction of SCOD (here 12%) removed via non-current generation pathways. To investigate to what extent these pathways contributed towards SCOD removal, a comparative study was carried out with both R1 and R2 operated in open circuit mode (action 12 on day 90, Figure 3.2). Surprisingly, after being switched into open circuit mode the SCOD removal of R1 decreased from 76.6% to 11%, which was only half of the SCOD removal of R2 (22.5%) (Figure 3.2E). This suggests that the established microbial community in the anode of R1 was highly specialised for current generation with the SCOD in wastewater.

Table 3.2 Performance of selected litre-scale BES processes operated with domestic wastewater and acetate.

Substrate	Anodic volume(L)	$R_{int}(\Omega)$	$P_{max}(mW m^{-3})$	CE (%)	HRT(h)	SCOD removal (%)	SS removal (%)	SCOD removal rate achieved by anodic biofilm(mg/l.h)*	Reference
Dual chamber MFC design, aerated cathode									
Domestic ww	9.64	2.7	1556	88.5	48	76.1	83	0.014Cin	This study
Domestic ww	2.9	11	1555	11	2.4	75	84	0.034Cin	(Lefebvre et al., 2011)
Dual chamber MFC design, open air cathode									
Acetate	7.5	NA	390	50	33.8	81	NA	0.012Cin	(Clauwaert et al., 2009)
Single chamber design MFC, open air cathode									
Domestic ww	4	NA	NA	NA	11.1	<53	NA	-	(Zhang et al., 2013a)
Domestic ww	4	NA	NA	10.7	11	70	50	0.007Cin	(Zhang et al., 2013b)
Acetate	2.4	7.02	15520	3.83	10-40	79	NA	0.003Cin	(Zhang et al., 2010)
Multi anode- cathode MFC design, open air cathode									
Domestic ww	20	175	170	0.3	20	80	NA	0.0001Cin	(Jiang et al., 2011)
NA, not available, *: $SCOD\ removal\ rate\ achieved\ by\ anodic\ biofilm = \frac{CE(\%)\cdot SCOD\ removal(\%)\cdot Cin}{HRT\ (h)}$, where Cin is the value of influent SCOD (mg/l).									

In open circuit mode, the microbial community was unable to readily use alternative pathways to metabolise the SCOD. On the other hand, the higher SCOD removal (22.5 %) recorded in R2 could be due to the established microbial community being acclimatised for these alternative pathways such as methanogenesis. Compared to R2, a lower SCOD removal of 15% was recorded in R3 (without electrode), most likely due to a higher biomass retainment with the carbon felt in R2 (Figure 3.2E).

In terms of nutrient removal, no measurable change in soluble phosphate was recorded in both R1 and R2 (approximately 6 mg-P/L). However, 52% of ammonium was removed in R1 (from 33 to 16 mg-N/L), most likely due to current-driven ammonia migration across the cation exchange membrane towards the cathodic chamber of R1 (Cord-Ruwisch et al., 2011). In contrast, the ammonium concentration in R2 was increased by 15% (from 33 to 38 mg-N/L), most likely due to organic matter hydrolysis. As expected, due to the absence of oxygen nitrate concentrations in the influent and effluent of both R1 and R2 were negligible (<0.05 mg- N/L).

3.3.1.4 Polarisation curve analyses revealed an improvement of electrochemical performance over time

Over the period of operation in stage 1, electrochemical properties (maximal current, power densities and internal resistance) of the BES filters were regularly examined using polarisation curve analyses (Figure 3.3). In general, the electrochemical performance of R1 increased progressively over time, whereas the performance of R2 remained poor. A maximum current and a power density of 13400 mA^m⁻³ and 877 mWm⁻³, respectively, was achieved together with a low internal resistance of 2.7 Ω by day 78 (Figure 3.3C). In contrast R2 showed a much lower maximum current and power density of 2150 mA^m⁻³ and 45.7 mWm⁻³, respectively (Figure 3.3B). The internal resistance of R1 is noteworthy as it is the lowest compared to other similar scale BES configurations operated with real wastewater (Table 3.2). The low internal resistance achieved with our configuration was most likely due to the close distance (*ca.* 2 cm) between the anode and the cathode (Ghangrekar & Shinde, 2007). While the design of BES would require further improvement to overcome challenges such as pH splitting, the high CE and low internal resistance of the design are promising features for practical application.

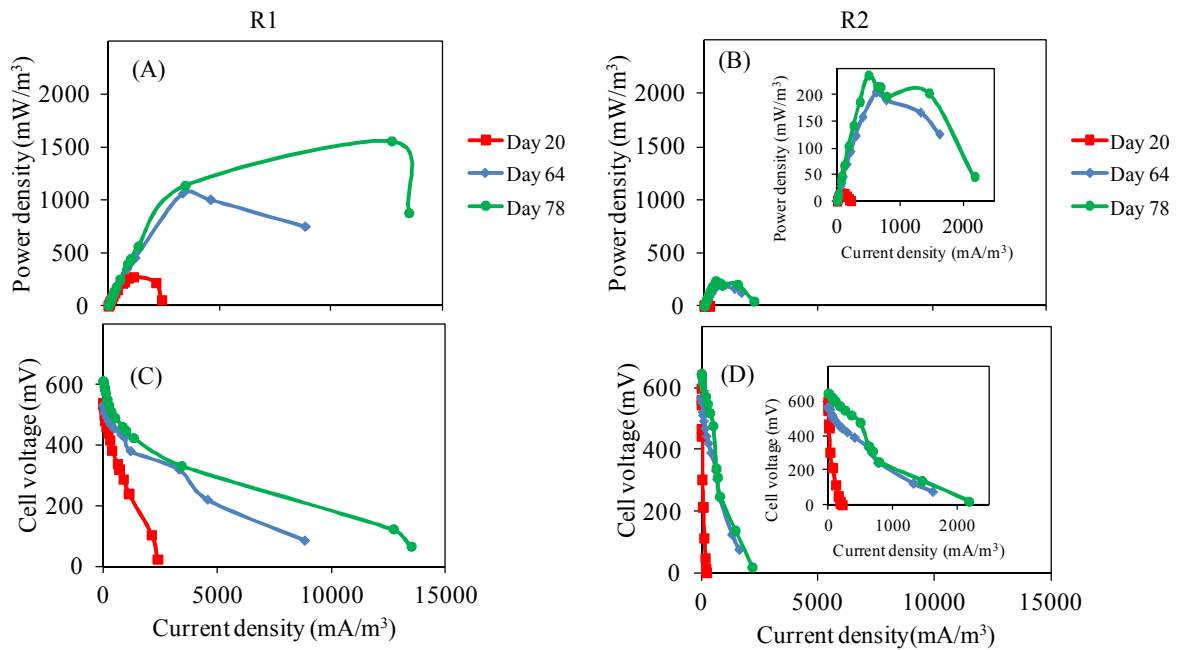


Figure 3.3 Comparison of (A and B), power curves, (C and D), polarisation curves of R1 and R2 at day 20, 64 and 78.

3.3.2 Stage 2 – Effects of organic loading rates on SCOD and particulate matter removal of the BES filter

A unique feature of the BES filter configuration was that the wastewater influent was forced to run through the anodic felt, whereby the SS in the influent could be physically removed. In stage 2 of this study the abilities of R1 and R2 to remove organics and particulate matter were compared at various SCODLRs (0.9, 0.42, 0.22, 0.11 and 0.05 kg/m³.d) (Figure 3.4A). Increasing the SCODLR (from 0.11 to 0.22 kg/m³.d) increased the current of R1 from 87.4 mA to 106.7mA, which was substantially (32%) lower than the expected current (156 mA) assuming a CE of close to 100 % recorded during the initial period (0 to 70 h in Figure 3.4A). Further increasing the SCODLR did not increase the current, suggesting that the existing microbial community had already reached its maximum capacity for anodic SCOD oxidation. In general, a lower SCODLR enabled a more complete removal of SCOD (Figure 3.4B). For instance, when the SCODLR was decreased from 0.9 to 0.11 kg/m³.d, the SCOD removal increased from 25 % to 65.5 % and 6.5% to 28.5%, for

R1 and R2, respectively (Figure 3.4B). The lower SCODLR enabled a higher contact time between the soluble substrate and the anodic biofilm, leading to the higher SCOD removal (Jiang et al., 2011).

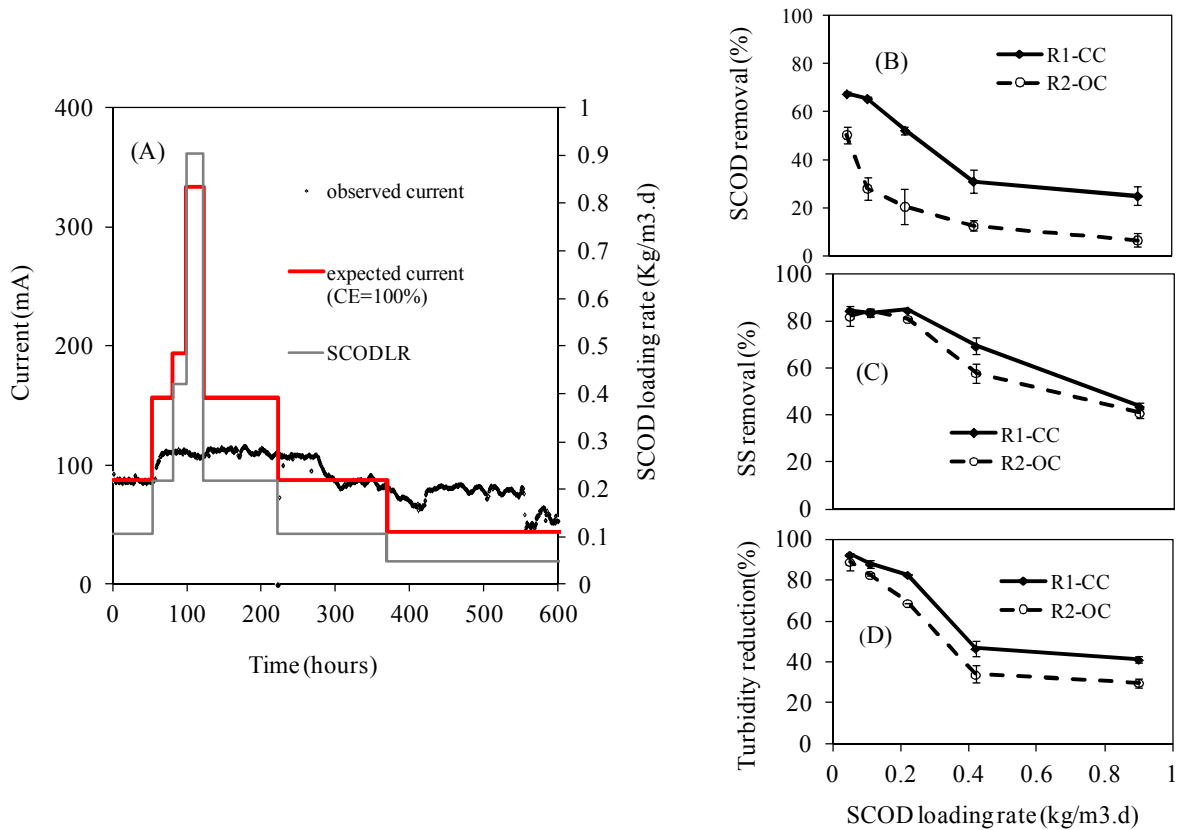


Figure 3.4 Effect of SCOD loading rate on (A) current production of R1; (B) SCOD removal; (C) SS removal; (D) turbidity reduction of R1 and R2. CE = Coulombic efficiency.

Interestingly, from 200 h onward reducing the SCODLR did not reduce the current and a CE of over 100 % was recorded (Figure 3.4A). The generation of this extra current (CE > 100%) signifies the presence of electron donors other than the loaded SCOD. Since the BES filter configuration was designed to facilitate entrapment of particulate matter in wastewater, the extra current recorded (from 200 h onward) could likely be due to oxidation of the entrapped particulate matter. Hence, SS removal and turbidity reduction in both R1 and R2 were quantified (Figure 3.4C & D). The influent SS concentration (110 - 150 mg/l) and turbidity (143-186 NTU) decreased to 18 mg/L (85% removal) and 9 NTU (94% removal), respectively in the effluent when the

SCODLR of R1 was 0.05 kg/m³.d. However, increasing the SCODLR to 0.9 kg/m³.d compromised both SS (94.5 mg/L, 42% removal) and turbidity (90 NTU, 40% removal). A similar effect was observed with R2 (Figure 3.4C and D). Since both R1 and R2 were predominately operated at the same SCODLR of only 0.1 kg/m³.d, both reactors achieved a satisfactory SS removal of 83 % (Figure 3.4C).

3.3.3 Stage 3 – Current production and enhanced Coulombic efficiency driven by the entrapped particulate matter

To determine if wastewater particulate matter could be exclusively used for current production and an increased CE, a spiking experiment was carried out with R1 over a 50 days period (Figure 3.5).

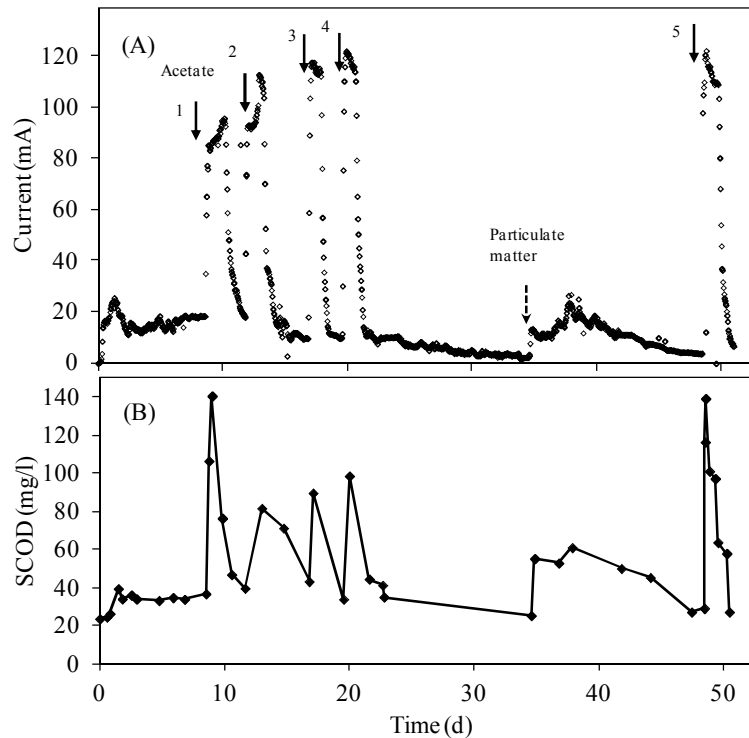


Figure 3.5 (A) Current production induced by the addition of soluble carbon (acetate) and wastewater particulate matter. (B) SCOD of R1. The addition of acetate and particulate matter is indicated by the arrows. Both the anolyte and catholyte pH were controlled at pH 7.

The experiment was initiated by first flushing the anodic chamber with plenty of organic-free DI water (see method section) to make the anode deprived from soluble organics. Immediately after this step, the current momentarily ceased (<1 mA) and the anolyte SCOD was approximately 20 mg/L. However, within 21 h the current increased to 18 mA and the SCOD of anolyte increased to 34 mg/L. Since R1 was operated for a prolonged period with the real wastewater (stages 1 and 2) prior to this experiment, it was likely that the anodic felt of R1 had already entrapped a substantial amount of particulate matter and may have caused the observed phenomenon (elevated background current). The anolyte SCOD concentration and current remained at the elevated background levels until the first acetate spike (Figure 3.5). The addition of acetate spikes induced current peaks, indicating that the established biofilm was highly active. After approximately three weeks, over which no particulate matter was loaded to the reactor, the baseline current declined to 3 mA by day 35 (Figure 3.5). At this

point, a pre-washed SCOD-free particulate matter aliquot was injected to the anodic influent stream, and within a short time the current increased and continued to rise reaching a maximum of 27 mA after 3 days. Compared to the acetate spikes, the particulate matter triggered a lower current, but over a longer period of time (331 hours). The prolonged prevalence of a low current could be indicative of a slow microbial hydrolysis of particulate matter in the anodic chamber, as hydrolysis is often considered as the rate-limiting step of anaerobic degradation of organic particulate matter (Rezaei et al., 2007).

Coulombic analysis of the different substrate spikes further affirms the role of the anodic filter in driving the oxidation of particulate matter (Figure 3.6). With acetate spikes of 1 to 4, decreasing CEs (106.7 % to 80.6 %) were observed. A CE greater than or near 100 % (spike 1) can only be explained by considering a release of SCOD (i.e. the extra electrons) from the entrapped particulate matter on carbon felt. A decrease of CEs (from spike 2 to 4) suggests a gradual decline of SCOD released from the hydrolysis of the entrapped particulate matter. With a spike of particulate matter, a CE of 365% was achieved which is attributable to particulate matter hydrolysis. A final spike of acetate (Spike 5) resulted in a CE slightly higher than 100%, suggesting that hydrolysis of the entrapped particulate matter could still be continuing.

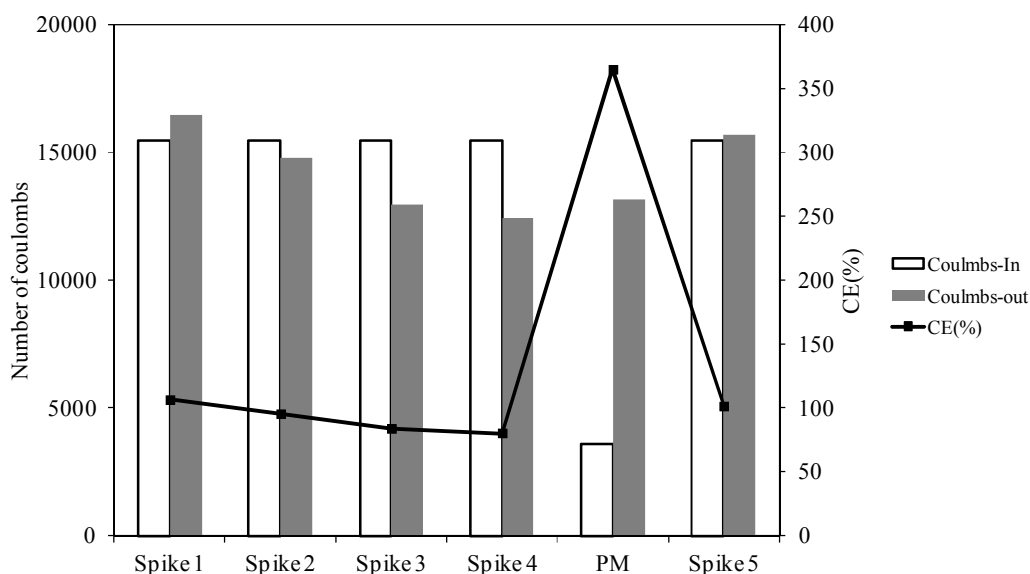


Figure 3.6 Coulombic balance and efficiencies of various substrate-spikes in Figure 3.5. Spikes 1-5= sodium acetate; PM= particulate matter. Note: the Coulombs-In is calculated based on soluble COD only.

There have been several studies reporting the CE of BES systems with domestic wastewater containing particulate matter. For instance, (Lefebvre et al., 2011) reported a SS removal of 84%, but a low CE of 11% with their BES unit loaded also with particulate matter containing municipal wastewater (Table 3.2). In the present study, a similar removal of SS (83%) was recorded, but at a remarkably higher coulombic efficiency of more than 80%, which is the highest CE reported thus far using real wastewater as the feedstock. The main discrepancy between the two BES designs is the filtration feature of our configuration, which enables the solubilisation of the entrapped particulate over prolonged operation of the BES filter. The spiking experiment further corroborates the contribution of the filtering mechanism to the increased CE. Overall, the results suggest that the BES filter could physically remove particulate matter from wastewater, and the decomposition of the entrapped particulate matter could be facilitated *in situ* via current production.

3.3.4 Implication of the findings

This study demonstrates the use of BES to remove both soluble and particulate organic matter from wastewater. The unique feature of the tested BES unit is the use of

electrode (anode) to both a physical filter and oxidise organic matter. Our results showed that the BES filter could remove or retain bulk of the particulate matter (83 %) from the effluent, and the degradation of the entrapped particulate matter was found to be electrochemically facilitated via current at an acceptable rate preventing clogging and not necessitating any back wash of BES filter. This overall contributed to the higher coulombic efficiencies that were observed and compared to similar studies, the coulombic efficiencies of this study is of significance (Table 3.2). There was no measureable change of flow rate in effluent of BES filters during the period of operation for over 200 days suggesting that a self- cleansing mechanism existed in BES filters. This is an important feature of the BES filter configuration as it highlights the ability of the unit to function as a modular, self-cleansing filtration device. It is worth noting that the continuous loading of wastewater also did not lead to severe clogging in the control reactor (R2), suggesting that part of the entrapped particulates was also degraded in situ inside the electrode-filter. Since the wastewater sample used in this study had already undergone primary sedimentation, which had removed most of the inert inorganic particles (e.g. sand), it is likely that the entrapped particulates were biodegradable and as such hydrolysed over time (as corroborated with the elevated ammonium concentration in the effluent of R2). However, further studies are required to confirm this.

Scaling up BES for municipal wastewater treatment has often been hindered by an increase of internal resistance (Clauwaert et al., 2008). The internal resistance of the BES filter was found to be in the lowest range (between 2 Ω and 20 Ω) amongst similar studies in the literature that also examined systems that had similar hydraulic throughputs (Table 3.2). Clearly, the use of stainless steel current collector and the short distance maintained between the electrodes are factors that should be considered in future designs. However, as in most other BES configurations, management of pH in both the cathode and anode chambers remains a technical challenge. While there were some efforts (Clauwaert et al., 2009) to address the pH splitting issue, more practical methods are needed to address this fundamental issue.

3.4 Conclusions

This study successfully characterised the BES filter configuration for its ability to remove organics and suspended solids. Based on the results, the carbon felt electrode used in this study could act as a filter for SS removal minimising the release of SS in the treated effluent. *In-situ* oxidation of the entrapped SS was facilitated via electrical current. Current production in the BES filter also remarkably increased SCOD removal (from 11 % to 77 %). High CE (>80%) and low internal resistance (2.7 Ω) were important features of the BES filter configuration. Sprinkling water on the cathode was an effective strategy to operate the cathodic chamber of the BES filter. Overall, this study affirms the potential of using BES to serve as both a physical filter and an oxidising media to polish WSP effluent.

Chapter 4

A bio-anodic filter facilitated entrapment, decomposition and *in situ* oxidation of algal biomass in wastewater effluent

Extended from:

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Chapter Summary

This study examined for the first time the use of bioelectrochemical systems (BES) to entrap, decompose and oxidise fresh algal biomass from an algae-laden effluent. The experimental process consisted of a photobioreactor for a continuous production of the algae-laden effluent, and a two-chamber BES equipped with a graphite granules and carbon-felt anodic filter facilitating the physical removal and oxidation of the algal biomass from the effluent. Results showed that the BES filter could retain *ca.* 90% of the suspended solids (SS) loaded. A coulombic efficiency (CE) of 36.6% (based on particulate chemical oxygen demand (PCOD) removed) was achieved, which was consistent with the highest CEs of BES studies (operated in microbial fuel cell mode (MFC)) that included additional pre-treatment steps for algae hydrolysis. Overall, this study suggests that a filter type BES anode can effectively entrap, decompose and *in situ* oxidise algae without the need for a separate pre-treatment step.

4.1 Introduction

Waste stabilisation ponds (WSPs) are well suited for tropical climate areas to treat municipal wastewater especially from remote communities (Mara et al., 1998). Typically, a WSP system consists of serially-connected anaerobic, facultative and maturation ponds (Mara et al., 1992). Facultative ponds (FPs) facilitate much of the oxidation of organic matter through a mutualistic relationship between algae and bacteria, and the process relies heavily on natural factors (wind, sunlight, temperature) to fulfil the requirements of such mutualistic relationship (Pedahzur et al., 1993; Tharavathi & Hosetti, 2003). However, due to the reliance on these uncontrollable factors the removal of dissolved organic carbon (DOC) and suspended solids (SS, concentration of up to 200 mg L^{-1}) are often inadequate (Ellis & Mara, 1983; Mara et al., 1998; Mara et al., 1992). With recent enforcement of stringent discharge limits (e.g. $<30 \text{ mg L}^{-1}$ of SS), most utilities have considered using additional processes to polish up the WSP effluent (Mara & Johnson, 2007). Rock filters have been identified as a simple and an economical technology for this purpose (Mara & Johnson, 2006; Short et al., 2007). As WSP effluent passes through a rock filter, SS are physically retained and subsequently oxidised biologically over time. However, excessive accumulation of SS can obstruct passive aeration and creates anaerobic conditions inside the rock filter, compromising COD removal (Saidam et al., 1995). Hence, alternative treatment technologies that could overcome these challenges are desirable for the wastewater industry.

Bioelectrochemical systems (BES) are an emerging wastewater treatment technology that can facilitate anaerobic oxidation of organic matter. These systems typically consist of a separated anode and a cathode chamber. Electrochemically active bacteria oxidise organic matter in the anode chamber using an inert electrode such as graphite as a final electron acceptor (Logan et al. 2006). The electrons donated by the bacteria subsequently flow through an external circuit to the cathode, where the electrons are accepted by electron acceptors such as dissolved oxygen. The anodic compartment of a BES could be engineered to functionally resemble a rock filter, i.e. to entrap and oxidise SS and DOC in wastewater. In this study, graphite granules and felts in the anode chamber simulated filtration aspects of a rock filter and the graphite media similar to rock media facilitated the formation of biofilms. A forced passage of WSP effluent through the anodic filter bed enabled entrapment of SS such as algal biomass

in the anodic chamber. The hydrolytic, fermentative and electrochemically active bacteria resident on biofilm then facilitated hydrolysis, fermentation and oxidation of soluble organic matter and SS entrapped in the BES anode chamber under complete anaerobic conditions. Since COD removal is facilitated under complete anaerobic conditions, this BES configuration (here on referred to as a “BES filter”) addresses limitations of rock filters and could become a good alternative technology to replace rock filters.

The oxidation of DOC in a BES anode has been extensively reported in past literature (Hou et al., 2016; Kim et al., 2016; Venkidusamy et al., 2016). However, entrapment and oxidation of SS (specifically algal biomass) on a BES anode is yet to be fully investigated. There are a few studies in literature that have examined the potential use of a BES anode to oxidise algal biomass (Inglesby et al., 2012; Nishio et al., 2013; Strik et al., 2008). The algal feedstocks used in these studies, however, were subjected to a pre-treatment (thermal, physical, chemical and biological) step (Hur et al., 2014; Kondaveeti et al., 2014; Velasquez-Orta et al., 2009; Yong et al., 2015). This pre-treatment step was carried out with an assumption of difficulties to facilitate a hydrolytic, fermentation and/or a direct oxidation of algal biomass in a BES anode. For instance, a pre-treatment of algal biomass using ultrasound (3.5 W mL^{-1} for 20 min) enabled Wang et al. (2012) to achieve a coulombic efficiency (CE) of 25% using a dual chamber BES. Velasquez-Orta et al. (2009) also were able to achieve a similar CE (28%) in a single chamber BES by having a pre-treatment step that involved mechanical breakage of algal cells (drying and grinding). Walter et al. (2015) for the first time reported an attempt to continuously treat algal biomass using a BES and this required a continuous operation of a pre-digester that had a hydraulic retention time (HRT) of 10 days. The pre-digested algal biomass was continuously fed into the BES anode and current densities as high as 9.03 A m^{-3} were achieved. In their studies, the pre-digestion step was found to be critical to achieve higher current densities.

The aim of this study was to evaluate the use of the BES filter to entrap and oxidise untreated algal biomass without reliance on a separate pre-treatment step. This feature may be advantageous in practice as no additional pretreatment unit is required. To mimic algal discharge from a failed WSP, a reactor was operated in a continuous mode to enable an unrestricted supply of algal biomass to BES filters. The performance of the BES filter was assessed under two different settings: (i) close-circuit operation

with current generation; (ii) open-circuit operation without current generation. Over the period of reactor operation, parameters such as current, total COD (TCOD), soluble COD (SCOD), particulate COD (PCOD), SS, volatile fatty acids (VFAs) were determined and coulombic efficiency (CE) of this study was compared with others that used algae as a feedstock in BES.

4.2 Materials and Methods

Figure 4.1 illustrates the experimental setup of this study, which was composed of two reactors: (1) an algal reactor – that facilitated a continuous supply of algae and (2) a BES reactor – which entrapped and oxidised algae discharged from the algal reactor.

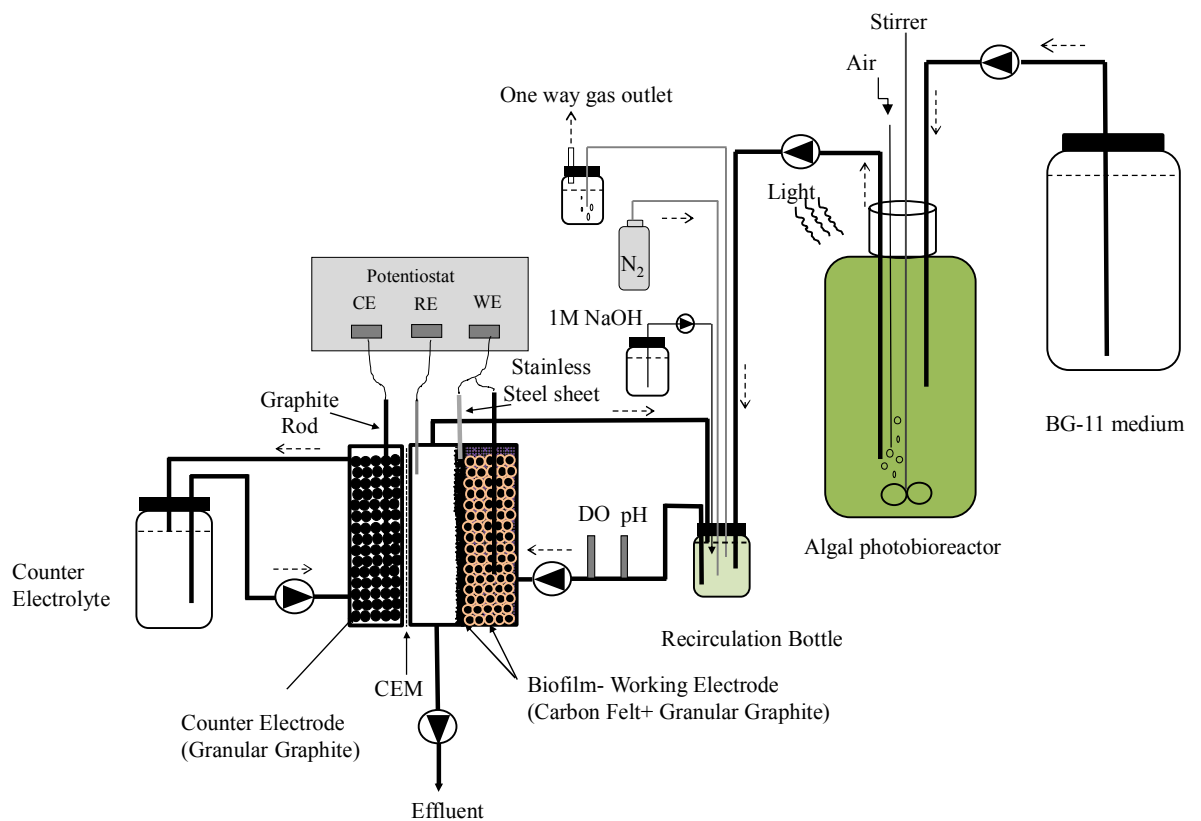


Figure 4.1 Schematic diagram of the BES filter operated in continuous mode. CE= counter electrode; RE= reference electrode; WE= working electrode; CEM= cation exchange membrane; BG-11 medium= algal growth medium.

4.2.1 Algal reactor design and operation

The algal biomass was continuously grown in a photobioreactor having a working volume of 14 L. An algal growth medium (BG-11) was continuously fed into the photobioreactor at a constant flow rate. The total flowrate from photobioreactor into the two BES filters (closed circuit reactor (R1) and open circuit (control) reactor (R2)) matched the influent (BG-11) flowrate into photobioreactor. The BG-11 medium adapted from Rippka et al. (1979) contained (per litre of de-ionized water) 1500 mg NaNO₃, 40 mg K₂HPO₄·3H₂O, 75 mg MgSO₄·7H₂O, 36 mg CaCl₂·2H₂O, 6 mg Citric acid, 6 mg Ferric ammonium citrate, 1 mg disodium magnesium ethylenediaminetetraacetic acid (EDTA), 20 mg Na₂CO₃ and 1 mL of trace element solution prepared as detailed in Cheng et al. (2008). Algal culture was obtained by exposing 5 L of primary effluent (Subiaco wastewater treatment plant, WA, Australia) to natural sunlight for a period of 14 days and 150 mL of the resulting culture was used as the inoculum for the algal bioreactor. The photobioreactor was initially operated in batch mode (with no continuous inflow of BG-11 medium) for a period of 17 days and was subsequently switched over to a continuous mode of operation. Two fluorescent lamps (24W; cool white, Philips), mounted at an approximate angle of 45° were placed 10 cm away from reactor to provide continuous light to the photobioreactor. Mixing was achieved using an overhead stirrer (250 rpm) and continuous aeration was carried out using an aquarium pump (4.2 L h⁻¹). Influent flow rate was set based on the growth rate of algae and the growth rate was determined by quantifying increase of biomass over time. A range of measurements (e.g. SS, TCOD, SCOD and optical density (OD₆₀₀)) were carried out to quantify increase of algal biomass.

4.2.2 The configuration of the BES filters

Two identical Perspex BES reactors were used in this study (Figure 4.1). The anodic chambers of the BES reactors (dual chamber) were further subdivided into two compartments (with each 14 cm × 12 cm × 2 cm in dimension) using two layers of graphite felt (a single layer thickness of ca. 5 mm and surface area of 168 cm², MGM-Carbon Industrial, Ltd Co., China). Close to the top of reactor, a T shaped stainless steel sheet (15 cm²) was firmly sandwiched between the two layers of graphite felt and was used as a current collector.

Algal biomass was fed continuously into the first compartment of the anodic chamber which was packed with graphite granules (3-5 mm in diameter, porosity 48%, KAIYU Industrial (HK) Ltd.). Two graphite rods (5 mm diameter, length 12 cm) were embedded in the granular bed and were also used as current collectors. The other compartment, which was adjacent to the cation exchange membrane (that separated the anodic and the cathodic chamber) was not packed with any media and the effluent port was located in this compartment. The location of the effluent port forced passage of algal media through both graphite granules and the felt that separated the two compartments enabling entrapment of algal biomass in the first compartment of the anodic chamber. The anolyte (algal medium, 480 mL) was continuously re-circulated (150 mL min⁻¹) from the second to the first compartment of the anodic chamber through a recirculation bottle (150 mL) using a peristaltic pump (Cole-Parmer, Victoria, Australia). The re-circulation bottle facilitated pH adjustment (feedback dosing of 1 M NaOH to control pH at 7) and maintenance of anaerobic conditions in anolyte (by sparging head space of the bottle with N₂ gas for 3 min at every 20 min interval). Online monitoring of pH was carried out using pH electrodes (Ionode, QLD, Australia) and pH control and recording of data was carried out with the assistance of a programmable logic controller (Compact-Rio, National Instrument, Austin, TX, USA) and a LabView software (National Instrument, Austin, TX, USA).

A silver-silver chloride (Ag/AgCl) reference electrode (MF-2079, RE-5B, BASi Bioanalytical Systems, Inc., IN, USA) was mounted in the second compartment of the anodic chamber and all electrode potentials (mV) were monitored in reference to the reference electrode (ca. +197 mV vs. standard hydrogen electrode). Of the two BES filters that were operated, one was operated in close circuit mode allowing current to be produced (R1) and the other was operated in open circuit mode with no current production (control, R2). To enable precise control of anodic potentials, minimise cathodic limitations and overcome ohmic limitations of the system, a poised potential of +200 mV was applied to the anode of R1 using a potentiostat (VMP3, BioLogic, Claix, France). The current produced in R1 and the working electrode potential (WE) of R2 was measured using the potentiostat and the programmable logic controller was used to control and record measurements of the potentiostat.

The cathodic chamber of the BES was also packed with graphite granules and two graphite rods (5 mm diameter, length 12 cm) were embedded in the granular bed as

current collectors for the cathode. A phosphate buffer of pH 7.05 (5.356 g L⁻¹ K₂HPO₄, and 2.62 g L⁻¹ KH₂PO₄) was used as catholyte and was continuously recirculated (150 mL min⁻¹) through the cathodic chamber using a peristaltic pump (Cole-Parmer, Victoria, Australia). All reactors were operated at ambient temperature (22-25°C).

4.2.3 Start up and operation of BES filters

The anodic chambers of R1 and R2 were inoculated with 1% (v/v of anodic chamber) of returned activated sludge (RAS, Subiaco wastewater treatment plant, Western Australia). The BES filter operation can be divided into five stages. Initially, the effluent of the photobioreactor was continuously fed into the anodic chambers of R1 and R2. At a flow rate of 0.34 mL min⁻¹ similar to influent reaching compartment 1 of anodic chamber, effluent was discharged from compartment 2 of anodic chamber using peristaltic pumps (Cole-Parmer, Victoria, Australia). This mode of operation continued for a period of 34 days (Stage 1). Both anodic and cathodic chambers of R1 and R2 were covered with black rubber to prevent light-dependent phototrophic activities.

While maintaining continuous mode of operation, on day 35, 1% (v/v of anodic chamber) anaerobic digester sludge (Beenyup wastewater treatment plant, Western Australia) was added into anodic chambers of R1 and R2 to introduce hydrolytic and fermentative bacteria into the system. Subsequently the reactors were closely monitored for a period of 39 days (Stage 2). After 74 days of operation at a poised potential of +200 mV, different anodic poised potentials were applied over a period of 8 days to R1 to examine electrochemical properties of the established biofilm (Stage 3). Stage 2 conditions were thereafter continued for another 22 days. During Stage 4 (starting on day 104), the BES filters were switched to batch mode operation for a period of 40 days (until current of R1 decreased approximately to 0 mA). On day 144 a concentrated volume of algal biomass was injected and reactor performance was monitored in batch mode until the current returned back to the same baseline level (Stage 5).

4.2.4 Assessment of electrochemical properties of R1 (stage 3)

To evaluate anodic activity of the established biofilm in R1, the poised potential was varied. In addition to OCP, potentials of -600, -500, -400, -200, 0 and +200 mV were examined over a period of 8 days (days 74-81). At each applied potential, current was allowed to reach steady state over a period of 24 h (1 HRT) and two anolyte samples were collected prior to change over to the next setting. To minimise possible shifts of anodic microbial community structure and examine the effect of applied potential on the biofilm activity, the duration of exposure to each of the applied potentials was restricted to 1 HRT. TCOD and SCOD were immediately measured on collection of the samples and PCOD was calculated by subtracting SCOD from TCOD. Volatile fatty acids (VFAs) measurements were carried out after filtering the samples through 0.22 μm syringe filters (Merck Millipore, USA). The samples were stored at -20°C until analysed for VFAs. All measured parameters were plotted against the electrode potentials.

4.2.5 Concentration of algal biomass for stage 5 injection

Algal biomass from photobioreactor was collected into Imhoff cones and was allowed to settle for 3 hours. The sediment layers at the bottom of cones were collected and centrifuged ($4000 \times g$ for 30 minutes) and supernatants were discarded. Pelleted algae were resuspended in deionised water and centrifuged once again and the supernatant was discarded. The algal pellet was then re-suspended in 25 mL of algal growth medium. TCOD and SCOD of the concentrated algal biomass were $13,125 \pm 121 \text{ mg L}^{-1}$ and $42 \pm 6.1 \text{ mg L}^{-1}$, respectively.

4.2.6 Analysis and calculations

SCOD and TCOD analyses were performed using HACH reagents (cat no. TNT 821; method 8000, LR) and a spectrophotometer (GENESYS 20, Thermo Scientific). Algal biomass densities were monitored measuring absorbance (A) at 600 nm using the spectrophotometer and normalising the absorbance values to optical density (OD) using optical pass length (L) of 1 cm and equation $\text{OD} = A/L$. Coulombic efficiency (CE) (i.e., the percentage of electrons recovered as anodic current from the PCOD removed) of the anodic reaction was calculated as detailed in literature (Logan et al.,

2006). Particulate matter was quantified by measuring SS. SS was measured as described in standard methods for examination of water and wastewater (APHA, 1992). VFAs were measured by an external laboratory (Department of Agriculture Western Australia, Australia) using a method detailed by Christophersen et al. (2008). In brief a gas chromatograph (GC) fitted with a flame ionization detector (Agilent 6890 series) and capillary column (HP-FFAP, 30 m × 0.53 mm × 1.0 m, Agilent) was used. The operational temperatures of the oven, injection port and the detector were 100°C, 260°C and 265°C, respectively. The data was processed with Chemstation software (Agilent) and the following VFAs were determined: acetic acid, propionic acid, iso-butyric acid, butyric acid, iso-valeric acid, valeric acid and caproic acid. The concentrations of individual VFAs was converted to SCOD. All analytical measurements were carried out in duplicate.

4.3 Results and Discussion

4.3.1 The photobioreactor for a continuous supply of algal biomass

In this study, a photobioreactor was used to provide a continuous supply of algal biomass to the BES filters. As shown in Figure 4.2, a maximum and stable optical density of approximately 0.2 nm cm⁻¹ was achieved after 14 days of process initiation. The OD₆₀₀ changes of the photobioreactor were analogous with PCOD and SS changes. Considering OD₆₀₀ is indicative of algal biomass abundance, the increase of SS and PCOD in this instance can be attributed to an increase of algal biomass in the reactor. The SCOD concentration remained relatively stable throughout the experimental period and hence the increase of TCOD was largely a result of an increase of particulate organic matter, which in this instance was algal biomass. Considering 14 days was required to achieve maximum biomass concentration, the specific growth rate of the algal biomass was estimated to be 0.07 d⁻¹. Based on this specific growth rate, the photobioreactor was operated in a continuous mode with inflow and outflow rates maintained at 0.69 mL min⁻¹ to achieve a HRT of 14 days. This enabled an algal biomass loading of 250 ± 11.3 mg L⁻¹d⁻¹ to each of the BES filters. The SS discharged from a failed WSP is largely in the form of algal biomass and according to Ellis and Mara (1983) the SS concentrations of such a pond could be

up to 200 mg L⁻¹. Accordingly, the photobioreactor of this study resembled a failed WSP.

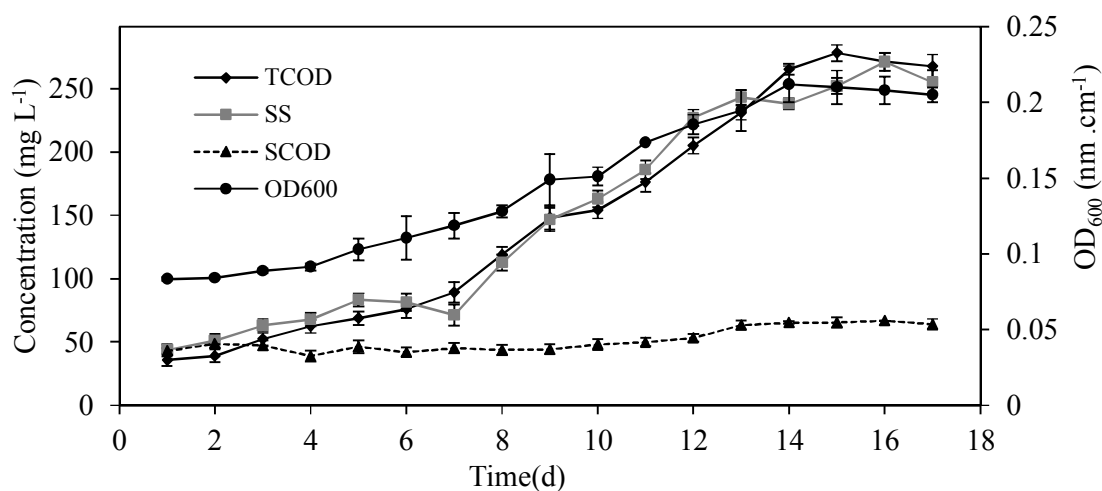


Figure 4.2 Changes in total chemical oxygen demand (TCOD), suspended solids (SS), soluble chemical oxygen demand (SCOD) and optical density measured at 600 nm (OD₆₀₀) of algal biomass in the photobioreactor. (Algal growth rate= 0.07 d⁻¹).

4.3.2 Process start up and initial examination of the BES performance (stage 1)

After inoculating both R1 and R2 BES filters with RAS, the anodic chambers of both reactors were continuously fed with algal biomass from the photobioreactor for a period of 34 days. Each reactor received algal biomass containing influent at a flow rate of 0.34 mL min⁻¹ and this enabled maintenance of a hydraulic retention time (HRT) of 1 day. According to past literature, a duration of 34 days is more than sufficient to enable establishment of an active anodophilic biofilm (Cheng et al., 2012a). During this period there was also an unlimited supply of organic matter for anodic oxidation due to entrapment of SS (> 50% of SS fed were entrapped) in the BES filters (Figure 4.3E). However, R1 only showed a marginal increase of current (<1 mA) and the anodic potentials of R2 also did not show a significant decrease and remained at approximately -70 mV (Figure 4.3B). Walter et al. (2015) also reported a similarly low current (0.03 ± 0.006 mA) with direct input of algal biomass into BES anode. Although algal biomass (approximately 4.2 g loaded over 34 days) is a source of organic matter, it does not appear to be readily oxidisable by the anodic bacteria.

There was no measurable change of SCOD and VFAs in effluent of both R1 and R2 during this period of operation indicating a limited hydrolysis of algal biomass. This suggested a limited abundance of hydrolytic and fermentative bacteria in the inoculum (RAS) used.

When the efficiency of the BES filters to entrap and oxidise algal biomass was quantified, an effective removal of SS was noted in both reactors. The SS removal gradually improved over time from approximately 50% to a maximum of 80% over the period of 34 days. The entrapment of algal biomass in the BES filters may have improved the further retention of algal biomass. However, when CE was calculated based on total amount of coulombs loaded (derived from PCOD removed) and coulombs recovered (as measurable current) only a 4.1% efficiency was noted during the initial 34 days of operation. This further confirmed the limited ability of the anodic biofilm to retrieve electrons from oxidation of retained algal biomass.

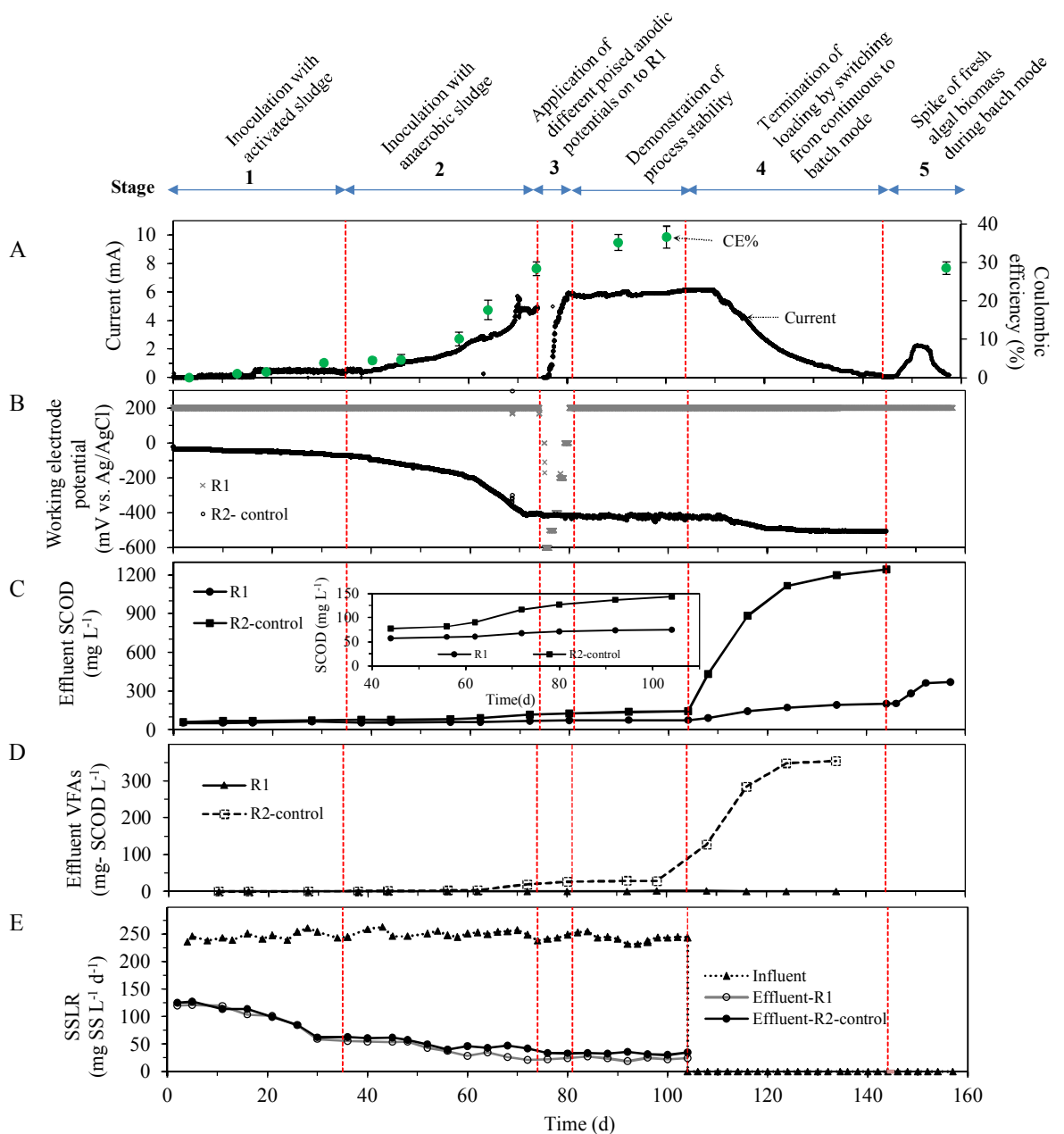


Figure 4.3 (A) Current generation and coulombic efficiency, (B) working electrode potential of R1 and R2, (C) soluble chemical oxygen demand (SCOD) in R1 and R2 effluents, (D) volatile fatty acids (VFAs) in R1 and R2 effluents calculated as SCOD, and (E) suspended solids loading rate (SSLR) and suspended solids removal of R1 and R2 over time. Numbers (1-5) represent different stages of operation used for the BES filters. (R1: close circuit reactor, R2: open circuit reactor- control, CE: coulombic efficiency).

4.3.3 Addition of anaerobic sludge enhanced current generation (stage 2)

With previous data suggesting inability of the resident bacteria in the anodic chamber to facilitate hydrolysis and fermentation of algal biomass, it was decided to re-inoculate both R1 and R2 with some anaerobic digester sludge. The inoculation with digester sludge was to increase the abundance of hydrolytic and fermentative bacteria in the anodic chambers of both R1 and R2 to facilitate the hydrolysis and fermentation steps, which appeared to be limiting the current generation as indicated by the low VFAs concentration in the BES filter effluents (Figure 4.3).

On inoculating with anaerobic biomass on day 35, an increase of anodic current was noted within a very short period of time (<5 days) (Figure 4.3A). The working electrode potential of the open circuit control (R2) also gradually declined from -70 to a steady -420 mV after 35 days of inoculation (Figure 4.3B). These results suggested an increased availability of electron donor for the anodic bacteria and the digester biomass appeared to have contributed towards this increase by releasing the reducing power entrapped in algal biomass. Algal biomass is largely composed of complex proteins, carbohydrates and lipids and past literature demonstrates the importance to hydrolyse these compounds to simple monomers before they could be oxidised by bacteria (Middelboe et al., 1995; Nishio et al., 2013; Vergara-Fernandez et al., 2008). Over a period of 70 days the current increased up to 6.2 ± 0.15 mA with a stable SS loading rate of approximately 250 ± 13.3 mg L⁻¹ d⁻¹.

The increase of current in R1 was expected to coincide with an increase of SCOD in R2 effluent. While no significant increase of SCOD was observed in R1 effluent, a gradual increase of SCOD (from 75.5 ± 6.1 mg L⁻¹ to 144 ± 9.3 mg L⁻¹) was noted in the effluent of R2 during stage 2 of reactor operation (Figure 4.3C). When SCOD of R2 effluent was further analysed for VFAs, VFAs increase from 0.7 ± 0.2 mg - SCOD L⁻¹ to 28.3 ± 3.8 mg - SCOD L⁻¹ was observed during the same period of operation. There were no measurable concentrations of VFAs in R1 BES filter effluent. Compared to R2 control, of the low SCOD in R1 effluent was likely a result of SCOD oxidation in anodic chamber of R1 via current generation pathways.

To infer the prevalence of SCOD removal pathways in R2, a coulombic balance was calculated between R2 and R1. Since the loading of TCOD (algal biomass) in both R1 and R2 were identical, the total coulombs available for both R1 and R2 were also

identical. If one assumed that the lower amount of SCOD in R1 (compared with that in R2) was exclusively caused by current production, then one would expect the coulombic balance between this amount of SCOD (16,960 coulombs) and the current (19,890 coulombs) to be close. However, a noticeable difference of 2,930 coulombs was noted due to a shortfall of coulombs in SCOD of R2. Such a shortfall may be due to unaccountable electron sinks such as methanogenesis in R2. Further studies are required to verify this.

4.3.4 The influence of anodic potential on the performance of BES filter (stage 3)

On inoculation of BES filters with anaerobic biomass the current generation of R1 gradually increased at stage 2. To investigate to what extent anodic current production could influence effluent quality (quantified as TCOD, SCOD, PCOD and VFA), R1 was exposed to different anodic potential set points (OCP, -600, -500, -400, -200, 0 and +200 mV). Figure 4.4A and B detail how effluent quality and current production changed in response to different set points. The increase of anodic potential increased current production (from 0 mA to 5.78 ± 0.14 mA) demonstrating the prevalence of an active anodic biofilm in R1. The current negatively correlated with both SCOD and PCOD concentrations in the R1 effluent. Specifically, an increase of current from 0 to 5.78 ± 0.14 mA resulted in a SCOD and PCOD reduction from 137 ± 3.8 to 78 ± 0.5 mg L⁻¹ and from 10.3 ± 0.3 to 5.2 ± 0.1 mg L⁻¹, respectively (Figure 4.4A and B). While the influence of current on R1 effluent SCOD concentrations was apparent, the influence of current on R1 effluent PCOD concentrations remained unclear. One explanation could be given on the lines of a feedback inhibition of hydrolytic bacteria (Wang et al., 2012). The exposure of anode to unfavourable anodic potentials could potentially have caused feedback inhibition of hydrolytic bacteria due to a build up of SCOD with low current generation, resulting in a higher discharge of PCOD from R1. An accumulation of SCOD in R1 with an application of unfavourable potentials confirms co-existence of hydrolytic and fermentative pathways with current generation pathways. According to Kondaveeti et al. (2014), the hydrolysis of algal biomass produces a range of different compounds and acetate is one of the major end products. In this study under open circuit conditions, acetic and propionic acids were

observed accumulating in R1 at a rate of $28.1 \pm 1.3 \text{ mg-SCOD L}^{-1} \text{ d}^{-1}$ and $5.2 \pm 0.88 \text{ mg-SCOD L}^{-1} \text{ d}^{-1}$, respectively. No other VFAs were observed in noticeable concentrations. When exposed to favourable anodic potentials, VFAs accumulation was almost non-existent in R1 suggesting that these two VFAs (acetate and propionate) in particular may be oxidised anodically via current generation pathways. Being a non-fermentable substrate, the decrease of acetate in particular has to occur via current generation pathway. Further, under open circuit, the SCOD concentration ($137 \pm 3.8 \text{ mg L}^{-1}$) far exceeded the total VFAs concentration ($28.1 \pm 1.3 \text{ mg-SCOD L}^{-1}$) in R1. This confirms the prevalence of other forms of organic carbon as SCOD. When exposed to favourable potentials, the SCOD in R1 decreased from $137 \pm 3.8 \text{ mg L}^{-1}$ to $78 \pm 0.5 \text{ mg L}^{-1}$ (close to the SCOD levels observed in effluent of the photobioreactor).

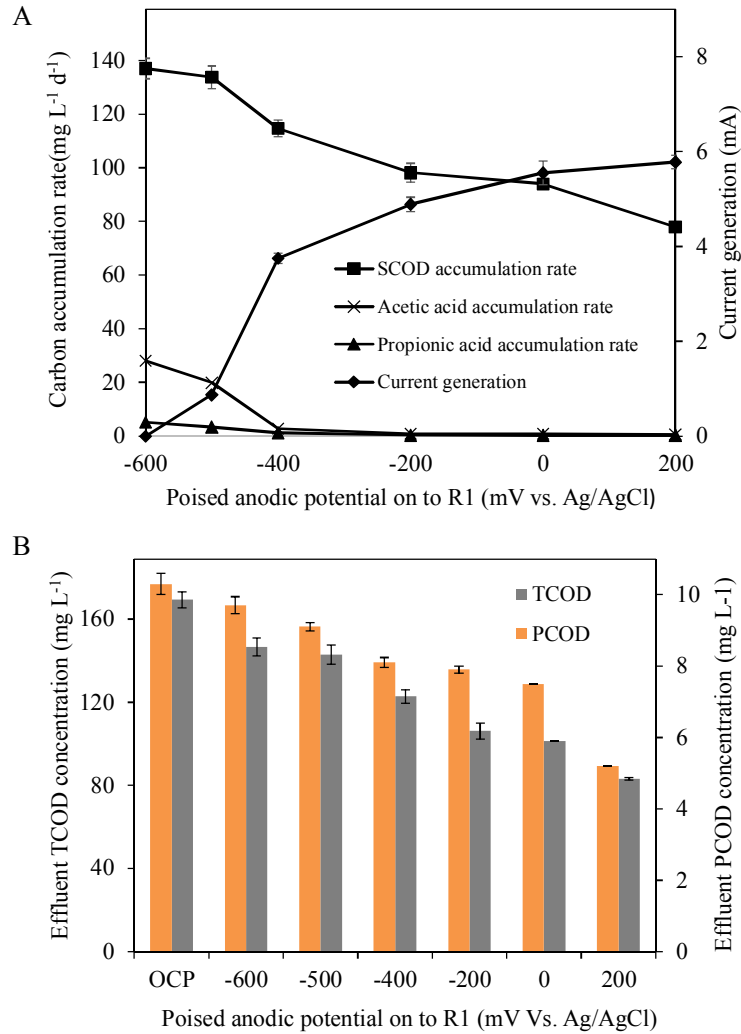


Figure 4.4 (A) Current generation and carbon (soluble chemical oxygen demand (SCOD), acetic acid and propionic acid) accumulation rate at anodic potentials ranging from -600 to +200 mV. The error bars of current profile are indicative of the stable current measured over the latter 5 h of a 24 h exposure to a set potential. (B) Total (TCOD) and particulate (PCOD) chemical oxygen demand (COD) concentrations at open circuit potential (OCP) and anodic potentials ranging from -600 to +200 mV.

4.3.5 The BES filter is a self-cleansing filter (stage 4)

The BES-filter successfully removed up to 92 % of algal biomass (SS removal) that was continuously loaded over a period of 104 days (Figure 4.3E). If the entrapped algae was not continuously removed through some mechanisms, inevitably the filter should have clogged. Even with continuous loading of algae ($250 \pm 13.3 \text{ mg L}^{-1}\text{d}^{-1}$)

for 104 days, the BES-filter showed no signs of clogging suggesting that a self-cleansing mechanism existed in both R1 and R2. A self-cleansing mechanism in this instance refers to mechanisms that involves decomposition of algae into gases (i.e. CO₂ or CH₄) or soluble compounds. To demonstrate the self-cleansing ability of the BES-filters, the feeding of algal biomass into R1 and R2 was discontinued (stage 4 – from day 104 to 143). Thereafter, R1 continued to maintain the current (6.16 ± 0.23 mA) for a period of 4 days. Subsequently over a period of 40 days the current gradually declined to <1 mA (Figure 4.3A). In R2 the anodic potential gradually declined and became more negative (from -430 to -503 mV) (Figure 4.3B).

R2 BES-filter also showed accumulation of SCOD and at the end of 134 days a stable concentration of approximately 1198 ± 64.2 mg L⁻¹ was observed (Figure 4.3D). This corresponded to an average SCOD accumulation rate of 35.1 mg L⁻¹d⁻¹. A similar trend was recorded for VFAs accumulation (10.76 mg-SCOD L⁻¹ d⁻¹). In contrast only a marginal increase of SCOD (from 75 ± 5.8 to 193 ± 12.8 mg L⁻¹; accumulation rate 3.93 mg L⁻¹ d⁻¹) was observed in R1 BES filter. This confirms an efficient removal of SCOD in R1 and it also implies a marginal dilution impact of SCOD with a continuous feed of algal biomass. The dilution impact in R2, however, could have been more profound as a significant increase of SCOD was observed during stage 4 operation. If continuous mode of operation can be assumed to minimise occurrence of a feedback inhibition of hydrolytic pathways (by preventing excessive build up of SCOD), feedback inhibition may be one explanation to the non-linear accumulation of SCOD during stage 4 (no continuous feeding) operation of R2 (Wang et al., 2012). Other contributing factors may be a possible increase of methanogenesis (due to increase of SCOD concentrations) and a gradual exhaustion of substrate (i.e. algal biomass). The build up of SCOD in R2 was likely due to hydrolysis and/or fermentation of the entrapped algal biomass. VFAs, also quantified, is a subset of SCOD, and this fraction only accounted for 30% of the total SCOD. The remaining 70% was likely constituted by chlorophyll, amino acids, sugars, alcohols and other fermentation products (He et al., 2009; Lee et al., 2008; Velasquez-Orta et al., 2009). The low SCOD concentration in R1 suggested that the anodic bacteria were capable of oxidising some of these compounds. Although SCOD concentrations of R1 were low during stage 4 operation, a gradual increase of SCOD was noted possibly due to an accumulation of the non-anodically oxidisable SCOD fraction. In continuous mode of operation the SCOD

released from algae was diluted with new influent, and hence the SCOD concentrations in both the influent and effluent of R1 were only marginally different.

4.3.6 The coulombic efficiency of R1 – a calculation suited for a BES filter

This study for the first time reports of a BES filter designed to trap and anodically oxidise algal biomass without any separate pre-treatment. Unlike in most BES studies reported in past literature the influent COD of this study was primarily in the form of PCOD. Hence, calculation of CEs was carried out based on PCOD (TCOD – SCOD) entrapped (PCODIN – PCODOUT) in the BES filter. To date there are no reports of any BES that has been directly fed with algal biomass as previous studies have used hydrolysed algal biomass. Since no SS was introduced, CEs in these BES were calculated based on SCOD only. SCOD removed (SCODIN – SCODOUT) was considered as the coulombs removed and the current produced was used to calculate coulombs recovered. Accordingly, a comparison of CE of this study with those of others should be done with caution and with an understanding of this difference in the calculation of CEs.

From stage 1 to the beginning of stage 4 (a total of 104 days), the BES filters were operated in continuous mode and the algal biomass loading rate into the BES filters was approximately 250 ± 13.3 mg-SS L⁻¹d⁻¹. Accordingly, each BES filter would have received 12.6 g-SS of algal biomass throughout this period. Of this 12.6 g-SS, the BES filters were able to retain 9.9 g-SS of algal biomass. This 9.9 g-SS algal biomass was equivalent to 8.2 g of PCOD. This approach was taken also to derive algal biomass retention (quantified as PCOD) at regular time intervals and was used to report CEs (calculated based on an average current measured between time intervals) over time (Figure 4.3A). Accordingly, a gradual increase of CE was observed and during steady state of operation, the system achieved a CE of 36.6 %. During stage 4, continuous loading of algal biomass was terminated by switching the system from continuous to batch mode. Interestingly, even without the supply of carbon, the system continued to produce current for a period of 40 d. This suggests an in situ supply of electrons and confirms the prevalence of hydrolytic and fermentative pathways in the anodic chamber of R1.

To further consolidate response of anodic biofilm to algal biomass a concentrated mass (TCOD and SCOD $13,125 \pm 121 \text{ mg L}^{-1}$ and $42 \pm 6.1 \text{ mg L}^{-1}$ respectively) of algae was injected to R1 in stage 5. As can be seen on Figure 4.3A, the current gradually increased from 0 mA to 2.2 mA over a period of 8 days and subsequently declined to previous background levels within the next 7 days (i.e. by day 158). The CE for stage 5 operation was 28.5 %. This further confirms the anodic biofilm's ability to decompose and in situ oxidise algal biomass.

To examine whether CEs calculated using PCOD is a reasonable measure of efficiency of the BES filter, CEs were also derived over time using TCOD measurements. Since SCOD in influent and effluent were quite similar, CEs calculated based on TCOD removal were only marginally different to CEs calculated based on PCOD (data not shown). For example, during steady operation of BES filter a CE of 36.6 % and 35.5 % was observed when PCOD and TCOD were used respectively for CE calculations.

4.3.7 Implication of the findings

This study proposed a new BES configuration that could potentially polish WSP effluent contaminated with high levels (up to 200 mg L^{-1}) of algal biomass. The aim was to propose a technology that would enable overcome limitations of rock filters. Based on the filtration concept of a rock filter, for the first time, Mohammadi Khalfbadam (2016) demonstrated a BES filter configuration that could remove and oxidise particulate and soluble organic matter from municipal wastewater. This study extended the previous findings by demonstrating that algal biomass also could be entrapped (up to 92 %) and decomposed anaerobically via electrochemical pathways in these BES filters. This is the first report of a BES anode that enabled algal biomass decomposition and oxidation. Past researches to date stressed the importance of having a pre-treatment step prior to anodic oxidation of algae. The CE (36 %) of this study was consistent with CEs of BES operated in MFC mode (e.g. a CE of 28 % and 25% by Velasquez-Orta et al. (2009) and Wang et al. (2012) respectively) that used a pre-treatment step to enable solubilisation of algae. However, the BES of this study was operated in microbial electrolysis cell (MEC) mode. If the BES of the above studies were also operated in MEC mode to overcome ohmic resistance and cathodic limitations, it is likely that these studies would likely have achieved higher CEs to that

of what is reported in the present study (Cusick et al., 2010). The findings of this study could have economic (due to the elimination of the pre-treatment step), environmental (elimination of the pre-treatment may reduce footprint) and process implications (a finely tuned symbiotic relationship of hydrolytic, fermentative and anodic bacteria could enhance oxidation of algae) by eliminating the need for a separate pre-treatment process.

4.4 Conclusions:

For the first time a BES filter was demonstrated to replace the need of a pre-treatment step to facilitate anodic oxidation of algae. Showing no signs of clogging, the BES filter was able to entrap 92 % of SS from influent. The results indicate *in situ* hydrolysis, fermentation and anodic oxidation of entrapped algal biomass and a CE of 36.6 % was noted during stable operation of reactor. In addition to VFAs, the anodic biofilm was able to successfully oxidise other organic compounds.

Chapter 5

Sequential solid entrapment and *in situ* electrolytic alkaline hydrolysis facilitated reagent-free bioelectrochemical treatment of particulate-rich municipal wastewater

(This chapter has been submitted for consideration of a provisional patent application)

Chapter Summary

This study proposed and examined a novel process for the treatment of particulate-rich wastewater. A two-stage combined treatment process, consisting of an electrolysis filter and a bioelectrochemical system (BES) configuration was designed and evaluated to remove particulate and soluble organic matter from municipal wastewater. The system was designed such that the electrolysis step was used as a filter enabling physical removal and *in situ* alkaline hydrolysis of the entrapped particulate matter. The alkaline effluent enriched with the hydrolysed soluble compounds (soluble chemical oxygen demand, SCOD) was subsequently loaded into the BES for removal via bio-anodic oxidation. The coupled system was continuously operated with a primary sedimentation tank effluent (suspended solid (SS) ~200 mg/L) for over 160 days, during which SCOD and total COD (TCOD), SS removal and current production were evaluated. With no sign of clogging the process was able to capture near 100% of the SS loaded. A high coulombic efficiency (CE) of 93%, (based on overall TCOD removed) were achieved. Results also suggest that the SCOD-laden alkaline liquor from electrolysis step compensated for the acidification in the bio-anode and the final effluent containing low COD with neutral pH was achieved. Overall, since the system can effectively entrap, *in situ* hydrolyse and oxidise organic matter without external chemical dosing for pH control, it has desirable features for practical application.

5.1 Introduction

Waste stabilisation ponds (WSPs) are commonly used to treat municipal wastewater particularly that of remote communities (Mara et al., 1998). However, maintenance of stable effluent quality of WSPs is often a challenge and additional treatment processes are often required to minimise discharge of suspended solids (SS) (mostly in form of algal biomass) and dissolved organic carbon (DOC) into the environment (Ellis & Mara, 1983; Mara et al., 1992). Rock filters are one of the widely used downstream polish up technologies designed to entrap and oxidise both particulate and DOC discharged from WSPs. They rely on passive diffusion of oxygen from atmosphere to facilitate aerobic biological oxidation of the entrapped organic matter. However, excessive biomass growth and particulate matter accumulation can hinder passive aeration and could result in anaerobic conditions in the filter compromising organic matter removal and hydraulic throughput of the treatment unit. Hence, alternative technologies are desirable for efficient treatment of particulate-rich liquor such as those emanating from failed WSPs.

Recently, there has been effort to develop new technologies to substitute rock filters (Khalfbadam et al., 2016b). Khalfbadam et al. (2016b) proposed a filter-type bioelectrochemical system (BES) termed as “BES filter” to retain and oxidise high particulate matter and soluble chemical oxygen demand (SCOD) effluent. The tubular, dual chamber BES prototype is composed of an outer anodic chamber that encircles an inner cathodic chamber and the two chambers are separated with a cation exchange membrane. The outer anodic chamber was designed as a filtration unit, whereby a carbon felt was installed as both a physical filter and a bioanode to entrap and bio-electrochemically oxidise the suspended organic matter from the wastewater. The study successfully demonstrated the ability of the BES filter to oxidise SCOD in wastewater with a high coulombic efficiency (CE) of >80% (based on the SCOD removed). The study also demonstrated effective removal of organic particulate matter from municipal wastewater (83% of SS removal). However, if the CE calculation was based on the coulombs derived from the entrapped particulates, the CE would be very low (~1%). Such a low CE was most likely due to inefficient microbial hydrolysis of the entrapped particulate matter. Indeed, the system proposed by Khalfbadam et al. (2016b) was suffered from the following limitations: (1) inefficient hydrolysis of entrapped particulate matter; (2) the need for active control of pH both in the cathodic

and anodic chambers of BES; and (3) a huge overpotential for reduction of oxygen at BES cathode. It is imperative to overcome the above limitations should this innovative design be considered as an effluent polish up technology for WSPs.

Generally, hydrolysis is often the rate-limiting step in biological treatment processes for waste streams rich in organic solids. Various pre-treatment methods (physical, chemical, biological, and electrochemical) have been examined to improve hydrolysis of organic particulate matter. For instance, Khalfbadam et al. (2016a) effectively harnessed hydrolytic bacteria in anaerobic sludge to increase *in situ* oxidation of algal biomass in a BES. Chu et al. (2001) found that ultrasound pre-treatment (sonication at 0.33 Watt/mL, 2 h) significantly increased the SCOD content of a waste activated sludge (WAS) (from 42 to 1084 mg SCOD/L). Alternatively, drastically altering the pH of the feedstock by dosing acids or alkali could also enhance hydrolysis of organic particulate matter (Chen et al., 2007; Huang et al., 2016; Yi et al., 2013). However, these methods require either substantial retrofit of infrastructure or usage of chemicals, and hence may not be desirable for practical application. Recently, Charles et al. (2013) investigated the use of a dual chamber electrochemical cell to enhance anaerobic digestibility of a WAS. With an applied voltage of 12 V, the acidic and alkaline conditions created by the electrolytic reactions in the anodic and cathodic chambers remarkably increased the SCOD in the WAS by 31% and 34%, respectively. Since this method could effectively use electrodes to hydrolyse particulate matter without dosing external chemicals, it may be suitable for addressing the abovementioned limitations in the BES-filter process of Khalfbadam et al. (2016a).

In this study, we proposed that by operating the BES-filter as an electrolytic cell, alkaline hydrolysis of the entrapped particulate matter could be driven *in situ* at the electrode (filter). This process would create an effluent with elevated SCOD and alkalinity, which could be a suitable feed stock for a subsequent bioelectrochemical (anodic) treatment. Figure 5.1A depicts the concept of the proposed two-stage process. In the first stage, the particulate-rich wastewater is fed to the module, whereby the filter-electrode physically removes (filtering) the particulate organic matter from the wastewater. The filter-electrode loaded with particulate matter is then cathodically-driven to create a localised alkaline condition (≥ 12), facilitating *in situ* alkaline hydrolysis of the entrapped particulate matter. The elevated SCOD and alkalinity are expected to facilitate current production and help neutralise the acidity liberated from

the anodic oxidation reaction at the subsequent stage. Overall, the sequential process is expected to yield a better quality final effluent with a much higher total COD removal efficiency.

The aim of this study was to validate the proposed combination of electrolysis and anodic oxidation for effective removal of particulate and soluble organic matter from municipal particulate-rich wastewater. Specifically, the following hypotheses were tested:

- (1) The increased cathodic pH created by the electrolysis step (first stage) can trigger alkaline hydrolysis of the particulate matter entrapped at the filter-electrode;
- (2) The alkaline effluent with elevated SCOD content can be harnessed as a more suitable feedstock for the subsequent anodic carbon oxidation step, negating the need of dosing external chemicals (e.g. NaOH) for pH control;
- (3) The acidity generated at the anodic reaction (captured in the counter electrolyte) of the first stage can be used to facilitate the cathodic reaction of the second stage, alleviating the overall reliance on external chemicals for pH control.

The coupled process was operated in a continuous mode with different hydraulic loadings of municipal primary sedimentation tank (PST) effluent for over 150 days, during which the performance of the system was quantified for a range of parameters such as total COD (TCOD), soluble COD (SCOD), particulate COD (PCOD) and SS removals; electrical current, coulombic efficiencies and energy consumption.

5.2 Materials and Methods

5.2.1 Configuration of the two-stage reactor process

Figure 5.1 illustrates the experimental process used in this study. The process consisted of two identical, hydraulically connected dual-compartment electrochemical reactors (Figure 5.1). The first reactor (R1) was operated as an electrolytic cell facilitating both entrapment and *in situ* alkaline hydrolysis of the entrapped particulate solids; the second reactor (R2) was operated as a typical BES for bioanodic oxidation of soluble organic matter. Specific configurational details of the reactor and the electrode materials have been described in Khalfbadam et al. (2016b). In brief, each

reactor had a height of 1.5 m (internal diameter 0.1 m) and consisted of two concentric cylindrical stainless steel mesh columns, one with a diameter of 6 cm and the other one with a diameter of 4 cm. The two columns were served as both electrical current collector and physical support for the anode and the cathode, respectively. The two compartments were isolated by a cation exchange membrane (Ultrex CMI 7000, Membrane International Inc.), which was firmly mounted onto the outer side of the inner stainless steel mesh column and was sealed with epoxy glue to create a water-tight compartment within the module. Carbon felts (MGM-Carbon Industrial, Ltd. Co., China) were used as both the anodic and cathodic electrode materials. The anodic surface area was 0.33 m². The carbon felts were mounted onto the stainless steel current collectors inside the reactors. A short distance (approximately 2 cm) was maintained between the anode and the cathode, creating a void volume where the wastewater influent was introduced at the bottom end of the unit. Since the inner column was completely enclosed, the influent wastewater was compelled to channel through the carbon felt facilitating physical removal of SS from the wastewater (Figure 5.1C). In this study, it was proposed that the particulate-rich wastewater was first processed in R1 for particulate matter removal and electrolytic alkaline-hydrolysis of the entrapped particulate; the alkaline effluent created by R1 was further processed in R2 for bioelectrochemical treatment before the treated effluent was finally discharged (Figure 5.1C).

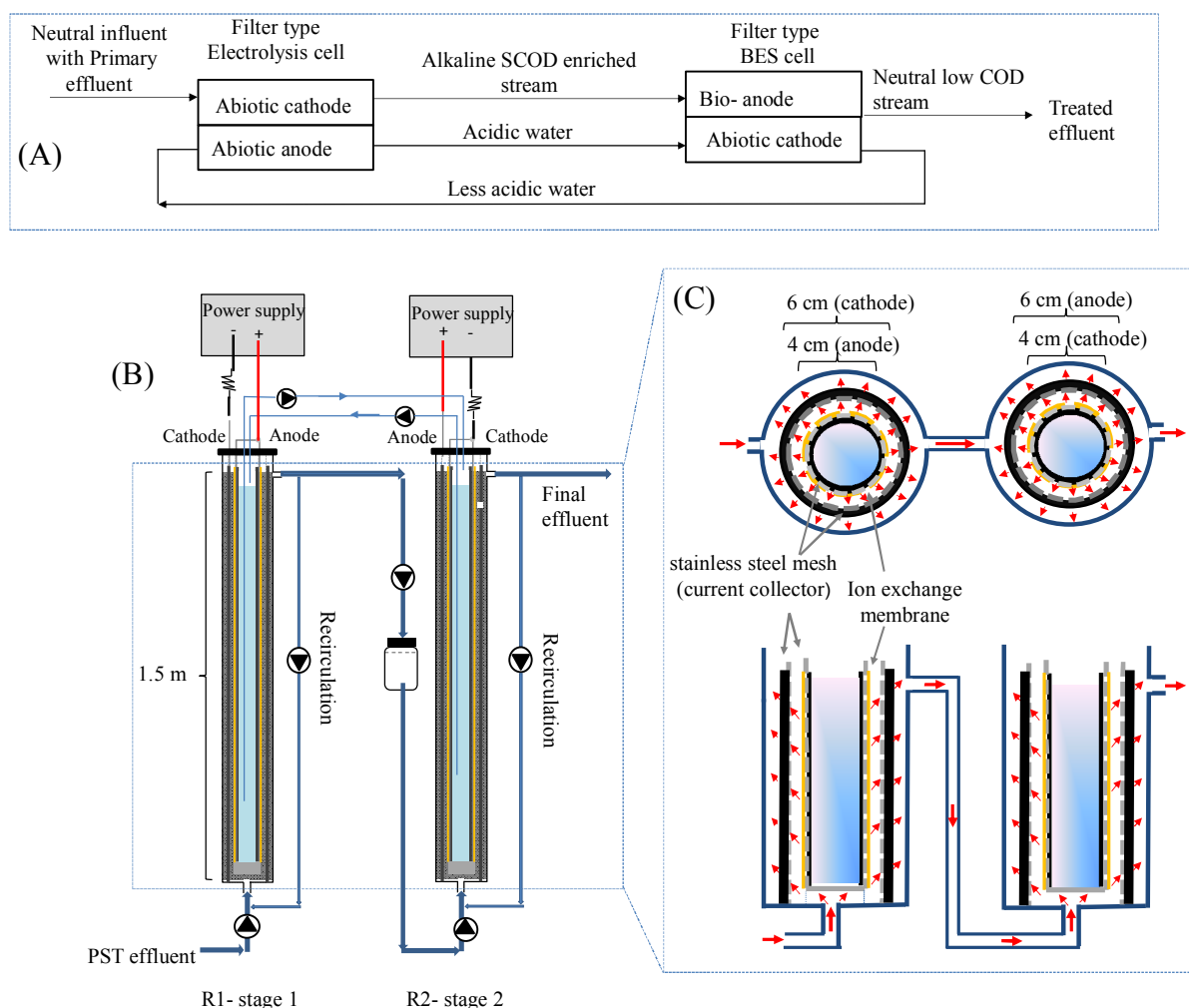


Figure 5.1 (A, B) Schematic diagram of the two- stage sequential solid entrapment and *in situ* electrolytic alkaline hydrolysis particulate-rich wastewater treatment process; (C) cross and top sections of the two stages (red arrows show wastewater flow path).

5.2.2 General operation of the process

To mimic effluent of failed WSPs, primary sedimentation tank (PST) effluent (200 mg-SCOD/L, 150 mg-SS/L) of a local municipal wastewater treatment plant was used. The effluent was collected weekly and stored in a fridge (4°C) to minimise compositional changes. The wastewater was continuously fed to the bottom of R1 at a defined flow rate (first stage). The effluent of R1 was withdrawn from a port located near the top of the reactor through a peristaltic pump and introduced to the bottom of

R2 (second stage). The final effluent was discharged from the outer (anodic) chamber of R2 by hydraulic pressure via an effluent port located near the top of the reactor. The wastewater in the outer chambers of both reactors was continuously recirculated (38 L/h). Two peristaltic pumps (Cole-Parmer, Victoria, Australia) operated at a same flow rate (17 ml/min) were used to mix the two counter electrolytes (in the inner chambers) between the two reactors, with one pump transferring the electrolyte from R1 to R2, and the other one returning the electrolyte from R2 to R1. This step was to facilitate the use of the acidity created by the anodic reaction of R1 for neutralising the alkalinity created by the cathodic reaction of R2.

Two adjustable digital power supplies (Array 3645 A; Array Electronics, Australia) were used to separately apply electrical voltage to both reactors. The positive and negative poles of the power supplies were connected to the anode and cathode, respectively (Figure 5.1B). To enable measurement of electrical current in both reactors, an external resistor (1 ohm) was connected between the cathode of both reactors and their respective negative terminals of the power supply. Electrical current was determined from the voltage measured across the resistor according to Ohm's Law. A silver-silver chloride (Ag/AgCl) reference electrode (MF-2079, RE-5B, BASi Bioanalytical Systems, Inc., USA) was mounted in the anodic chamber of R2 to enable measurement of the anodic potential of the BES. All electrode potentials (mV) reported in this study refer to values against Ag/AgCl reference electrode (ca. +197 mV vs. standard hydrogen electrode). The process was operated at ambient pressure and temperature (22-25°C).

5.2.3 Determination of the optimal pH for enhancing particulate matter hydrolysis (serum bottle experiment)

A separate experiment was first conducted to determine the susceptibility of the particulate matter in the PST effluent for acid/alkaline hydrolysis, and to define the optimal pH for enhancing the SCOD content in the PST effluent. Freshly collected PST effluent was loaded into four 1-L Imhoff cones and was allowed to settle for one hour. Thereafter, two distinct sediment layers were visualised at the bottom of each cone. The lower layers, which contained mostly inert sand-like particles were carefully discarded through the decant port of each Imhoff cone. The upper layers were carefully

collected and pooled together for experimentation. The TCOD and SCOD contents of the composite particulate matter sample were 5361 mg/L and 251.3 mg/L, respectively. Hence, the SCOD/TCOD ratio was 4.7%.

To evaluate the impact of acidic and alkaline pH on solubilisation of particulate matter, the composite particulate matter sample (630 mL) was equally divided into seven serum bottles (90 ml each). The initial pH value in bottles 1–6 was adjusted to 2, 5, 7, 8, 10 and 12, respectively, by adding sodium hydroxide (1M NaOH) or hydrochloric acid (1M HCl). The bottle 7, in which the pH was not adjusted, was used as the control (pH = 7.05). The bottles were incubated on an orbital shaker (room temperature, 225 rpm) for 24 h. Samples were taken from each bottle at 0, 3, 7 and 24 h over a 24 h period for SCOD analysis. Percent solubilisation of particulate was calculated for each setting according to: $(\text{SCOD measured} - 251.3 \text{ mg/L}) / 5361 \text{ mg/L} \times 100\%$.

5.2.4 Impact of applied voltage on solubilisation of entrapped particulate matter in R1

The impact of various applied voltages (0, 3, 6 and 10 V) on the hydrolysis of entrapped particulate matter in the filter type electrolysis unit (R1) was evaluated before connecting both R1 and R2 as a coupled process. This experiment was to determine the most suitable applied voltage for driving the alkaline hydrolysis of the entrapped particulate matter in R1. Fresh PST effluent was continuously loaded into R1 at a hydraulic retention time (HRT) of 32 h (flow rate of 5.02 mL/min) over a period of 14 days. After each voltage and prior to the next setting, the applied voltage was set to zero and the HRT was reduced to 6 h for a period of at least 24 h, to ensure the electrode-filter was recharged with sufficient organic particulate matter prior to the next applied voltage setting. Current, working electrolyte pH and effluent SCOD for various settings were monitored and compared.

5.2.5 Influence of applied voltage on the performance of R2

Prior to this study, R2 was started up and had been operated for approximately two years in microbial fuel cell (MFC)-mode as reported in Khalfbadam et al. (2016b). It was identified that the current production and SCOD removal efficiency were largely

limited by the poor cathodic reaction (Khalfbadam et al. 2016b). Hence, in this study R2 was coupled with an external power supply to overcome such limitation. This mode of operation (i.e. as a microbial electrolysis cell (MEC)) was evaluated before connecting both R1 and R2 as a coupled process. The effects of various applied voltages (0, 150, 250, 400, 600 and 800 mV) on R2 were evaluated over a period of 60 hours. Current production, electrode potentials, electrolyte pH and anodic SCOD removal rate were recorded. In order to ensure the supply of COD was not limiting, the R2 was continuously fed with fresh municipal PST effluent at a HRT of 6 hours, corresponding to a flow rate of 26.8 ml/min. To eliminate the impact of pH changes, both the anolyte and catholyte were maintained at pH 7 by feedback-dosing NaOH (4M) and HCl (1M), respectively. Similar to the previous study, the counter electrolyte of R2 was aerated to ensure that the cathodic reaction was not limited by dissolved oxygen.

5.2.6 Evaluation of the effect of hydraulic retention time (HRT) and applied voltage on the performance of the sequential process

After separately testing the R1 for alkaline hydrolysis of the entrapped particulate matter and R2 for bioanodic oxidation of SCOD, the performance of the coupled process was assessed. As described above, the two reactor modules were hydraulically connected (Figure 5.1). Applied voltages (setting 1: 6 and 0.5 V for R1 and R2, respectively (6V/0.5V); setting 2: 10 and 0.6 V for R1 and R2, respectively (10V/0.6V)) and HRT (6, 12, 18, 24 and 32 h) were selected as the process variables. The coupled process was evaluated in continuous mode over a period of 150 days. Freshly collected PST effluent was loaded into R1 at different flow rates (26.8, 13.4, 8.9, 6.7 and 5 ml/min) to achieve the respective HRTs of 6, 12, 18, 24, 32 h in R1. The final effluent was discharged from R2 at the same flow rate and hence both R1 and R2 were operated at identical HRT. Each set of applied voltage and HRT was maintained for 15 days to ensure steady-state operation. Process parameters such as TCOD removal, SCOD removal, working electrolyte pH, current production and CE were quantified for each stage and were compared amongst various settings.

5.2.7 Effect of spiking algal biomass to the influent of R1 on current production in R2

The effectiveness of using the coupled process to entrap and hydrolyse algal biomass for current production was evaluated in a separated experiment. The concentrated algal biomass was prepared from a synthetic algal medium as described in Khalfbadam et al. (2016a). The algal biomass containing medium was loaded into Imhoff cones, and the biomass was allowed to settle for 3 hours before collection. The collected sediments were centrifuged ($4000 \times g$ for 30 minutes) and the supernatants were discarded. The pelleted algal solids were resuspended in deionised water, centrifuged again and the supernatant was discarded. This step was to remove SCOD. The pelleted algae was finally resuspended in a medium (300 mL). The TCOD and SCOD concentrations of this algae-containing medium were 8981 mg/l and 51 mg/l, respectively. Prior to the spiking test, the coupled process was steadily operated with municipal PST effluent for at least one week (HRT 32 h). When the current of R2 was stable, the pre-concentrated algae-containing medium was injected to the influent line of R1. The same procedure was repeated when the current of R2 had returned to the baseline level for >1 HRT. Coulombic efficiencies (CE) were determined using the current induced by the spikes and the TCOD content of the spikes.

5.2.8 Analyses and calculations

The voltage (i.e. the potential differences between the anode and the cathode) (V) was measured using a digital multimeter placed across the external resistor and the anodic and cathodic potentials were measured against respective reference electrodes (Ag/AgCl). pH was monitored using a portable pH meter (TPS, Australia). The current (I , mA) of R1 was determined from the cell voltage according to Ohm's Law, $I = \frac{V}{R}$, where V (mV) is the measured cell voltage across an external resistor R (Ω). Power (P , μ W) was calculated according to equation $P = V \times I$. It was used to calculate electrical energy consumption of R1 and R2 over a specified period of time (h). SCOD and TCOD analyses were performed using HACH reagents (cat no. TNT 821; method 8000, LR) and a spectrophotometer (GENESYS 20, Thermo Scientific). CE (i.e., the percentage of electrons recovered as anodic current from the TCOD removed) of the anodic reaction was calculated as detailed in literature (Logan et al., 2006). Particulate

matter was quantified by measuring SS. SS was measured as described in standard methods for examination of water and wastewater (APHA, 1992). All analytical measurements were carried out in duplicate.

5.3 Results and discussion

5.3.1 Increasing pH to 12 enabled efficient hydrolysis of PST effluent particulate

A comparative study was conducted to examine the effect of pH (2 to 12) on the hydrolysis of PST particulate matter. Figure 5.2 shows how SCOD concentration and percent solubilisation of particulate matter changed as a function of pH. Clearly, both acidification (pHs 2 and 5) and basification (pHs 10 and 12) could increase SCOD concentration and solubilisation of the PST particulate matter. However, compared with other pHs, pH 12 enabled the highest solubilisation of the particulate matter (13%) (Figure 5.2B). Also, at pH 12 the SCOD concentration was significantly increased by 4-fold within a short time (from 235.2 to 948 mg/L in 3 hours) (Figure 5.2A). The slight decreases in SCOD recorded near circum-neutral conditions (pH 7, 8 and control) could be a result of microbial degradation of soluble organic matter. Overall, the result confirmed that pH 12 was the most effective condition to facilitate hydrolysis of the PST particulate matter.

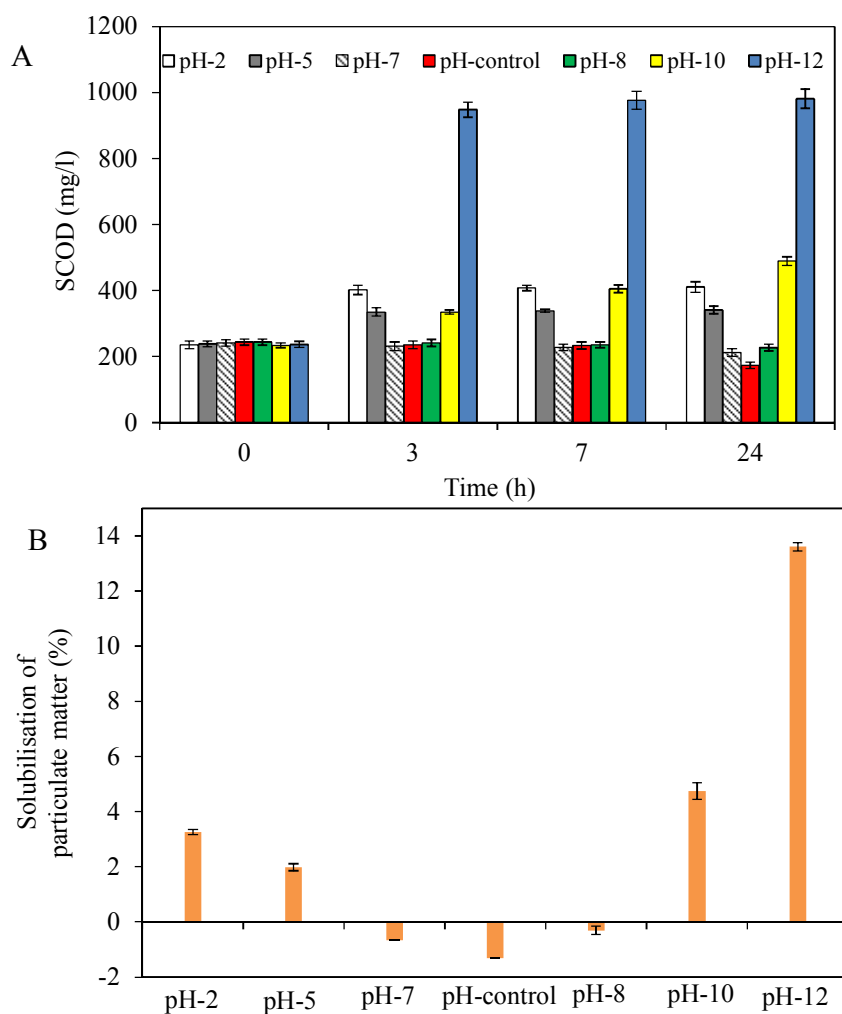


Figure 5.2 Changes in (A) SCOD concentration over time and (B) solubilisation of organic particulate matter at different pHs.

5.3.2 Cathodic-driven alkaline hydrolysis of entrapped particulate matter in R1

With previous experiment confirming the effect of alkaline pre-treatment for improving hydrolysis of the PST particulate matter, it was decided to couple the R1 with an external power supply to approach the desired alkaline condition. To determine how much applied voltage was needed, the changes in SCOD, pH of working electrode and current production in R1 with different applied voltages (0, 3, 6 and 10 V) were quantified (Figure 5.3).

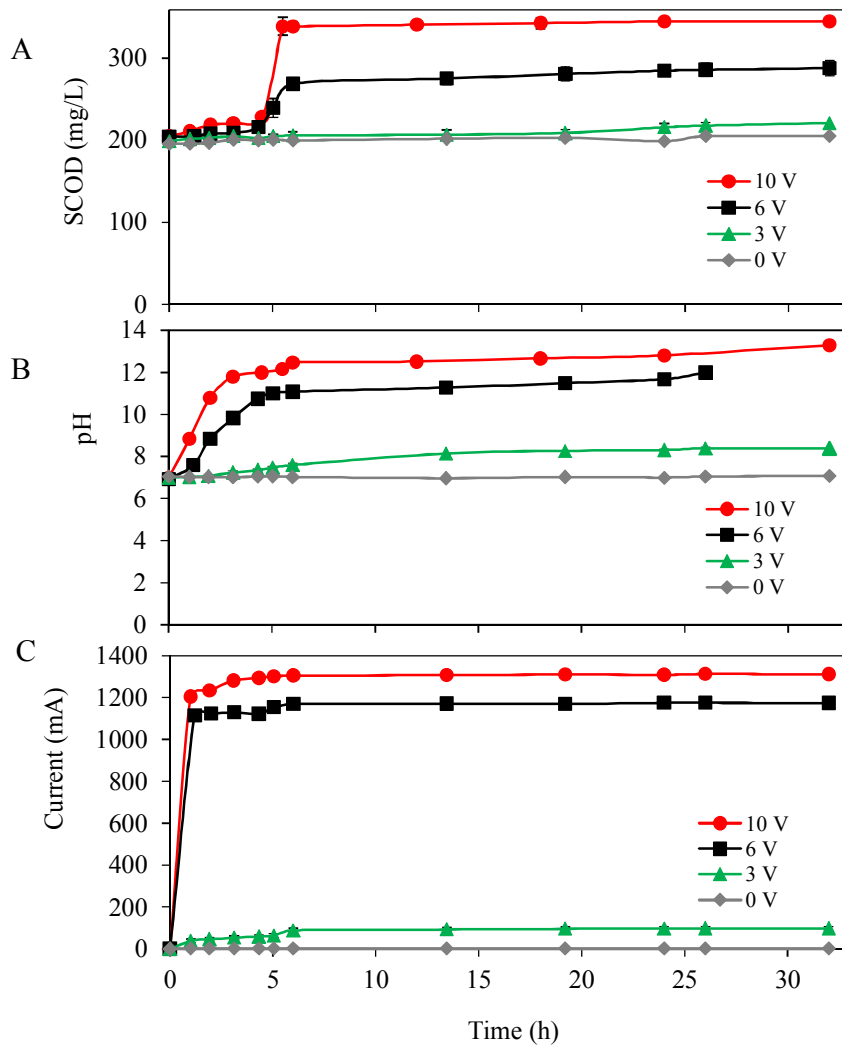


Figure 5.3 Effect of applied voltage on (A) SCOD content (B) working electrolyte pH and (C) current production of the filter type electrolysis unit (R1).

Although applying 3 V increased the current of R1 from 0 mA to 98 mA, no remarkable change in both working electrolyte pH and SCOD were recorded compared to the control (no applied voltage) (Figure 5.3A, C). In contrast, doubling the applied voltage to 6 V remarkably increased the pH from 6.94 to 11.0 within 5.5 h (Figure 5.3B). This also coincided with an increase in current (from 0 to 1154 mA) and SCOD (from 196 to 271 mg/L). Further increasing the applied voltage to 10 V resulted in a more rapid basification of the catholyte (from 7.0 to 12 within 4.5 h), and more profound increases in both current (from 0 to 1294 mA) and SCOD concentration (from 205 to 335 mg/L) (Figure 5.3).

Since applying 6 and 10 V enabled the SCOD concentration in R1 to approach plateau within ≤ 6 h (Figure 5.3A), it would be sufficient to operate R1 with the applied voltage for a shorter time frame. Overall, the results confirmed that the alkaline condition ($\text{pH} > 11$) could facilitate hydrolysis of the entrapped particulate organics. Such condition could be created by driving the electrode-filter of R1 as a cathode with an external voltage of $\geq 6\text{V}$.

5.3.3 Augmenting R2 with an applied voltage to enhance SCOD removal rate

It was previously shown that COD removal by R2 was limited by the poor cathodic oxygen reduction (Khalfbadam et al. 2016b). One way to overcome this constrain was to switch the operation into MEC mode, whereby external voltage is applied to increase reaction kinetics at the bioanode (Cheng et al., 2012b). Hence, before connected with R1, R2 was examined with different applied voltages (0, 150, 250, 400, 600 and 800 mV) and the corresponding effects on anodic potential and COD removal were quantified (Figure S5.1; Appendix 2). The results indicated that addition of voltages (up to 400 mV) effectively increased the anodic potential (from -570 mV to -430 mV), which favoured a higher biogenic electrical current (from 100 to 310 mA) (Figure S5.1A and B; Appendix 2). Such improvement also coincided with a notable rise (>3 fold) in SCOD removal rate. With an applied voltage of 400 mV, the SCOD removal rate increased from 0.08 to 0.25 $\text{kg/m}^3\cdot\text{d}$ (HRT 6 h) (Figure S5.1D; Appendix 2).

This experiment confirmed that the activity of the established anodic biofilm in R2 was largely hindered by the cathodic reaction, and that by augmenting with electrical voltages, SCOD removal could be markedly improved. Nonetheless, it must be mentioned that in this experiment the process was operated with active pH corrections (i.e. dosing of NaOH), which should ideally be omitted for practical application.

5.3.4 Characterisation of the sequential process and influence of hydraulic retention time and applied voltage

The above experiments showed that R1 and R2 could effectively facilitate *in situ* alkaline hydrolysis of the entrapped particulate matter and bioanodic oxidation of

SCOD, respectively. Hence, a subsequent experiment was conducted with the two modules connected hydraulically as a sequential process (see Figure 5.1). The process was operated in continuous mode for a long period (150 days) with various HRTs (6, 12, 18, 24 and 32h) and applied voltages (6V/0.5V; 10V/0.6V). Key process variables were quantified (Figure 5.4).

5.3.4.1 The sequential process could enable an excellent SS removal, and R1 (stage 1) was responsible for the majority (>60%) of removal

The results again confirmed that the “electrolytic electrode-filter” of R1 could effectively remove SS (Figure 5.4D). For both applied voltage settings tested, increasing the HRT of R1 (from 6 to 32 h) also improved SS removal (from 62% to 96%) in R1 (data not shown). Extending the HRTs beyond 6 h may have offered an extra SS retention (e.g. settling) leading to the improved SS removal recorded (Figure 5.4D, at days 15 and 90). As expected, further SS removal was attained by R2, resulting in a near complete overall SS removal (>99%) (Figure 5.4D). Similar trends for SS removal efficiencies were recorded with the higher applied voltage setting (10V/0.6V, days 75 to 150). These results suggested that the sequential process could enable an excellent SS removal, and R1 (stage 1) was responsible for the majority (>60%) of removal.

5.3.4.2 Current, COD removal and pH

In general, increasing the HRT did not notably affect the current and SCOD augmentation in R1, as only slight decreases in current and slight increases in SCOD were recorded (Figure 5.4A and E). The result also corroborates with the previous conclusion (in Section 5.3.2) that the two voltages tested (6 and 10V) were suitable to allow efficient cathode-driven alkaline hydrolysis, and that a short HRT of 6 h was adequate for R1 to attain good efficacies. Clearly, at all tested settings, R1 could create the desirable alkaline conditions (pH 11.9-13.8) for *in situ* hydrolysis of the entrapped SS, resulted in a higher SCOD in the R1 effluent (Figure 5.4C, E). Also, with a higher applied voltage (10 vs. 6V), both the R1 current and SCOD concentrations in R1 effluent were generally higher (20%) (Figure 5.4A, E). This further highlights the

functional feature of R1 as an electrolytic-filter for particulate organics removal and hydrolysis.

In contrast, the current of the subsequent stage (R2) decreased with increasing HRT, indicating that the bioanode activity of R2 was likely limited by the SCOD from R1 (Figure 5.4A). Yet, in terms of overall COD removal (both SCOD and TCOD), operating the process at higher HRT appeared to be essential, as only by extending the HRT to 32 h the overall removal of SCOD and TCOD could reach >80% (Figure 5.4E, F). When R1 was applied with 6 V and 10 V, increasing the HRTs (from 6 to 32 h) decreased the current of R2 from 390 mA to 235 mA and from 430 mA to 258 mA, respectively (Figure 5.4A). These trends coincided with an increase in CE from 38.8 % to 93.3 % (with applied voltage of 6 V/0.5V) and from 44.6 to 84.8 % (with applied voltage of 10 V/0.6 V) (Figure 5.4B). For both voltages, the highest CEs were achieved with the longest HRT (32 h), suggesting that operating the process at higher HRTs is also favourable to obtain higher CEs.

Although current production is a proton producing reaction, it did not result in acidification at the bio-anode due to accumulation of protons released from microbial oxidation of organic matter. However, the pH of working electrolyte was gradually decreased from 11.3- 13.3 to 6.87- 7.33 (Figure 5.4C). The results suggest that even without external chemical dosing for pH control, the detrimental impact of acidification of anodic oxidation process was not encountered and neutral pHs were observed at R2 effluent.

The regular electrolyte renewals did not retard the rapid acidification of the R1 counter electrolyte, as a sharp decrease in pH (pH ~2) was recorded immediately (<2 h) (Figure 5.4C). Circulation of both counter electrolytes in a close loop enabled the neutralisation of hydroxyl ions in counter electrolyte of R2. Since the current of R1 was much faster (~4x) than that of R2 (Figure 5.4A), the rate of acidification in R1 counter electrolyte was much faster than alkalisation of R2 counter electrolyte. Hence, throughout the operation both counter electrolytes remained acidic (pH 2-3) (Figure 5.4C). In Chapter 3, it was demonstrated that the performance of the BES-filter could be improved when the catholyte was actively maintained (by adding HCl) in acidic conditions (Khalfbadam et al. (2016b)). In this study, the acidity generated in the electrolysis step (stage 1) could be effectively harnessed to facilitate the cathodic

reaction in the BES (stage 2) without the need of dosing HCl. Considering also the fact that no external chemicals are needed for sustaining the bioanode activity, the proposed sequential process is suitable for practical application.

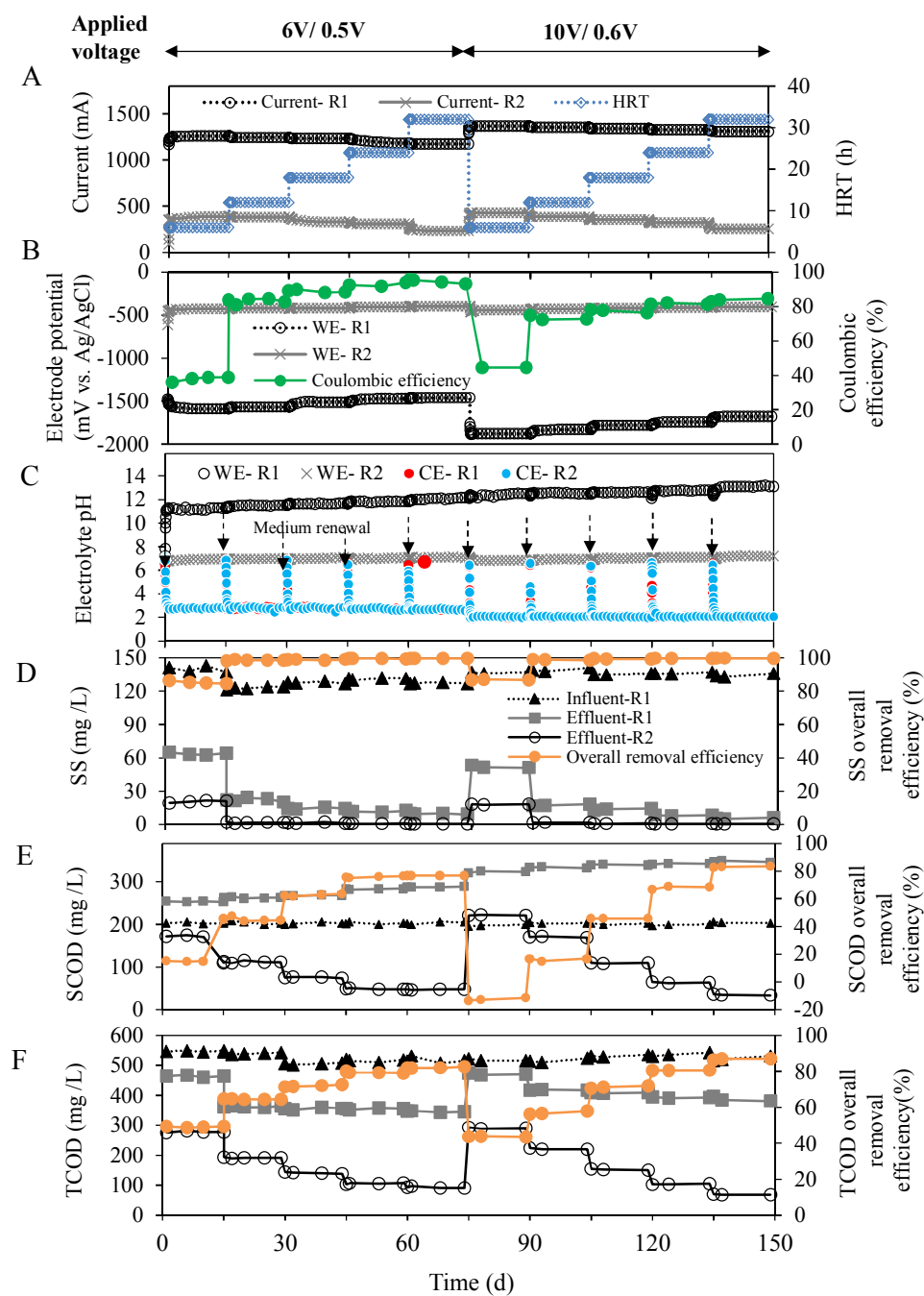


Figure 5.4 Effect of HRT and applied voltage on (A) current production of R1 and R2; (B) working electrode potential of R1 and R2 and coulombic efficiency of R2; (C) working and counter electrolytes pH of R1 and R2; (D, E, F) suspended solids (SS), soluble chemical oxygen demand (SCOD) and total chemical oxygen demand (TCOD) concentrations of R1 and R2, and overall removal efficiency of the whole process. (WE: working electrolyte; CE=counter electrolyte; R1: electrolysis filter, R2: BES filter).

5.3.5 The sequential process could effectively hydrolyse algal cells for more efficient bio-anodic oxidation

To test if the sequential process could readily treat fresh intact algal biomass for current generation, a spiking experiment was carried out (Figure 5.5). The experiment was started by first operating the process with municipal wastewater in a continuous mode with HRT of 32 h. After approximately 7 days, the current of R2 became stable at around 260 mA (Figure 5.5A). At this point, an algal biomass aliquot was added to the influent stream of R1, and within 3.5 h the current of R2 increased and continued to rise reaching a maximum of 420 mA after 16 h. Subsequently, the current returned gradually to the initial background level. Similar trends was recorded when the experiment was repeated with the same amount of algal injection (Figure 5.5A). The two current peaks also coincided with slight decreases in the working electrolyte pH of R2 (from 7.6 to 6.4), which were probably caused by the additional protons released from the faster anodic reaction (Figure 5.5B). The two algae-induced current peaks corresponded to an average CE of 41%.

Overall, the results suggested that the sequential process could effectively hydrolyse fresh algal cells for bio-anodic oxidation (removal). Future studies are necessary to further develop the process for algae-laden streams treatment.

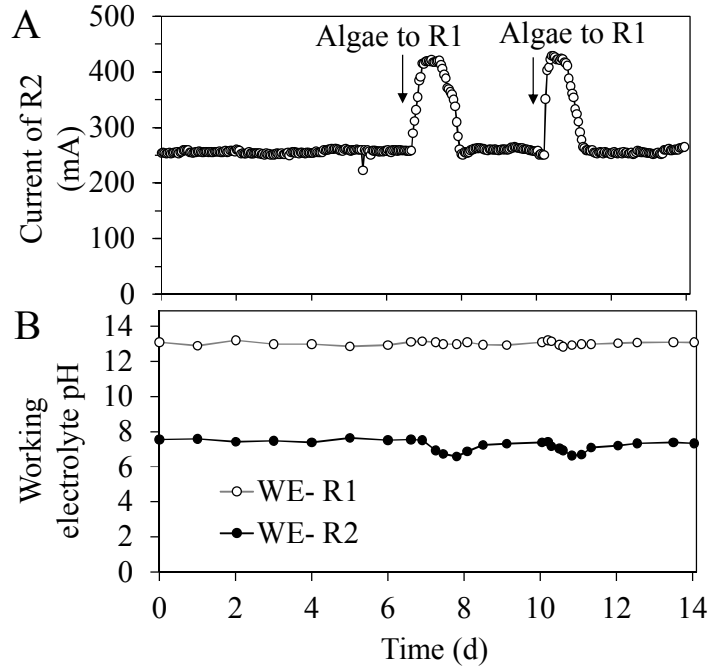


Figure 5.5 Current generation in R2 induced by the addition of algal biomass at R1. The vertical arrows indicate addition of the algal biomass. (HRT= 32 h, applied voltages= 10 V for R1 and 0.6 V for R2).

5.3.6 Energetic consideration for the sequential treatment process

In this study, electrical energy was consumed to facilitate alkaline hydrolysis (stage 1) and bioanodic oxidation (stage 2). Figure 5.6 and Table S5.1 summarise the treatment and energetic performance of the sequential process. In general, the energy consumptions in both stages were dependent on both HRT and applied voltage. Also, as expected, R1 consumed significantly (two orders of magnitude) more energy than R2 (Figure 5.6A, B). For stage 1 electrolytic hydrolysis (R1), increasing the HRT from 6 to 32 h increased the energy consumption from 92.1 to 274.7 kWh/kg SCOD_{increased} and 67.5 to 303.7 kWh/kg SCOD_{increased} with applied voltage of 6 and 10 V, respectively (Figure 5.6). Noteworthy, these values are lower than that reported for alternative particulate matter hydrolysis pre-treatments. For instance, an approximately two-fold higher energy consumption of 633 kWh/kg SCOD_{increased} was reported by Chu et al. (2001), who used ultrasound as a pre-treatment method to enhance SCOD in WAS (from 42 mg/L to 1084 mg/L). Hence, operating the electrode-

filter to achieve *in situ* alkaline hydrolysis of particulate can be considered realistic in terms of energy requirement.

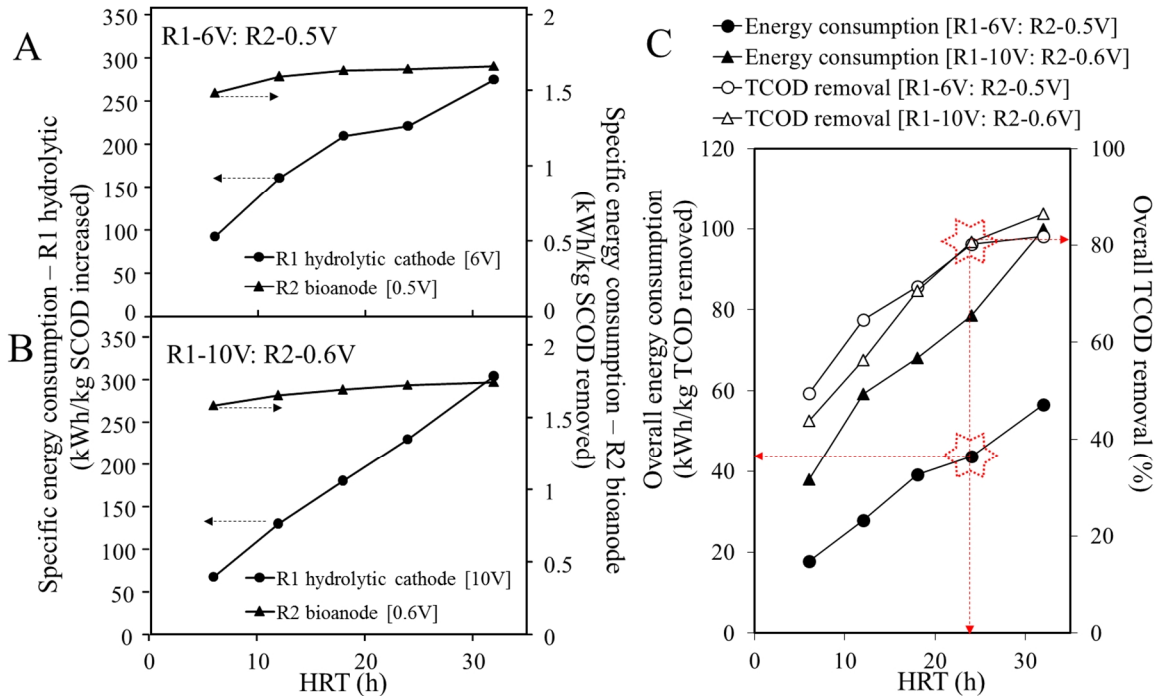


Figure 5.6 Energetic consideration of the sequential process operated with different HRT and applied voltages. A and B: specific energy consumption in each stage; C: overall energy consumption and TCOD removal. Dotted hexagons in C identify the most suitable HRT of 24 h for achieving TCOD removal (80% removal at 44 kWh/kg TCOD_{removed}).

Unlike in R1, increasing the HRT of R2 (6 to 32 h) only slightly increased the energy consumption, from 1.48 to 1.66 kWh/kg SCOD_{removed} (12%) and 1.58 to 1.74 kWh/kg SCOD_{removed} (10%) with applied voltage of 0.5 and 0.6V, respectively (Figure 5.6A, B). This suggests that changing the HRT did not markedly affect the energetic performance of R2 bioanode in terms of SCOD removal. Further, the energetic performance of R2 (stage 2) is comparable with other wastewater treatment MEC processes. For example, an energy input of 2.59 kWh/kg SCOD_{removed} was recorded by Ivanov et al. (2013) in their MEC process to enable SCOD removal (74%) from a municipal wastewater.

In fact, the energy consumption by R1 is within the range of energy demand in conventional activated sludge processes (0.7-2 kWh/kg SCOD_{removed}) (Pant et al., 2011; Tchobanoglous & Burton, 1991). Hence, augmenting R2 with applied voltage could be a viable option to remove SCOD hydrolysed from the entrapped particulate (R1). However, it should be stressed that it is still more preferable to operate R2 as a MFC with the aim to recover energy (as electricity), as this could further improve the overall energetic performance of the sequential process. Future studies towards this objective are warranted.

In terms of TCOD removal, increasing HRT and applied voltage generally increased the overall energy demand of the sequential process (Figure 5.6C). Of all tested settings, the most suitable setting was HRT 24 hours with applied voltages of 6V (R1):0.5V (R2), which enabled a high TCOD removal (80%) with relatively low energy consumption, 44 kWh/kg TCOD_{removed} (Figure 5.6C). Since the sequential process developed here is the first of its kind to enable simultaneous removal, hydrolysis and oxidation of particulate organics from wastewater, no comparable processes are available for direct comparison.

5.3.7 Implication and perspective

This study clearly demonstrated the effectiveness of the proposed sequential process (Figure 5.1). The findings also illustrated several key advantages of this approach: (1) the use of electrode as a physical filter ensured a more reliable SS removal (here close to 100%) and offered a pre-concentration mechanism to localise the SS at one place (i.e. electrode-filter in R1); (2) the use of applied voltage to drive cathodic production of alkaline in the vicinity of the electrode-filter enabled efficient hydrolysis of the organics; (3) the cathode-driven hydrolysis step created an alkaline SCOD enriched stream, facilitated a more efficient TCOD removal. The alkaline stream could be effectively neutralised in the subsequent BES process without reliance on external chemical dosing for pH control, enabled a discharge of a pH neutralised final effluent. The need of dosing chemicals for sustaining process operation has been a well-known stumbling block for BES technology (Rozendal et al., 2008). A complete negation of this requirement represents as a step forward towards practical application.

The present work demonstrates feasibility of using the proposed sequential process to polish particulate matter- laden effluent such as algal biomass emanating from WSPs. Although the complexity of the system and the need of energy usage may not seem comparable to the simplicity of a rock filter, one unique feature of the proposed process is the use of the electrode-driven hydrolysis step to enable the filtration unit (R1) to be a self-cleansing filtration device. Similar to a rock filter, the hydrolysis step (R1) filtered out most of the particulate matter from the effluent. However, instead of relying on natural decomposition of the entrapped particulate, the use of electrolytic-cathode continuously enable the solubilisation of the particulate matter at an acceptable rate, preventing clogging and not necessitating any back wash of the filter. This feature is desirable for maintaining longevity of the treatment unit.

Although this study has significantly contributed to the advancement of BES technology, further studies will be required to optimise the performance of the individual and combined stages. For instance, in this study, the two reactors in both stages 1 and 2 were operated with identical HRT. However, results suggested that the optimal operational regime of the coupled process may be achieved by coupling the two stages with their respective optimal HRTs, which could be different. For instance, the optimal HRTs for R1 and R2 were found to be 6 h and 24 h, respectively. Such HRTs may be provided by changing the reactors volume or combining different numbers of modules for the two stages. To this end, the modular configuration of the electrochemical-filter could be a promising feature for up-scaling consideration. Further research is certainly required to develop the technology.

5.4 Conclusions

This study reports for the first time a combination of an electrolysis filter and a BES process particulate and soluble organic matter removal from municipal wastewater. Based on the results, the following points are concluded:

- The first step electrolysis filter could remove near 100% of SS from wastewater influent. Electrolysis enhanced *in situ* hydrolysis of entrapped particulate matter in the filter.

- The use of alkaline cathodic effluent after electrolysis step as anodic influent of BES process eliminated the need of active pH control.
- Electrochemically assisted alkaline hydrolysis enhanced the subsequent anodic oxidation process which resulted in high overall TCOD removal of 87% and a CE of 93%.
- The electrolysis stage generated acidic solution (pH~2) in the counter electrolyte which was harnessed by the subsequent proton- requiring cathodic reaction.
- This study also shows that the energy consumptions for driving both hydrolysis and BES steps are lower than that values reported in past studies.

Chapter 6

Conclusions and future works

Overall, this thesis has made distinctive contribution to the development of bioelectrochemical systems (BES) technology for wastewater treatment. Arguably, it is the first PhD thesis specifically devoted to advancing BES technology for the treatment of particulate-rich wastewater such as those emanating from waste stabilisation ponds (WSPs). This final Chapter summaries the major findings and implications of the thesis. Recommendation for future research and limitations of the thesis are also highlighted.

6.1 A sediment- type BES configuration is not a good alternative for rock filters to polish WSPs effluent

This thesis commenced with evaluating the suitability of the simplest BES configuration (the sediment-MFC configuration) as an alternative to rock filters for polishing WSPs effluent (Chapter 2). One key finding is that by simply offering electrode surface for biomass retention, SCOD removal could already be markedly improved (from 25% to 66 %), albeit the fact that a majority (60%) of the removal was unrelated to current production. Although sediment-type configuration could be the simplest and cost-effective BES configuration to substitute rock filters, as identified in Chapter 2, it lacks at least two desirable design features, namely (1) the ability to allow a close distance between anode and cathode; and (2) the prevalence of low COD concentration near the cathode to enable efficient cathodic oxygen reduction. These features were considered in subsequent Chapters for designing a suitable BES configuration to polish WSPs effluent.

6.2 A novel filtration-type BES configuration for soluble and particulate organic matter removal from municipal wastewater

To address the limitations identified in Chapter 2, a new tubular dual chamber filter-type BES configuration, termed as “BES filter” was designed and characterised for its ability to retain and oxidise particulate matter and SCOD from municipal wastewater (Chapter 3). The BES prototype was composed of an outer anodic chamber that encircles an inner cathodic chamber and the two chambers are separated with a cation exchange membrane. This allows a very short distance (2 cm) to be maintained between the anode and the cathode. Another unique feature of this configuration was the use of porous conductive carbon felt as both physical filter and microbial oxidant. The BES filter could effectively remove (via filtration) the organic particulate matter from municipal wastewater (83% of SS removal). The process could also oxidise SCOD in wastewater with a high coulombic efficiency (CE) of over 80% (based on the SCOD removed), the highest CE reported thus far using real wastewater as the feedstock.

Besides, the internal resistance of the BES filter was between 2 Ω and 20 Ω , which is much lower than those reported in the literature (Clauwaert et al., 2009; Lefebvre et al., 2011; Zhang et al., 2013a; Zhang et al., 2013b) (Chapter 3). Given its scale (~10L working volume), the prototype tested has an attractive feature with such a low internal resistance, as scaling up of BES for municipal wastewater has often been hindered by increasing internal resistance (Clauwaert et al., 2008). The low internal resistance of the BES filter prototype was mainly attributed to the use of stainless steel current collector and the short distance maintained between the electrodes. These features should be incorporated in future designs.

Nonetheless, the BES filter tested in Chapter 3 was suffered from several limitations: (1) slow hydrolysis of entrapped particulate matter; (2) the need for dosing external chemicals for active pH control in both the cathodic and anodic chambers; and (3) a huge overpotential for cathodic oxygen reduction. Addressing these limitations are crucial and hence the subject of Chapter 5.

6.3 Entrapment and oxidation of fresh algal biomass at a BES anode

Further to the success in validating the filtration-concept with primary sedimentation tank effluent (Chapter 3), Chapter 4 confirmed that algal biomass (originated from municipal wastewater) could also be entrapped and decomposed anaerobically via electrochemical pathways. The findings confirmed for the first time that BES anode could directly treat fresh algal biomass. Prior to this study, for BES treatment of algae-laden wastewater a pre-treatment step has been considered essential. However, Chapter 4 suggested that a filter type BES anode could effectively entrap, decompose and anodically oxidise algal biomass without the need for a separate pre-treatment step. This is practically desirable particularly for the context of WSPs.

6.4 Sequential filtration and *in situ* electrolytic alkaline hydrolysis coupled with bio-anodic oxidation: A prominent concept for practical implementation

The BES filter developed in Chapter 3 was effective for polishing particulate matter-laden effluent. However, as mentioned above the system was suffered from the following limitations: (1) inefficient hydrolysis of entrapped particulate matter; (2) the need for active control of pH both in the cathodic and anodic chambers of BES; and (3) a huge overpotential for oxygen reduction at the cathode.

To address these issues, a unique two-stage process was designed and successfully validated in Chapter 5. This process consists of a first stage of entrapping particulate matters (via a filtration mechanism) from a particulate-rich wastewater stream on an electrode structure, whereby *in-situ* alkaline hydrolysis (i.e. release of soluble organics from solid organics) of the particulate is triggered electrochemically (i.e. by imposing electrical voltage to the electrochemical cell that houses the electrode), facilitating the formation of hydroxyl ions (alkali) by the electrode which could induce *in-situ* alkaline hydrolysis of the entrapped particulate. To our knowledge, this is the first example that combines filtration and electrolysis to simultaneously achieve concentration (entrapment or immobilisation) and alkaline hydrolysis of wastewater particulates in a single process.

The wastewater effluent generated from the electrochemical cell contains elevated soluble organics and alkalinity (pH>10). This thesis proposes that such alkaline stream could be further processed in a subsequent bioelectrochemical treatment step (stage

2), whereby the organics could be further oxidised by the anodic biofilm established at a different electrode akin to the one used in the preceding electrolytic step. This is a novel combination of two electrochemical processes, one abiotic and another one biotic (i.e. electrolytic alkaline hydrolysis step and bioelectrochemical soluble organic oxidation step), to enable efficient treatment of particulate-rich wastewater streams.

Scenario A- estimation of the footprint required for an up- scaled two- stage coupled process if implemented in full-scale. In this estimation, it is assumed that:

- Flow rate of effluent of a failed WSP: $100 \text{ m}^3/\text{d} = 4.17 \text{ m}^3/\text{h}$
- Effluent TCOD: 550 mg/L
- Seepage and evaporative losses are negligible.

Electrolysis step (R1):

TCOD concentration in the influent of the electrolysis step: 550 mg/L

HRT of electrolysis step: 6 h

Total volume of electrolysis step (m^3) = $4.17 \text{ m}^3/\text{h} \times 6 \text{ h} = 25 \text{ m}^3$

Reactor working volume: $10 \text{ L} = 0.01 \text{ m}^3$

Number of electrolysis filter = $25 \text{ m}^3 \div 0.01 \text{ m}^3 = 2500$

Reactor foot-print: 0.0078 m^2 (diameter 10 cm)

Footprint for electrolysis step: $2500 \times 0.0078 \text{ m}^2 = \mathbf{19.6 \text{ m}^2}$

BES step (R2):

Total expected current for bioanode:

TCOD at effluent of electrolysis step = 0.283 kg/m^3 , CE = 91.7%

TCOD loading: $0.283 \text{ kg/m}^3 \times 100 \text{ m}^3/\text{d} = 28.3 \text{ kg/d}$

Electron loading = 884.4 mol COD/d ($\div 32 \text{ g O}_2/\text{mol O}_2$)

$$\begin{aligned}
 &= 3537.5 \text{ mol e/d} && (\times 4 \text{ mol e/mol O}_2) \\
 &= 3243.9 \text{ mol e/d} && (\times 0.917; \text{CE}) \\
 &= 312986485 \text{ C/d} && (\times 96485 \text{ C/mol e; Faraday's constant}) \\
 &= 3622.5 \text{ C/s} && (\div 86400 \text{ s/d})
 \end{aligned}$$

Current= **3622.5 A**

- Experimental bioanode performance (Chapter 5): HRT= 24 h, Current= 312 mA.

$$\begin{aligned}\text{TCOD removed rate} &= 26956800 \text{ mC/d} \quad (\times 86400 \text{ sec/d}) \\ &= 279.4 \text{ mmol e/d} \quad (\div 96485; \text{Faraday's constant}) \\ &= 69.8 \text{ mmol O}_2\text{/d} \quad (\div 4 \text{ mmol e/mmol O}_2) \\ &= 2235.1 \text{ mg/d} \quad (\times 32 \text{ mg O}_2\text{/mmol O}_2) \\ &= 2437.4 \text{ mg/d} \quad (\div 0.917; \text{CE}) \\ &= 0.0024 \text{ kg/d} \quad (\div 1000000 \text{ kg/mg}) \\ &= \mathbf{0.244 \text{ kg/m}^3\cdot\text{d}} \quad (\div 0.01 \text{ m}^3, \text{ BES working volume})\end{aligned}$$

The number of BES needed= 11610 $(28.3 \text{ kg/d} \div 0.0024 \text{ kg/d})$

Footprint for BES step: $11610 \times 0.0078 \text{ m}^2 = \mathbf{90.6 \text{ m}^2}$

Total footprint for electrolysis and BES step: $19.6 + 90.6 = \mathbf{110.2 \text{ m}^2}$

Scenario B- estimation of the footprint required for a rock filter if implemented in full-scale. In this estimation, it is assumed that:

- Typical HRT within the relevant literature: 5 days; Flow rate= $100 \text{ m}^3\text{/d}$; typical depth= 1.5 m, void space= 50 %

Footprint needed for rock filter: $= (100 \text{ m}^3\text{/d} \times 5 \text{ d}) \div (1.5 \text{ m} \times 0.5) = \mathbf{667 \text{ m}^2}$

Clearly, the footprint of the proposed coupled system could be remarkably lower (~6x) than that of a typical rock filter (Figure 6.1). However, one drawback when scaling up the proposed coupling strategy is the reliance on pumping, which would inevitably elevate the operational cost. The prototype tested requires the wastewater to be recirculated and continuously transferred from the bottom to the top of reactors. This concern needs to be considered as a limitation for up- scaling of the proposed configuration. Future studies should be encouraged to consider negation of this requirement.

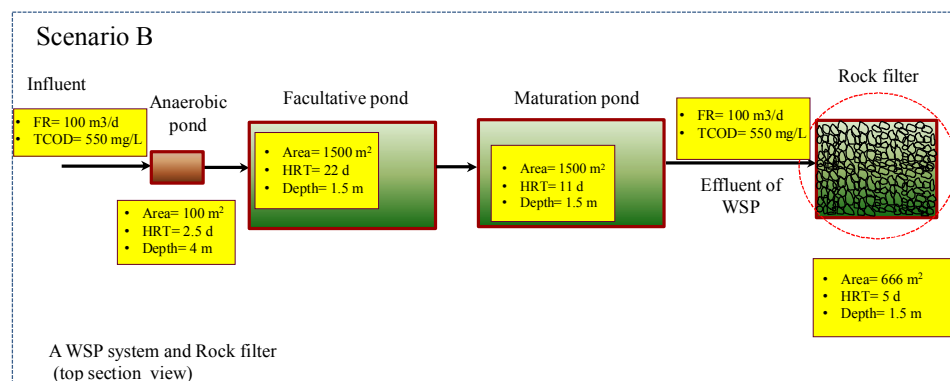
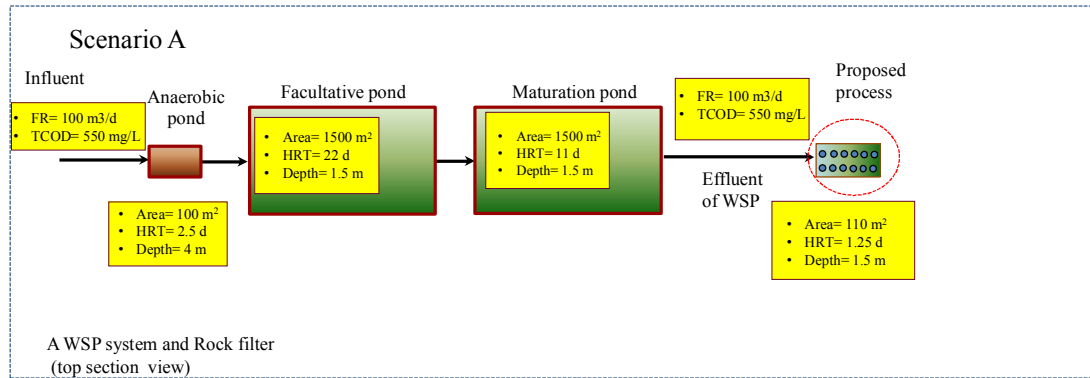


Figure 6.1 Process flow sheet, horizontal and top view of (scenario A) for the proposed coupled process and (scenario B) the rock filter for polishing a WSP effluent.

6.5 Recommendation for future works

Overall, the thesis has developed a novel process for particulate-rich wastewater treatment. The process enables the wastewater industry to effectively manage discharge of particulate matter with effluent of wastewater treatment facilities. A specific application includes the management of algae discharge from waste stabilisation ponds. Practically, the new process may create a platform to enable BES to be broadly examined for removal of organic solids. The electrochemical filter system (Chapter 5) could also be used to generate a stream rich in organics from various type of particulate organic matter (e.g. abattoir solids, diary solids, leather industry solids), by trapping and hydrolysing the particulate matter in the cathodic chamber and thereafter neutralising the organic rich stream with the acidic anolyte. Further, such organic rich stream may also be used for removing contaminants (e.g. nitrate, sulfate, selenate) from wastewater or industrial process waters by using the soluble organics as an electron donor for microbes. The generated organic rich stream

may also be used for recovering valuables such as phosphorus, metals, energy and other resources from waste streams.

Although the development of the novel proposed process creates an avenue to overcome most of current limitations of BES technology further studies may be required to optimise the performance of the individual and combined stages. For instance, the modular configuration of the electrochemical-filter could be a promising feature for large scale implementation. Other parameters such as cost-benefit and life-cycle analyses are required to assess the applicability of the coupled process in a real situation.

6.5.1 Other aspects (research questions) closely related to WSPs

Future research may focus on other issues in the context of WSPs. Some remaining questions for future works:

- Can the BES filter also facilitate removal of nutrients? The goal of the thesis was primarily aimed at suspended solids and COD removal. The potential of using BES technology for nutrient removal has been broadly embraced in the literature (Cord-Ruwisch et al., 2011; Zhang et al., 2014). It is worthwhile exploring the possibility of using the proposed BES filter process for nutrient removal and/or recovery.
- Can the use of the coupled system (Chapter 5), be able to alleviate unwanted release of methane from WSPs? As noted in Chapter 1, the release of methane as fugitive gases is likely taking place already in most existing WSPs around the world. A study by Hernandez-Paniagua et al. (2014) reports that some full-scale WSPs have been observed to loose almost 30% of influent organic carbon as methane. Methane is a greenhouse gas (GHG) and it has potential consequences on climate change. Hence, it is recommended investigating the potential of the proposed BES filter to mitigate methane emissions.
- Can we engineer the process to achieve disinfection of WSP effluent? It has been demonstrated that hydrogen peroxide (H_2O_2) can be produced from BES cathode, and could be used for disinfection of wastewater effluent (Arends et al., 2014). It will be interesting to further develop the technology to enable

disinfection of WSP effluent. In particular, the possible use of the BES filter module for active control of the growth of cyanobacteria and their toxin should be further explored. The configurations tested in this thesis may be considered too complex to achieve these goals. Hence, more suitable configuration should be identified and developed.

- What microorganisms are associated with the BES filter and which are playing the key role in the process? Knowing the microbial diversity is essential to further understand the functional feature and potential of the process. Ideally, effort should be made to establish the functional links between microbial diversity and process variables.

7. References

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Appendix 1

Supporting document to chapter 3

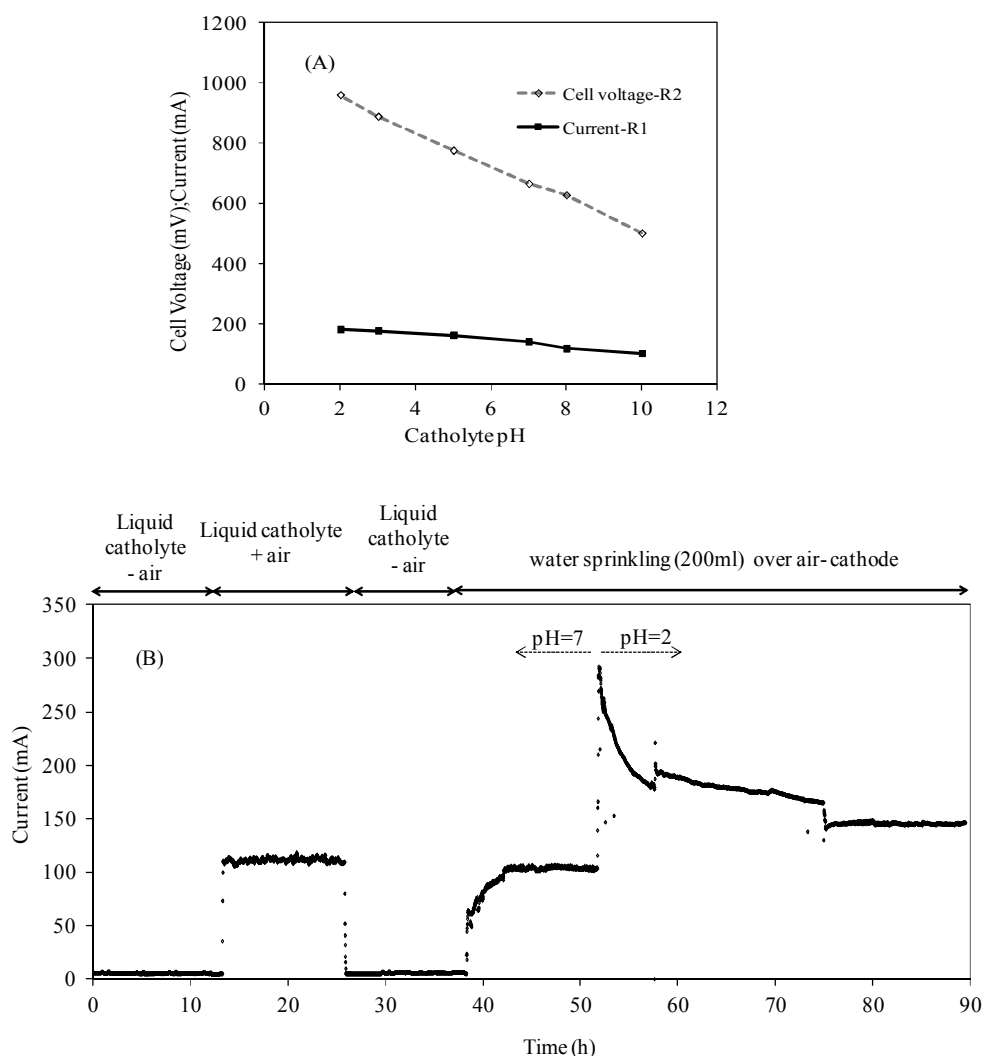


Figure S3.1 (A) Effect of catholyte pH on the current of R1 and open circuit voltage of R2, (B) Current production of R1 with different modes of operating the cathodic chamber: fully-loaded with aerated or non-aerated catholyte; partially-loaded (*ca.* 10% of the total cathodic chamber volume) with recirculated catholyte sprinkling over the air cathode. The catholyte pH was controlled at either 7 or 2 with 1M HCl over the periods as indicated in the figure. Anodic pH was controlled at 7 with 4M NaOH.

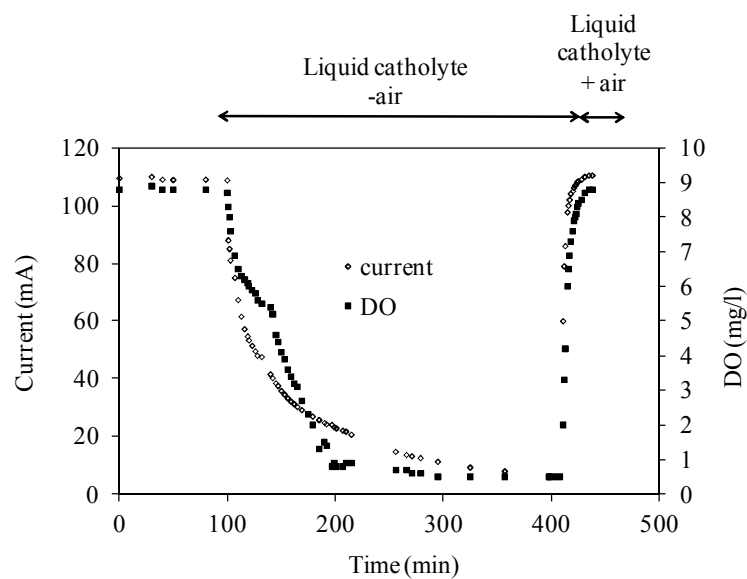


Figure S3.2 Current and dissolved oxygen concentration in the catholyte during the experiment of testing the effect of aeration inside the cathodic chamber. The cathode was aerated in the first 100 minutes. Aeration was terminated from 100 to 400 min. Aeration was resumed at 400 min.

Appendix 2

Supporting document to Chapter 5

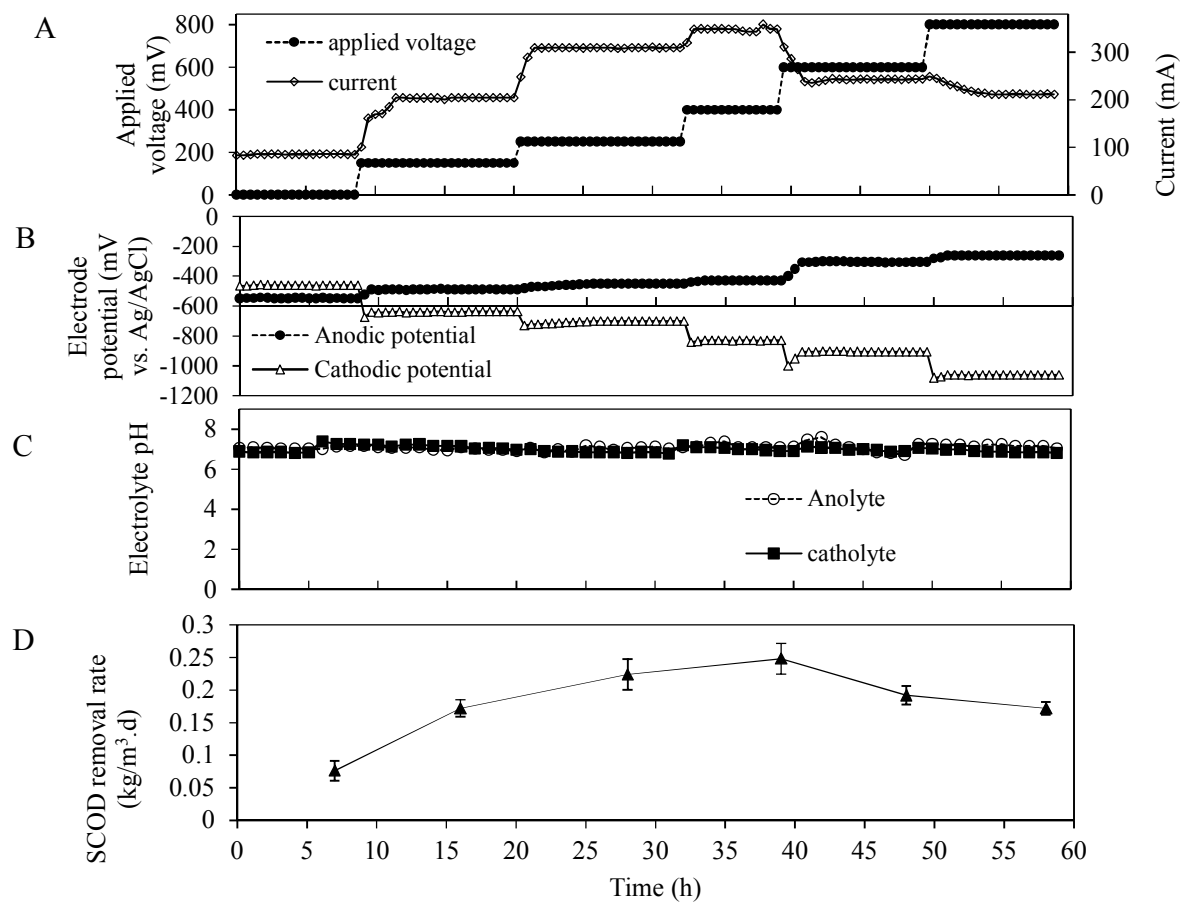


Figure S5.1 Changes in (A) applied voltage and current production; (B) electrodes potential; (C) electrolyte pH; (D) SCOD removal rate in the BES filter over the step-change of applied voltage experiment.

Table S5.1 Treatment and energetic performance of the sequential process

HRT (h)	R1- hydrolysis step			R2- MEC step			Overall energy consumption (kWh/kg. TCOD removed)	Overall TCOD removal rate (kg TCOD/m3.d)	Overall TCOD removal (%)
	Applied voltage (V)	Mean current (A)	E1 (kWh/kg. SCOD increased)	Applied voltage (V)	Mean current (A)	E2 (kWh/kg. SCOD removed)			
6	6	1.261	92.1	0.5	0.39	1.48	17.8	1.08	49.5
12	6	1.245	160.4	0.5	0.384	1.59	27.8	0.7	64.6
18	6	1.233	209.4	0.5	0.332	1.63	39.2	0.48	71.5
24	6	1.184	221	0.5	0.312	1.64	43.8	0.42	80.2
32	6	1.175	274.7	0.5	0.235	1.66	56.7	0.31	81.8
6	10	1.367	67.5	0.6	0.43	1.58	37.9	0.91	43.8
12	10	1.354	129.7	0.6	0.388	1.65	59.2	0.58	56.4
18	10	1.339	180.29	0.6	0.356	1.69	68.1	0.5	70.6
24	10	1.328	229.6	0.6	0.322	1.72	78.6	0.43	80.6
32	10	1.311	303.7	0.6	0.258	1.74	99.8	0.33	86.4

Appendix 3

Laboratory photos



Figure S3.1 Attachment of membrane and carbon felt on the stainless steel mesh



Figure S3.2 Construction of (A) the sediment- type BES reactors, (B) BES filters reactors

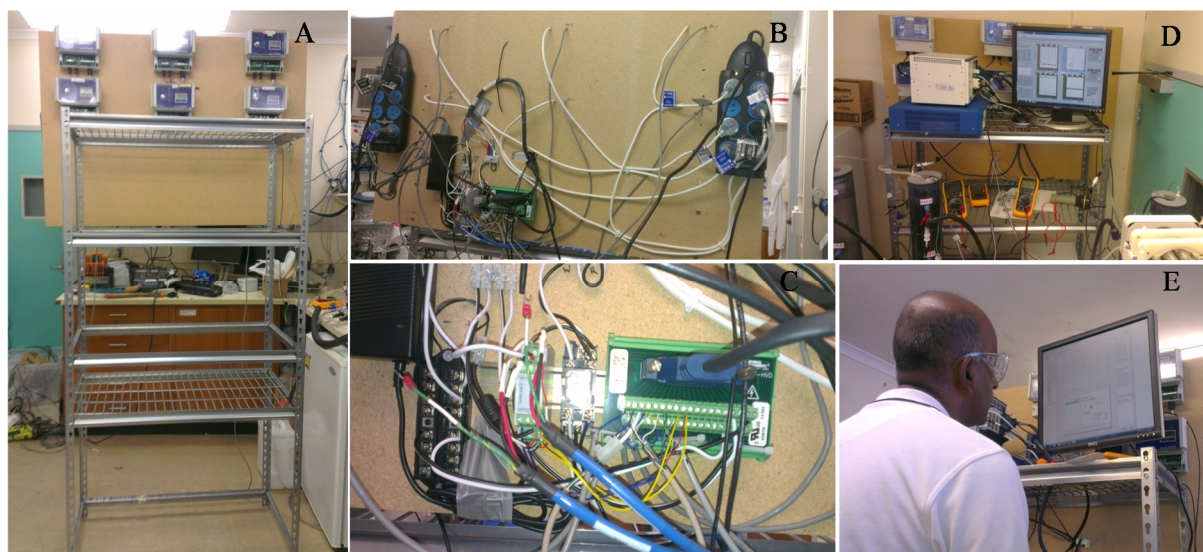


Figure S3.3 Construction of experimental station at CSIRO (significant effort made on setting up the experimental station with advanced process monitoring capability). (A) scaffold for mounting of the pilot-scale reactors; (B, C) monitors and electronic peripheral settings; (D, E) computer-programming for online process monitoring.



Figure S3.4 (A) Wastewater (PST effluent) collection at Subiaco WWTP, (B) transportation of samples to the wastewater laboratory.



Figure S3.5 Operation of the BES filters



Figure S3.6 The algal BES filter reactors