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Research article

Integrating bioelectrochemical system with aerobic bioreactor for organics removal and caustic recovery from alkaline saline wastewater

Tharanga N. Weerasinghe Mohottige [a,b,c], Maneesha P. Ginige [a], Anna H. Kaksonen [a,d,e], Ranjan Sarukkalige [b], Ka Yu Cheng [a,f,*]

[a] CSIRO Environment, Floreat, Western Australia, Australia
[b] School of Civil and Mechanical Engineering, Curtin University, Bentley, Western Australia, Australia
[c] The College, Western Sydney University, Kingswood, New South Wales, Australia
[d] Western Australian School of Mines: Minerals, Energy and Chemical Engineering, Curtin University, Bentley, Western Australia, Australia
[e] School of Engineering, University of Western Australia, Crawley, Western Australia, Australia
[f] Environment and Energy, Murdoch University, Murdoch, Western Australia, Australia

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ABSTRACT

Bioelectrochemical systems (BES) are increasingly being explored as an auxiliary unit process to enhance conventional waste treatment processes. This study proposed and validated the application of a dual-chamber bioelectrochemical cell as an add-on unit for an aerobic bioreactor to facilitate reagent-free pH-correction, organics removal and caustic recovery from an alkaline and saline wastewater. The process was continuously fed (hydraulic retention time (HRT) of 6 h) with a saline (25 g NaCl/L) and alkaline (pH 13) influent containing oxalate (25 mM) and acetate (25 mM) as the target organic impurities present in alumina refinery wastewater. Results suggested that the BES concurrently removed the majority of the influent organics and reduced the pH to a suitable range (9–9.5) for the aerobic bioreactor to further remove the residual organics. Compared to the aerobic bioreactor, the BES enabled a faster removal of oxalate (242 ± 27 vs. 100 ± 9.5 mg/L.h), whereas similar removal rates (93 ± 16 vs. 114 ± 23 mg/L.h, respectively) were recorded for acetate. Increasing catholyte HRT from 6 to 24 h increased the caustic strength from 0.22% to 0.86%. The BES enabled caustic production at an electrical energy demand of 0.47 kWh/kg-caustic, which is a fraction (22%) of the electrical energy requirement for caustic production using conventional chlor-alkali processes. The proposed application of BES holds promise to improve environmental sustainability of industries in managing organic impurities in alkaline and saline waste streams.

1. Introduction

Aluminium is a crucial commodity for many industries, such as transportation, construction and electronics due to its unique properties such as light weight, corrosion resistance, flexibility, recyclability and durability (Meyers, 2004; Miller et al., 2000). Aluminium is industrially produced from refined alumina (Al_2O_3). According to International Aluminium, the world alumina (Al_2O_3) production reached 134,432 thousand metric tons in the year 2020 (International Aluminium, 2021). Alumina refining is most commonly conducted via Bayer processing which uses a hot concentrated caustic solution to digest alumina-bearing mineral known as bauxite. Gibbsite ($Al(OH)_3$) is separated from the digested alkaline bauxite solution via precipitation through a series of sand and inorganics removal steps. The spent liquor, rich in caustic is recycled to the digestion step. As the final step, the precipitated gibbsite is calcined to produce Al_2O_3, the end product of the Bayer process (Hind et al., 1999; Meyers, 2004).

Although the Bayer process has been widely used by the alumina industry, the process is still hampered by several technical challenges. One of the key challenges is the accumulation of organic impurities in process liquor. Bauxite typically contains 0.1–0.3% organics, and in some cases organic content can be up to 1% (Hind et al., 1999; Power et al., 2012). The organics in the bauxite are extracted into the process liquor during digestion. If not removed (oxidised), these organic compounds accumulate with repeated re-use of process liquor in the refining circuit. Sodium oxalate has been widely recognised as the key organic

* Corresponding author. CSIRO Environment, Floreat, Western Australia, Australia.
E-mail address: kayu.cheng@csiro.au (K.Y. Cheng).

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impurity in the Bayer process liquor (Power et al., 2012). It severely reduces the alumina yield and quality, resulting in the generation of undesirably fine alumina particles, loss of caustic due to formation of organic sodium salts, as well as increased scale formation (Smeulders et al., 2001; Soucy et al., 2013). Therefore, many alumina refineries already adopted strategies to remove organics from their process water. Conventional strategies are predominately based on physical (e.g., thermal destruction such as liquor burning) and chemical unit processes (e.g. wet oxidation, precipitation) (Power et al., 2012). However, these methods are energy-intensive and incur significant cost (Zhang et al., 2020). The Australia alumina industry spends an estimated $AU 500 million per year to manage organic impurities in the Bayer process liquor (Power and Loh, 2010).

Over the past years, alumina refineries have explored chemical and biological processes to manage accumulation of organics in Bayer process liquor (Bangun and Adesina, 1998; Tilbury, 2003; Yingwei et al., 2011). Biological processes in particular have received much attention because of their ability to remove oxalate and other organic compounds in an environmentally friendly manner. In fact, some alumina refineries in Australia have already implemented commercial-scale aerobic bioreactors to destruct oxalate that is chemically and physically removed from the Bayer circuit (McKinnon and Baker, 2012; McSweeney et al., 2009). In these bioreactor processes, the metabolic activities of microorganisms are harnessed to aerobically oxidise oxalate into carbon dioxide (CO_2) and/or carbonate under alkaline conditions (pH 9–10) (McKinnon and Baker, 2012; Morton et al., 1991) (reaction 1).

$$2\ C_2O_4^{2-} + 4\ OH^- + O_2 \rightarrow 4\ CO_3^{2-} + 2\ H_2O \quad (1)$$

Although aerobic oxalate biodegradation has been proven as an effective bioreactor treatment option, it does not allow caustic soda recovery for reuse in the Bayer process. Further, the process requires a pre-acidification (carbonation) step to reduce the influent pH to a level suitable for microbial activity, and it requires nutrients (ammonia and phosphorus) addition to promote microbial growth (McKinnon and Baker, 2012). Moreover, the aeration requirement in the existing bioreactor process not only incurs a high energy cost, but it also increases volatilisation of ammonia under alkaline condition, leading to the loss of ammonia-N to the atmosphere. Accordingly, a liquor treatment technology that (1) requires minimal aeration (energy); (2) prevents undesirable loss of ammonia; and (3) allows the recovery of caustic soda for reuse in the refining process, is desirable.

Bioelectrochemical systems (BES) (also known as microbial electrochemical technology, MET) represent a promising technology for a wide range of environmental applications, including wastewater treatment and resources recovery. A key feature of this technology lies in the effective use of electrodes to stimulate and control microbial conversion of substrate or degradation of organic compounds (Cheng, 2009; Logan et al., 2006; Rozendal et al., 2008). In BES, organic compounds are degraded by electroactive microorganisms that can transfer electrons liberated from organic compounds to an insoluble anode surface. Driven by an electrical potential gradient, these electrons flow across an external circuit to a cathode. The electroneutrality of the BES is maintained through migration of ions between the anode and the cathode. With the use of a cation exchange membrane (CEM) separating the electrode pair, the electroneutrality of a BES is predominately maintained through the transmembrane migration of the dominant cations present in the anolyte (e.g. Na^+, K^+) instead of protons (H^+) liberated from the anodic reaction (Cheng et al., 2010; Rozendal et al., 2006). Consequently, the protons accumulated in the anolyte need to be neutralised by the influent alkalinity. Otherwise, the anolyte pH may drop to a level that would severely impact the bioelectrochemical activity of the microbes, thereby impeding the organics degradation.

In the context of alumina process liquor treatment, the BES process can be an attractive option based on the following reasons. Firstly, as the anodic reaction is proton-producing, it may help maintain a suitable pH within the bioprocess without a pre-carbonation step or addition of acids for neutralising the high alkalinity (pH > 12) of the influent. Secondly, the cathodic reaction of a BES process is proton-consuming, which allows the formation of hydroxyl ions (OH^-) in a sodium-rich catholyte, thereby facilitating the recovery of a caustic soda-enriched stream that can be recycled to the Bayer process. This can reduce the demand of new chemical (caustic soda) for the refinery. Thirdly, the oxidation of organic compounds occurs with an insoluble electron acceptor (i.e. anode) instead of dissolved oxygen (DO). This reduces not only the demand of active aeration, but also reduces the undesirable ammonia volatilisation (via air-stripping) and minimises energy consumption.

The feasibility of using BES for treating a saline and alkaline synthetic Bayer process liquor has been demonstrated in our previous studies (Weerasinghe Mohottige et al., 2017a). It was found that an aerobic biofilm pre-cultured onto graphite granules in a packed-bed aerobic bioreactor could use the same graphite granules as an electron acceptor in a BES anode for oxalate degradation. However, in terms of oxalate removal rate the BES was notably less efficient (17%) compared to the packed-bed aerobic bioreactor (19.6 vs. 25.5 kg/m^3.d) (Weerasinghe Mohottige et al., 2018). This suggests that in terms of organics removal, aerobic bioreactor is a reasonable choice that also justifies the existing full-scale use of aerobic bioreactors for the treatment of organics in alumina refinery liquor (McKinnon and Baker, 2012). Nonetheless, considering the aforementioned drawbacks associated with aerobic bioreactor processes, it seems promising to apply BES as an auxilary process for overcoming these limitations, and to create benefits. To our knowledge, no studies have considered using BES to improve the performance of aerobic bioreactor treatment of high salinity and alkalinity liquors.

In light of the above, it was hypothesised that a BES could serve as a preconditioning step to reduce the influent pH to a range favourable for a subsequent aerobic biotreatment step (Fig. 1a). The effluent from the aerobic bioreactor can then be discharged as a treated effluent, and a portion of the effluent can be used to capture the caustic soda generated by the BES cathode for recovery and reuse. As such, the aim of this study was to validate this hypothesis. We examined the use of a BES as an add-on unit to facilitate organics removal, as well as anodic acidification and cathodic causticisation of the influent and the effluent of the aerobic bioreactor process, respectively. For proving the proposed concept, an organic-rich influent that simulated the alumina refinery liquor in terms of alkalinity (above pH 12.5) and salinity was tested. A synthetic liquor was used in this study as real industrial wastewater (Bayer liquor) was not accessible. The synthetic liquor was continuously fed to the BES anode chamber for acidification and organics removal. The effluent of the anodic chamber was further processed in an aerobic bioreactor to remove the remaining organic compounds. The aerobic bioreactor effluent was fed to the BES cathodic chamber to recover caustic soda as the final product of the process. It is envisaged that this integrated process may help alumina industry to achieve multiple benefits, including (1) improved alumina quality and yield; (2) more environmentally sustainable management of organic waste impurities; and (3) less demand on chemicals (e.g. caustic soda).

2. Materials and methods

2.1. Synthetic influent and reactor electrolyte

A synthetic medium which simulated the Bayer liquor alkalinity and salinity was used in this study. Unless stated otherwise, sodium oxalate 3.35 g/L (25 mM) and sodium acetate 2.0 g/L (25 mM) were used as the carbon sources to represent the Bayer process organic impurities, and NaCl 25 g/L was added to increase the solution salinity. The pH value of the influent solution was maintained at above 12.5 by adding 2 M NaOH solution to mimic the alkalinity of the Bayer liquor according to the experimental requirements. The nutrients medium used consisted of (mg/L): NH_4Cl, 130; $NaHCO_3$, 125; $MgSO_4{\cdot}7H_2O$, 51; $CaCl_2{\cdot}2H_2O$, 15;

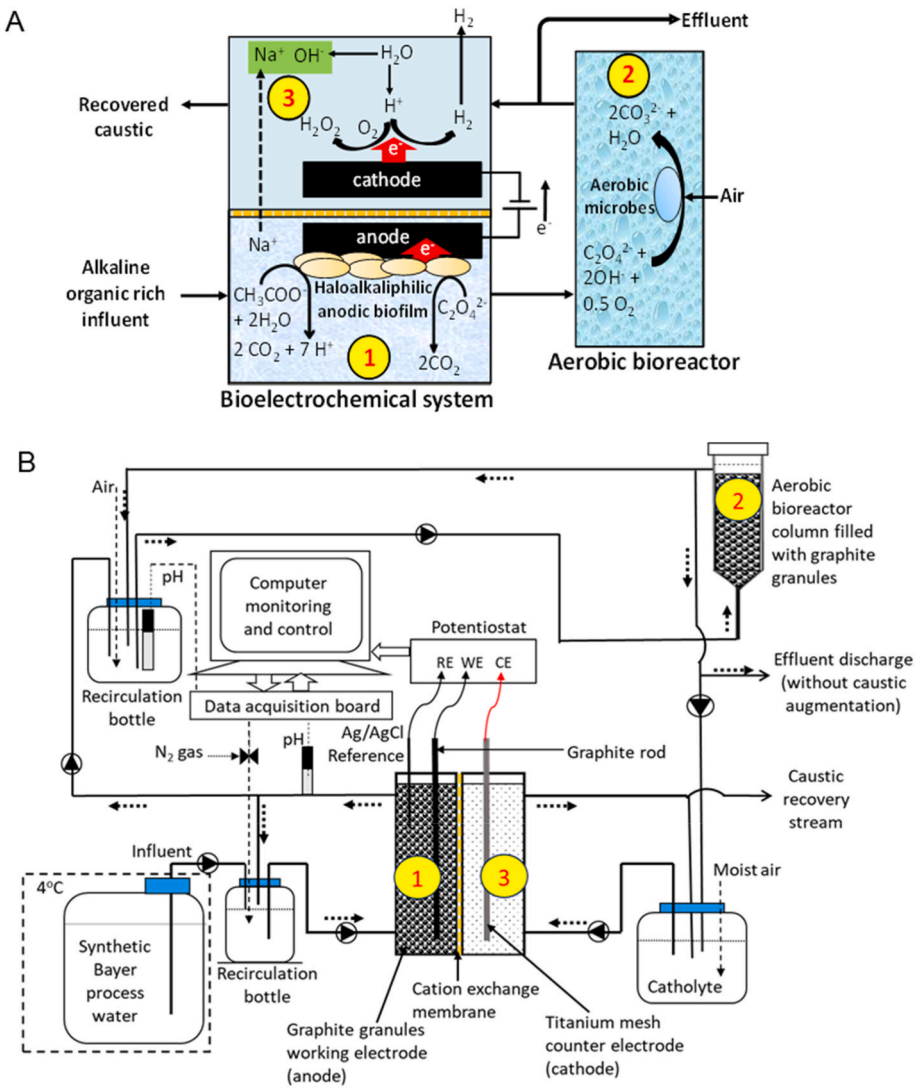

Fig. 1. (A) Process schematic of the proposed integrated process consisting of a BES and an aerobic bioreactor for organics destruction and caustic soda recovery from saline and alkaline liquor. (1) anodic chamber; (2) aerobic bioreactor (optional); (3) cathodic chamber. (B) A schematic diagram of the integrated process. RE-reference electrode, WE-working electrode (Anode) and CE-counter electrode (Cathode).

and $K_2HPO_4 \cdot 3H_2O$, 20.52 and 1.25 mL/L of trace element solution which had the composition of (g/L): $ZnSO_4{\cdot}7H_2O$, 0.43; $FeSO_4{\cdot}7H_2O$, 5; $CoCl_2{\cdot}6H_2O$, 0.24; $MnCl_2{\cdot}4H_2O$, 0.99; $CuSO_4{\cdot}5H_2O$, 0.25; $NaMoO_4{\cdot}2H_2O$, 0.22; $NiCl_2{\cdot}6H_2O$, 0.19; $NaSeO_4{\cdot}10H_2O$, 0.21; ethylenediaminetetraacetic acid (EDTA) 15, H_3BO_3, 0.014; and $NaWO_4{\cdot}2H_2O$, 0.05 (Cheng et al., 2010). Similar medium composition was successfully employed in previous studies for establishing active alkaliphilic microbial biofilms in bioreactors (Weerasinghe Mohottige et al., 2017a, 2017b, 2019). Unless stated otherwise, this medium was used as the influent solution in the anodic chamber throughout the entire study.

2.2. Process set-up and general operation

A two-compartment BES reactor coupled with an aerobic packed bed column reactor was used for the experiments (Fig. 1B). The BES reactor consisted of two identical half cells (14 cm × 12 cm × 2 cm). A cation exchange membrane (surface area 168 cm^2) (Ultrex CMI-7000, Membrane International Inc.) was used to separate the two cells. The anodic half-cell was filled (packed bed volume 250 mL) with biofilm coated conductive graphite granules (3–5 mm diameter, specific area 1.308 ± 0.003 m^2/g, KAIYU Industrial (HK) Ltd.) collected from an active oxalate removing aerobic column reactor (Weerasinghe Mohottige et al., 2017a). Four graphite rods (5 mm diameter, length 12 cm) were inserted into the anode half-cell to act as the current collector. Graphite was chosen as the anode material as it is structurally robust and inert to many solution environments, and it can support the growth of electroactive microbial biofilms in BES (Logan et al., 2006). In the cathode chamber, a titanium mesh (125 mm × 120 mm; NMT electrodes Pty Ltd., Australia) was mounted as a cathode and connected to the external circuit. The titanium mesh was selected as it is highly conductive, minimising internal resistance of the BES (Rozendal et al., 2008). The BES was connected to a potentiostat for electrode potential control, current and applied voltage measurement (VMP3, BioLogic) (Cheng et al., 2010). It was operated as a three-electrode system. A silver-silver chloride (Ag/AgCl) reference electrode (MF-2079 Bioanalytical Systems, USA) was used to facilitate the control of the working electrode at a defined potential using the potentiostat. The reference electrode was embedded within the granular graphite bed within the working electrode cell to minimise the distance with the anodic graphite bed. The cathodic potential was determined from the difference between the applied voltage and the anodic potential measured from the potentiostat. Both the anode and cathode half cells were connected to two separate external recirculation glass bottles (total electrolyte volume

500 mL each) via recirculation lines with recirculation rate of approximately 14 L/h.

The aerobic packed bed column bioreactor was made of glass with 45 mm internal diameter and 300 mm height. Similar to the BES anode chamber, the glass column was packed with biofilm coated graphite granules (packed bed volume 200 mL) collected from the same oxalate degrading aerobic reactor as the BES anode granules. The column bioreactor was connected to a recirculation bottle (total liquid volume 500 mL) and recirculation line. The solution within the recirculation bottle was aerated and was continuously recirculated through the packed bed column in an up-flow direction at a flow rate of 14 L/h. The inlet of the aerobic reactor was connected to the outlet line of the BES anode chamber and the effluent line of the aerobic reactor was connected to the cathode recirculation bottle as the cathode feed stream (Fig. 1B).

The integrated process was operated in continuous mode as specified below. The synthetic medium (maintained at 4 °C in a refrigerator) was continuously loaded at a specified flow rate into the anode recirculation bottle. Concurrently, an equal volume of anolyte was withdrawn from the anode chamber and pumped to the aerobic reactor recirculation bottle from the anode recirculation line (Masterflex® Cole-Parmer L/S pump drive fitted with a Model 77,202-60 Masterflex® pump head; Norprene® tubing 06404–14) (Fig. 1B). Notably, the process influent was not actively maintained anaerobic, as it was considered that any residual dissolved oxygen present in the influent would not be detrimental to the BES anodic biofilm.

Unless stated otherwise, during the entire study, the anode chamber and aerobic reactor hydraulic retention times (HRTs) were both maintained at 6 h. The effluent from the aerobic reactor was pumped to the cathode recirculation bottle at a specified flow rate depending on the experimental requirements, and the solution was recirculated through the cathodic chamber to capture the produced caustic soda. Concurrently, an equal volume of the catholyte was extracted from the catholyte recirculation line as a caustic soda recovery stream. The entire process was operated at 22±2 °C.

The working electrode potential and current of the BES were monitored via the potentiostat. All electrode potentials (mV) reported in this paper refer to values against Ag/AgCl reference electrode (*ca.* +197 mV vs. standard hydrogen electrode (Bard and Faulkner, 2001)). The pH of the anolyte, aerobic reactor liquor and catholyte were continuously monitored using in-line pH sensors (TPS Ltd. Co., Australia). All signals were regularly recorded to an Excel spreadsheet via the computer programme interfaced with a National Instrument™ data acquisition card.

2.3. Experimental procedures

2.3.1. BES process start-up with biofilm acclimatised in aerobic conditions

Initially, the BES reactor was operated as a stand-alone process to establish electricity-producing activity of the aerobically grown biofilm attached on the graphite granules. After the BES anode chamber was filled with biofilm coated granules, the reactor electrodes were connected to the potentiostat to control the anode potential at −300 mV vs. Ag/AgCl as this potential could facilitate efficient bioelectrochemical oxidation of organics by the biofilm (Weerasinghe Mohottige et al., 2017a). Initially, the influent solution contained sodium oxalate (25 mM) as the sole carbon and energy source and was continuously pumped to the anode chamber at an HRT of 12 h. After 14 h of operation, the HRT of the anode chamber was decreased to 6 h to test if a higher organic loading rate enabled a higher current. On day 2, sodium acetate (15 mM) was added to the influent and the acetate concentration was gradually increased to 25 mM over a 4 days period. After the anodic current production became stable on day 7, the aerobic bioreactor was hydraulically coupled with the BES as an integrated treatment system.

2.3.2. Operation of the integrated process with oxalate and acetate as carbon sources

The performance of the integrated BES-aerobic bioreactor process was examined by analysing liquid samples collected from different locations of the process over an approximately three weeks stable operation period. During this period, the process influent (pH 12.5) containing sodium oxalate (25 mM) and sodium acetate (25 mM) was continuously loaded into the anode chamber at HRT of 6 h. Concurrently, the anode effluent was pumped at a same rate to the aerobic reactor, and the effluent of the aerobic reactor was fed to the BES cathode chamber to facilitate the generation of a low-organics, caustic soda-enriched recovery stream. To cope with the anode flow rate, the aerobic reactor and the cathode compartment flow rates were maintained at a similar HRT of 6 h.

2.3.3. Effect of increasing cathode chamber HRT on cathodic pH and alkalinity

An effective approach for increasing the caustic soda concentration in the recovery stream is beneficial for practical application of the proposed process. Hence, an experiment was conducted to investigate the effect of cathodic chamber HRT on the pH and alkalinity of the caustic soda recovery stream. After 30 days of operation, the cathode chamber HRT was increased from 6 h to 12 h, while keeping the BES anode and aerobic reactor HRTs at 6 h. Thereafter, the cathode chamber HRT was doubled to 24 h. During this experiment, the BES was continuously operated as an integrated process with the aerobic bioreactor. When the catholyte HRT was increased beyond 6 h, a designated portion of the aerobic reactor effluent was discarded to avoid liquid accumulation in the aerobic reactor. At selected time points the catholyte total and hydroxide alkalinities were quantified to establish their relations with the catholyte HRT.

2.4. Chemical analysis

Performance of the BES and aerobic bioreactor were monitored by measuring the changes of chemical oxygen demand (COD), oxalate, acetate and cation concentrations at various locations of the process over time. Liquid samples collected from the BES and aerobic bioreactor were immediately filtered through a 0.22 μm filter (0.8/0.2 μm Supor® Membrane, PALL® Life Sciences) upon collection and were stored at 4 °C prior to analysis. COD was measured using a closed reflux dichromate COD method (HACH Method 8000, HACH Ltd). Anolyte, catholyte and aerobic reactor solution pH were also monitored continuously throughout the experiment.

Acetate and oxalate were analyzed using a Dionex ICS-3000 reagent free ion chromatography (RFIC) system equipped with an IonPac® AS18 4 × 250 mm column. The eluent was potassium hydroxide, with a flow rate of 1 mL/min. The eluent concentration was 12–45 mM from 0 to 5 min, 45 mM from 5 to 8 min, 45–60 mM from 8 to 10 min and 60-12 mM from 10 to 13 min. Ammonium (NH_4^+ –N), sodium (Na^+) and other cations were measured with the same RFIC with a IonPac® CG16, CS16, 5 mm column. The eluent was methansulfonic acid with a flow rate of 1 mL/min. The eluent concentration was 30 mM for a run time of 29 min. The two columns were maintained at the temperature of 30 °C during the run. Suppressed conductivity was used as the detection signal (ASRS ULTRA II 4 mm, 150 mA, AutoSuppression® recycle mode). The change in alkalinity along the process line was determined by potentiometric titration of liquid samples with 0.1 M HCl to pH 8.3 for hydroxide alkalinity and pH 4.5 for carbonate/bicarbonate alkalinity according to the standard methods (American Public Health Association, 1995).

2.5. Calculation of coulombic efficiency, caustic strength and energy consumption

Coulombic efficiency of caustic production ($CE_{caustic}$), caustic strength (CS) and energy consumption (EC) were calculated according

to equations (2)–(4), respectively.

$$CE_{caustic} = 100*(I*t)/(F*OH^{-}_{produced}) \quad (2)$$

Where $CE_{caustic}$ is coulombic efficiency of caustic production (%), I is averaged BES current (C/s), t is hydraulic retention time of the catholyte (s), t is hydraulic retention time for the batch operation (s), F is Faraday constant (96,485 C/mol), $OH^{-}_{produced}$ is the amount of hydroxide produced in the catholyte (mol) as measured by using the aforementioned titration method.

$$CS = (OH^{-}_{Alk} * MW_{NaOH})/10 \quad (3)$$

Where CS is caustic soda strength in the catholyte (% wt. NaOH/vol.), OH^{-}_{Alk} is catholyte hydroxide alkalinity (mol OH^{-}/L), MW_{NaOH} is molecular weight of NaOH (40 g/mol).

$$EC = (I*V*t)/1000 \quad (4)$$

Where EC is energy consumption per batch operation (kWh), I is averaged BES current (A), V is applied voltage (V), t is HRT of the catholyte for the batch operation (h).

3. Results and discussion

3.1. Establishment of anodophilic biofilm in oxalate-fed BES reactor

Soon after the BES anode chamber was packed with the active aerobic biofilm colonised graphite granules, the electrodes were poised at −300 mV and the biofilm was continuously fed with an oxalate-containing influent (HRT 12 h). This anodic potential was selected as it is within a typical potential range for establishing efficient anodophilic biofilms to oxidise organic compounds in BES (Cheng et al., 2008). Fig. 2 shows that an immediate increase in current production was recorded (maximum of 18 mA), indicating that the aerobic oxalotrophic biofilm could instantly switch the electron acceptor from dissolved oxygen to the solid graphite surface. This result confirmed the previous finding of Weerasinghe Mohottige et al. (2017a) which recorded a rapid start-up of a BES reactor with active aerobic biofilm colonised graphite granules for oxalate biodegradation. After 14 h from the onset of the experiment, the anode chamber HRT was reduced to 6 h, which resulted in a gradual increase in current from 18 to 48 mA. This confirmed that the biofilm could use oxalate as their sole electron donor for current generation. To test whether the anodic biofilm could also readily convert acetate into electrical current, after day 1, 15 mM of sodium acetate was added to the influent. The results showed that upon acetate addition the anodic biofilm instantly produced a higher anodic current (Fig. 2), indicating that acetate could be bioelectrochemically and readily oxidised. Further, during the start-up phase the anolyte pH was notably lower than the influent pH (*ca.* 12), and was fluctuated between 7 and 10, which was close to the optimum pH (*ca.* 9) reported for both aerobic and anodic biofilm under similar saline and alkaline condition for oxalate degradation (Weerasinghe Mohottige e al., 2017a and 2017b). After the anodophilic activity of the biofilm was successfully established, the BES anode was coupled with the aerobic bioreactor.

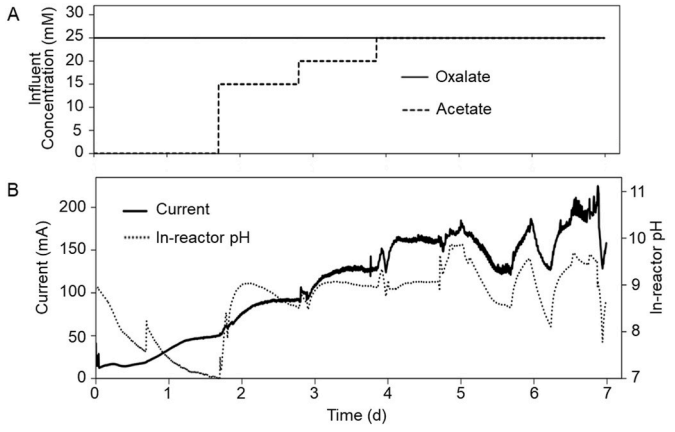

Fig. 2. Start-up of the BES with biofilm granules from an aerobic bioreactor. A. Change of influent oxalate and acetate concentrations. B. BES current generation and In-reactor pH profile. The BES was operated at anode potential of −300 mV vs. Ag/AgCl and HRT of 6 h in both anodic and cathodic chambers.

3.2. Coupling of the BES with the aerobic bioreactor as an integrated process

3.2.1. General process performance

After coupling the aerobic packed bed bioreactor to the BES, the integrated process was operated with sodium oxalate (25 mM) and sodium acetate (25 mM) in the influent at a constant HRT (6 h) for over 20 days. During this period, the BES was able to produce approximately 150 mA current from the oxidation of organics (Fig. 3A) at anode potential of −300 mV under alkaline and saline conditions. The cathode potentials recorded over this period fluctuated between *ca.* −1200 mV and −1400 mV, which were notably lower (more negative) than the theoretical potential that allows cathodic hydrogen formation at pH 13 (*ca.* −770 mV vs. standard hydrogen potential). As such, hydrogen gas may be generated at the cathode (reaction 5)(data not shown). Depending on the dissolved oxygen availability , another proton-consuming electrochemical reaction that may occur at the cathode is hydrogen peroxide formation (reaction 6). However, further study is required to characterise and understand the exact cathodic reactions in the process.

$$2\ H^{+} + 2\ e^{-} \rightarrow H_2 \quad (5)$$

$$O_2 + 2\ e^{-} + 2\ H^{+} \rightarrow H_2O_2 \quad (6)$$

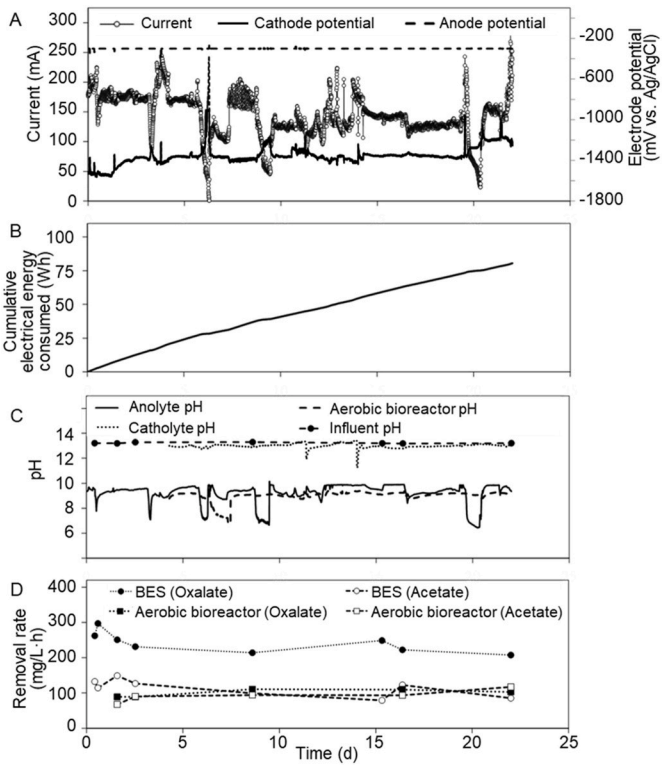

Fig. 3. Performance of the integrated process in long term operation at an HRT of 6 h in each of the BES chambers and the aerobic bioreactor. A. BES anodic current production and electrode potentials over the experimental time period. B. Cumulative electrical energy consumption of the BES over the experimental period C. Change of pH of the solution at different locations D. Oxalate and acetate removal rates in the two reactors.

Since the anode potential was constantly poised at −300 mV, the cathode potentials dictated the voltage applied to the BES, which amounted between 0.9 V and 1.1 V. Considering also the electrical current generated over time, a cumulative energy consumption of *ca.* 75 Wh by the BES was recorded after 22 days of operation (Fig. 3B). Noteworthy, although the BES reactor was fed with a highly alkaline influent (pH 12.5), the acidity generated from the anodic reaction was sufficient to maintain the desirable pH condition in the anolyte. The results suggested that both the BES anolyte and the aerobic bioreactor pH were predominately within the range of 9–10 (Fig. 3C), which was suitable for the acclimatised microbial activity for oxalate degradation in both BES and aerobic bioreactor. As such, no active pH correction strategy (e.g. regular dosing of acids) was required. This is advantageous as the integrated process did not require input of chemicals for pH control. Moreover, both the influent and the catholyte pH profiles were similar (Fig. 3C), suggesting that the proposed integrated process enabled recovery of alkalinity in the form of catholyte, which could potentially be recycled to the refinery process enabling cost and chemical savings.

In terms of organics removal, both the BES and the aerobic bioreactor enabled a stable removal of oxalate and acetate during continuous mode operation (Fig. 3D). However, the bioanode enabled a higher oxalate removal rate (2.4 times) compared to the aerobic bioreactor (242 ± 27 mg/L.h (n = 8) vs. 100 ± 9.5 mg/L.h (n = 5)) (Fig. 3D). Due to the difference in the packed bed volumes between the two reactors, where the BES anode contained initially 1.25 times more biomass than the aerobic bioreactor, the specific oxalate removal rate by the BES was nearly double (1.9 times higher) compared to the aerobic bioreactor. This result may be explained with the Michaelis-Menten reaction kinetics theory, whereby the substrate removal rate increases with the initial substrate concentration until a maximum (saturating) substrate concentration is reached. In fact, the oxalate-oxidising aerobic bioreactor, from which the aerobic oxalotrophic biofilm was originated, also exhibited this behaviour (Weerasinghe Mohottige et al., 2019). Therefore, it is likely that the oxalate concentration in the aerobic bioreactor influent was lower than the maximum oxalate concentration for the aerobic biomass, and hence the maximal oxalate removal rate could not be reached. In contrast, both the BES anode and the aerobic bioreactors had similar capacity to remove acetate (93 ± 16 vs. 114 ± 23 mg/L.h, respectively), despite the differences in influent acetate concentrations.

3.2.2. *Anodic acidification of the alkaline-saline influent and cathodic causticisation of the final effluent*

The performances of the BES and the bioreactor were further characterised to test whether the BES could alleviate external acid dosing for controlling the pH of the aerobic bioreactor influent, and to allow caustic soda recovery as an integrated process (Fig. 4A). The results showed that the oxalate, acetate and COD concentrations decreased along the treatment locations of the process, resulting in overall removal efficiencies of 86%, 97% and 88% for oxalate, acetate and COD, respectively (Fig. 4B). As expected, the final effluent collected from the BES cathode chamber outlet (process location 4 as depicted in Fig. 4A), was an alkaline solution (pH > 12.5) with minimal concentrations of oxalate and acetate (Fig. 4B). The pH profile also clearly shows the acidity generation from anodic organics oxidation and alkalinity recovery in the BES cathode. Even though the overall change in total alkalinity was negligible along the process (Fig. 4C), the hydroxide and carbonate/bicarbonate alkalinities were notably different in the influent and final effluent samples (Fig. 4C). The hydroxide alkalinity decreased in the anodic compartment as a result of neutralization of the protons generated from the anodic organic oxidation process, but increased again in the cathodic compartment as a result of hydroxide production. The carbonate/bicarbonate alkalinity increased in each step of the process as organics were oxidised to carbonate/bicarbonate.

Since the dominant cation in the catholyte was sodium (Na^+ >12 g/L) (Fig. 4D), the cathodic recovery stream was essentially a caustic soda

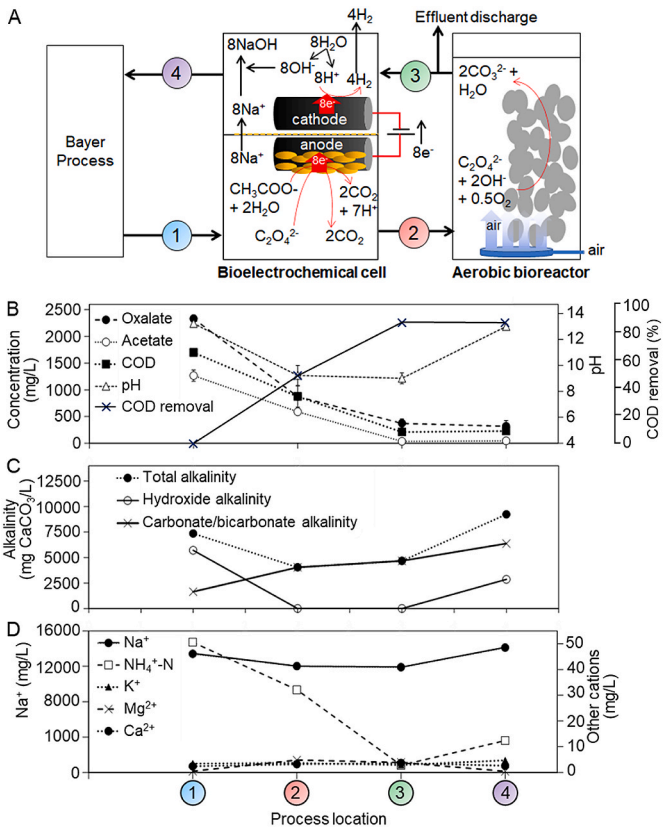

Fig. 4. Influent and effluent quality at different locations of the process at a HRT of 6 h in each of the BES chambers and the aerobic bioreactor. A. Schematic diagram of the sampling locations. B. Oxalate, acetate concentrations and pH. C. Total , hydroxide and carbonate alkalinities. D. Cation concentrations.

(NaOH) solution, which is a desirable chemical for alumina processing. The results also suggested that the impact of other major cations (namely K^+, NH_4^+, Mg^{2+}, Ca^{2+}) on the purity of the recovered caustic soda solution was negligible, as their concentrations were substantially low (<20 mg/L) (Fig. 4D). Nonetheless, it was found that some NH_4^+ (12 mg-N/L) had migrated from the anodic chamber to the cathodic chamber (Fig. 4D), which was likely caused by the steep concentration gradient (50 vs. 12 mg-N/L) across the CEM. Worth noting also is a decline in NH_4^+ concentration in the aerobic bioreactor, which may be due to both microbial assimilation for growth and volatilisation loss of NH_4^+ as NH_3 from the aerobic bioreactor at high pH (≥9.25, which is the pKa value of ammonia at 25 °C). Therefore, minimising the transmembrane NH_4^+ migration in the BES (e.g. by lowering the amount of ammonium-N supplied to the influent as a microbial nutrient, and exploring the use of other non-volatilisable nitrogen compounds (e.g. nitrate) as microbial nutrients for the aerobic bioreactor are meaningful for process improvement.

3.3. *Optimisation of the recovered caustic strength by increasing the HRT of the catholyte*

The results so far suggested that the integrated process enabled organics removal without the need to dose acid to the alkaline influent for neutralization. However, in terms of caustic recovery the process only enabled the generation of a caustic recovery stream with a strength of 0.22%. From a practical perspective, it is desirable to recover caustic at higher strengths (e.g. >4%) that can be directly returned to the Bayer process. Presumably, the caustic strength of the recovery stream could be augmented by increasing the HRT in the cathodic chamber of the BES. Thus, the integrated process was further optimised with increased HRTs

in the cathodic compartment (Fig. 5). Over a 12 days experimental period, the current production in the BES was rather stable (at approximately 110 mA) (Fig. 5B). When the HRT in the cathodic chamber was stepwise increased from 6 h to 24 h, the catholyte total alkalinity increased from 9000 mg $CaCO_3$/L to 20,000 mg $CaCO_3$/L (Fig. 5C). Accordingly, increasing HRT by 4 times increased the caustic strength of the recovery stream by 2 folds (Fig. 5C). A linear relationship could be established between catholyte HRTs (6–24 h) and the catholyte alkalinities (total and hydroxide) (Fig. 6).

In terms of caustic strength, when the BES was operated with a catholyte HRT of 24 h and a current of approximately 0.11 A, the caustic strength of the catholyte reached 0.86% (w/v). This value is lower than the caustic strength reported by Rabaey et al. (2010), who recorded a value of 3.4% (w/v) at a higher current (*ca.* 0.71 A) using their lamellar-type BES for treating a pH-neutral synthetic wastewater. However, in terms of electrical energy demand for caustic production, the alkaline wastewater fed-BES tested in the present study was more energy efficient, with 0.465 kWh/kg-caustic compared to 1.06 kWh/kg-caustic reported in Rabaey et al. (2010). Presumably, the higher energy efficiency achieved was due to better retention of the hydroxyl ion (OH^-) generated by the cathode in the cathodic recovery stream, as the cross-over of OH^- towards the anodic chamber became less favourable due to the alkaline nature of the anolyte (Du et al., 2018). In fact, compared to conventional chlor-alkali processes (0.465 vs. 2.10–2.15 kWh/kg-caustic) (Thiel et al., 2017), the BES tested in this study enabled caustic production only at a fraction (22%) of the electrical energy requirement for caustic production. Hence, the use of BES for recovering caustic from alkaline organics-containing influent is attractive.

In terms of coulombic efficiency (CE) for caustic production, a CE of 89% was recorded when the cathode chamber was operated at 6 h HRT. Further increasing the HRTs to 12 h and 24 h enabled up to 98% CE of OH^- production under both operational conditions. These CE values are higher than the maximal CE of 76% reported in Rabaey et al. (2010), supporting that increasing HRT of the catholyte is an effective strategy to increase the caustic soda strength of the recovery stream in the proposed integrated process. Nonetheless, further study is required to optimise the caustic strength for practical application.

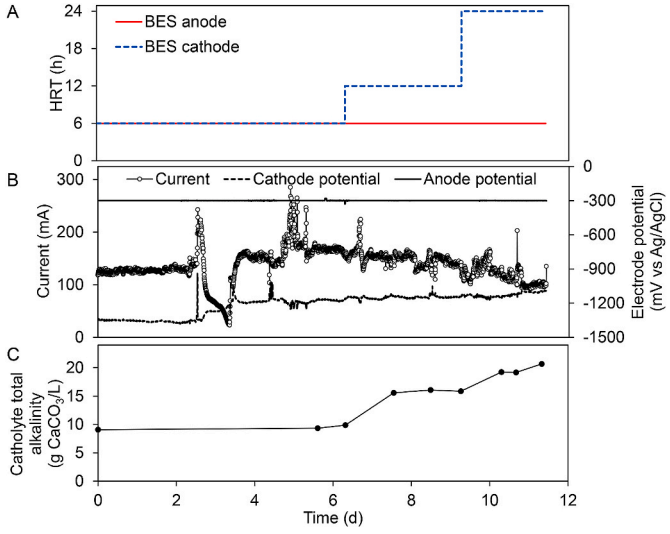

Fig. 5. The change of HRT in the cathodic chamber of the BES to increase the alkalinity of the catholyte. A. The change of HRT in different compartments of the reactor system. B. Anodic current production and change of electrode potentials. C. Catholyte total alkalinity increase over the experimental time.

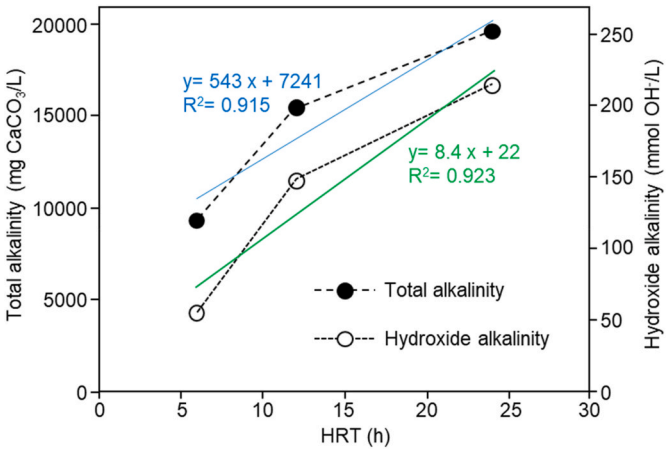

Fig. 6. The relationship of total alkalinity and hydroxide alkalinity with catholyte HRT.

4. Implications of the findings

Overall, this study demonstrated for the first time that a BES could serve as a preconditioning step to reduce the pH of a highly saline and alkaline wastewater to a range favourable for a subsequent aerobic biotreatment step for organics removal. The study confirmed that the BES bioanode could effectively acidify the alkaline influent while oxidising part of the organic impurities, thereby eliminating the need for dosing acidic chemicals and reducing the aeration requirement for the aerobic bioreactors. The ability of an aerobic oxalate-degrading biofilm to readily utilise a BES anode for bioelectrochemical oxidation of oxalate is practically beneficial, as this implies that when required the aerobic bioreactor could be a ready source of biocatalyst supplement for the BES anode (e.g. during circumstances such as reactor failure, or process inhibition).

In terms of caustic soda recovery, although the BES cathode was able to recover caustic soda, facilitating the production of an organic-free recovery stream, the process did not produce a strong caustic solution when the recovery step (cathode) was operated at a similar HRT as in the other steps. The finding that the caustic soda strength in the catholyte was doubled with increased catholyte HRT (6–24 h), implies that increasing HRT is a feasible approach to address the issue. However, based on the relationship obtained between HRT and alkalinity recovery, a lengthy catholyte HRT (4.8 days) would be required to recover 1 mol/L OH^- solution in the process, which is not desirable. Increasing HRT by increasing the BES cathodic chamber volume may not be a viable solution and would be cost-prohibitive. On the other hand, apart from cathode chamber HRT the caustic soda recovery may also depend on factors such as: (i) anodic current production, (ii) anolyte alkalinity, and (iii) anode to cathode chamber volume ratio. Hence, further investigation on these variables, particularly with the use of real alumina refinery process liquor, appears necessary for optimising the process.

5. Conclusions

An integrated process consisting of a BES and aerobic bioreactor was proposed and successfully validated for organics removal from an alkaline and saline influent. The treatment performance over a long-term operation (>20 days) was proven efficient for organics removal. The BES concurrently removed a majority of the influent organics and reduced the influent pH to a level conducive (pH 9–9.5) for the aerobic bioreactor, which enabled further organics removal. Organics removal rates in the BES were comparable to values recorded for the aerobic bioreactor. Further, the BES cathode represents an energy-efficient step for recovering caustic soda as an organic-free product stream for

beneficial industrial reuse.

Credit author statement

TWM: Investigation, Methodology, Visualization, Writing – original draft; MG: Conceptualisation, Methodology, Investigation, Supervision, Writing- Reviewing and Editing; AHK: Conceptualisation, Methodology, Funding acquisition, Supervision, Writing- Reviewing and Editing; RS: Supervision, Writing- Reviewing and Editing; KYC: Conceptualisation, Methodology, Funding acquisition, Project administration, Visualization, Investigation, Supervision, Writing- Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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